

Supporting Information

Synthesis, Characterization, and Photovoltaic Properties of a Low-Bandgap Copolymer Based on 2,1,3-Benzoxadiazole

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Experimental

Materials

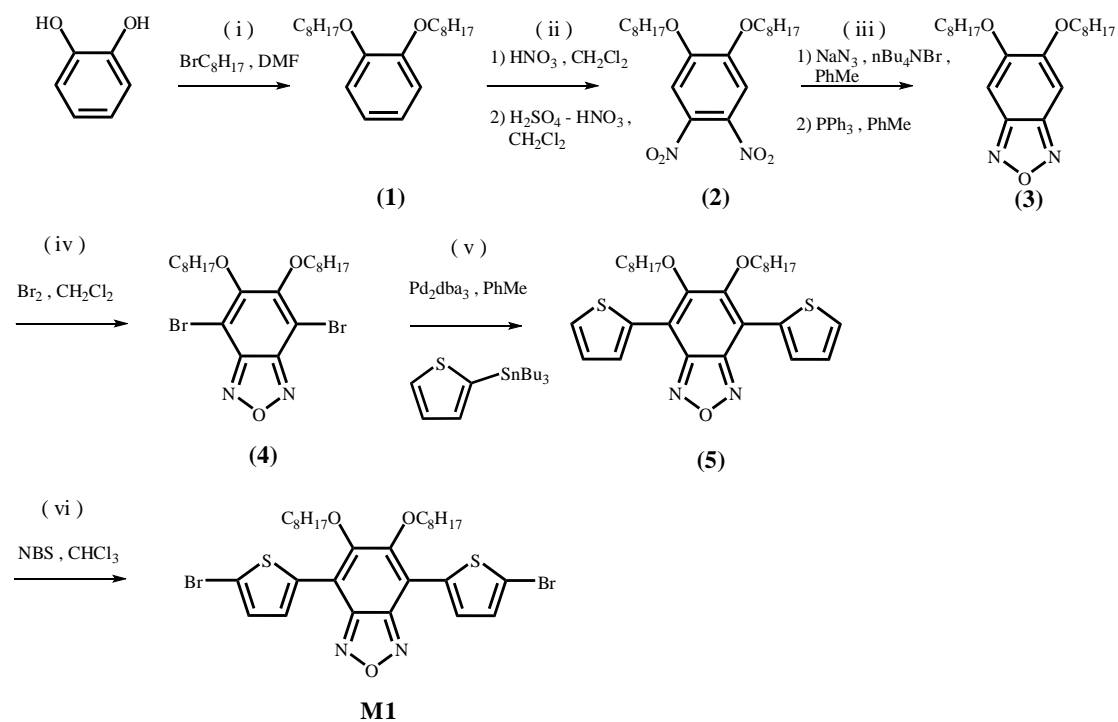
2,6-Bis(trimethylstannyl)-4,8-di(2-ethylhexyloxy)benzo[1,2-*b*:3,4-*b'*]dithiophene (**M2**)

was prepared according to reported procedures.¹ PC₆₁BM was purchased from

Solenne. All other reagents were used as received from commercial sources, without

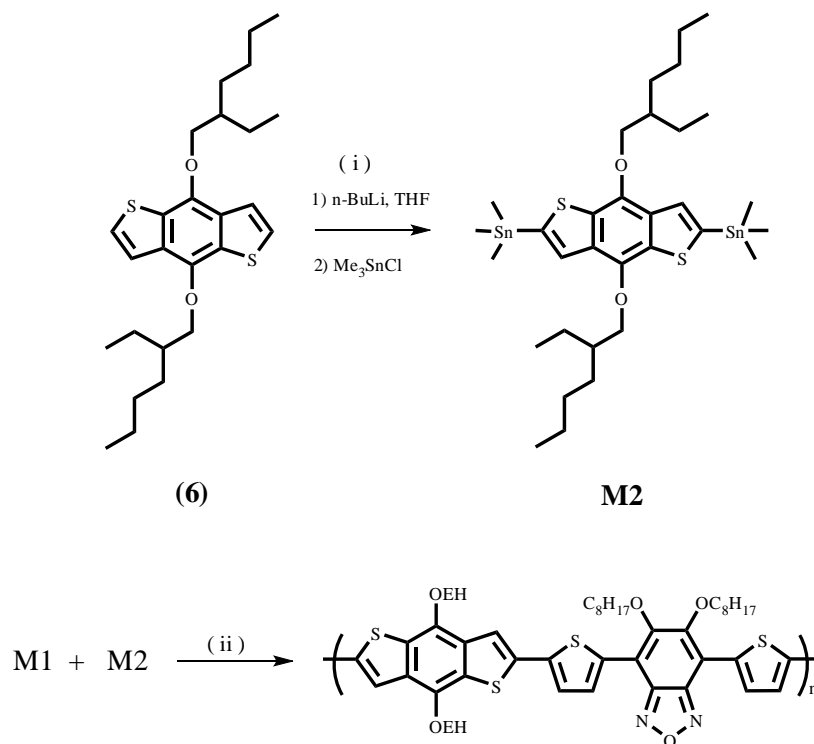
further purification.

Scheme S1 Synthesis of M1^a



^aReagents and conditions: (i) $\text{C}_8\text{H}_{17}\text{Br}$, K_2CO_3 , DMF, 100 °C, 40 h; (ii) 60% HNO_3 , CH_2Cl_2 , 10 °C, 1 h; then 100% HNO_3 , 40 h; (iii) NaN_3 , $n\text{-Bu}_4\text{NBr}$, toluene, 100 °C, 40 h; then PPh_3 , reflux, 24 h; (iv) Br_2 , AcOH, CH_2Cl_2 , RT, 3 days; (v) 2-(tributylstannyl)thiophene, Pd_2dba_3 , $\text{P}(o\text{-Tol})_3$, toluene, 90 °C, 16 h; (vi) NBS, CHCl_3 , 6 h.

Scheme S2 Syntheses of **M2** and **PBDTBO**^a



^aReagents and conditions: (i) $n\text{-BuLi}$, THF, $-78\text{ }^\circ\text{C}$, 2 h; then trimethylstannyl chloride, RT, overnight. (ii) Pd_2dba_3 , $\text{P}(o\text{-Tol})_3$, toluene, $90\text{ }^\circ\text{C}$, 24 h.

1,2-Bis(octyloxy)benzene (1)

A mixture of catechol (10 g, 0.091 mol), 1-bromooctane (40 g, 36 mL, 0.21 mol), and K_2CO_3 (38 g, 0.27 mol) in dry DMF (50 mL) was stirred at 100 °C under a N_2 atmosphere for 40 h. After cooling to room temperature, water (300 mL) was added; the organic layer was separated and the aqueous layer extracted with CH_2Cl_2 . The combined organic phases were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified through column chromatography (SiO_2 , hexane) to provide a colorless oil (27 g, 90%). 1H NMR (300 MHz, $CDCl_3$): δ 6.89 (s, 2H), 3.99 (t, $J = 6.9$ Hz, 4H), 1.84–1.77 (m, 4H), 1.49–1.29 (m, 20H), 0.90 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1, 120.9, 114.0, 69.2, 31.8, 29.4, 29.3, 29.2, 26.0, 22.6, 14.0.

1,2-Dinitro-4,5-bis(octyloxy)benzene (2)

65% HNO_3 (20 mL) was added dropwise to a two-neck round-bottom flask containing 1,2-bis(octyloxy)benzene (10 g, 29.9 mmol), CH_2Cl_2 (140 mL), and AcOH (140 mL) that was cooled at 10 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. The mixture was then cooled to 10 °C and 100% HNO_3 (50 mL) was added dropwise. The mixture was warmed to room temperature and stirred for 40 h before being poured into ice-water. The CH_2Cl_2 layer was separated and the aqueous

phase extracted with CH₂Cl₂. The organic phases were combined, washed sequentially with water, sat. NaHCO₃ (aq), and brine, and then dried (MgSO₄). Concentration under vacuum gave a crude product that was recrystallized from EtOH. Yield: 12 g (95%). ¹H NMR (300 MHz, CDCl₃): δ 7.29 (s, 2H), 4.09 (t, *J* = 6.6 Hz, 4H), 1.91–1.81 (m, 4H), 1.49–1.28 (m, 20H), 0.89 (t, *J* = 6.9 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 151.7, 136.4, 107.8, 74.7, 31.7, 30.1, 29.4, 29.2, 25.7, 22.6, 14.1.

5,6-Bis(octyloxy)benzo[*c*][1,2,5]oxadiazole (3)

A mixture of 1,2-dinitro-4,5-bis(octyloxy)benzene (**2**, 848 mg, 2.0 mmol), NaN₃ (650 mg, 10 mmol), and *n*-Bu₄NBr (130 mg, 0.4 mmol) was heated under reflux in toluene (10 mL) for 12 h. At this point, the starting material had been consumed (TLC); PPh₃ (630 mg, 2.4 mmol) was added and the mixture heated under reflux for an additional 24 h. The reaction mixture was cooled to room temperature and filtered through a short silica plug; the plug was rinsed with CH₂Cl₂. Evaporation of the solvents from the combined organic phases, under reduced pressure, afforded a crude solid that was recrystallized (EtOH) to yield an off-white solid (683 mg, 63%). ¹H NMR (300 MHz, CDCl₃): δ 6.79 (s, 2H), 4.05 (t, *J* = 6 Hz, 4H), 1.92–1.83 (m, 4H), 1.54–1.28 (m, 20H), 0.89 (t, *J* = 6.7 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 151.1, 146.7, 90.5, 69.3, 31.7, 29.2, 29.1, 28.5, 25.9, 22.6, 14.0.

4,7-Dibromo-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole (4)

AcOH (10 mL) and Br₂ (0.85 mL, 16.6 mmol) were added sequentially to a solution of 5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole (**3**, 1.504 g, 4.0 mmol) in CH₂Cl₂ (80 mL). The resulting mixture was stirred in the dark for 3 days at room temperature and then poured into aq. NaOH solution (10 g in 200 mL). The aqueous phase was extracted with CH₂Cl₂; the combined organic extracts were washed with brine and concentrated under reduced pressure to afford a crude solid that was purified through column chromatography [SiO₂, hexane/CH₂Cl₂, 9:1 (v/v)] to yield a white solid (2.2 g, 79%). ¹H NMR (300 MHz, CDCl₃): δ 4.13 (t, *J* = 9 Hz, 4H), 1.89–1.80 (m, 4H), 1.53–1.29 (m, 20H), 0.88 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 155.6, 147.4, 99.5, 75.3, 31.7, 30.1, 29.3, 29.2, 25.8, 22.6, 14.0.

5,6-Bis(octyloxy)-4,7-di(thien-2-yl)benzo[*c*][1,2,5]oxadiazole (5)

2-Tributylstannylthiophene (994 μL, 3.13 mmol) was added to a solution of 4,7-dibromo-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole (**4**, 665 mg, 1.25 mmol), Pd₂dba₃ (46 mg, 0.05 mmol), and tri-*o*-tolylphosphine (122 mg, 0.40 mmol) in dry toluene (10 mL) and then the reaction mixture was heated under reflux for 16 h under N₂. The reaction mixture was concentrated directly under vacuum. Dry column chromatography [SiO₂, hexane/CHCl₃, 10:1 (v/v)] afforded a yellow solid. Yield: 470

mg (70%). ^1H NMR (300 MHz, CDCl_3): δ 8.46 (d, $J = 3.6$ Hz, 2H), 7.50 (d, $J = 6.3$ Hz, 2H), 7.22 (t, $J = 4.5$ Hz, 2H), 4.14 (t, $J = 7.2$ Hz, 4H), 2.05–1.95 (m, 4H), 1.47–1.30 (m, 20H), 0.90 (t, $J = 3.3$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 151.6, 146.7, 132.8, 130.8, 128.0, 127.1, 113.0, 74.4, 31.8, 30.2, 29.5, 29.2, 25.8, 22.6, 14.0.

4,7-Bis(5-bromothien-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]oxadiazole (M1)

NBS (355 mg, 2 mmol) was added in one portion to a solution of 5,6-bis(octyloxy)-4,7-di(thien-2-yl)benzo[*c*][1,2,5]oxadiazole (**5**, 540 mg, 1 mmol) in CHCl_3 (40 ml) and glacial AcOH (40 mL) and then the mixture was stirred at room temperature for 20 h in the dark. The reaction mixture was concentrated directly onto Celite under vacuum. Dry column chromatography [SiO_2 , hexane/ CHCl_3 , 9:1 (v/v)] afforded an orange solid. Yield: 800 mg (92%). ^1H NMR (300 MHz, CDCl_3): δ 8.22 (d, $J = 4.2$ Hz, 2H), 7.15 (d, $J = 4.5$ Hz, 2H), 4.14 (t, $J = 7.5$ Hz, 4H), 2.04–1.94 (m, 4H), 1.47–1.30 (m, 20H), 0.90 (t, $J = 2.4$ Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3): δ 151.1, 146.1, 134.2, 131.1, 130.0, 116.3, 112.6, 74.7, 31.7, 30.1, 29.4, 29.2, 25.7, 22.6, 14.1. Anal. Calcd: C, 51.58; H, 5.48; N, 4.01. Found: C, 51.44; H, 5.47; N, 4.15.

PBDTBO

A mixture of **M1** (100 mg, 0.143 mmol), **M2** (110.6 mg, 0.143 mmol), and

tri-*o*-tolylphosphine (3.48 mg, 8.0 mol%) in dry toluene (4 mL) was degassed at 60 °C for 10 min. Tris(dibenzylideneacetone)dipalladium (2.6 mg, 2.0 mol%) was added to the mixture, which was then heated at 100 °C for 24 h. 2-Tributylstannylthiophene (0.09 mL) was added and then the mixture was stirred for 3 h. Subsequently, 2-bromothiophene (0.03 mL) was added to the mixture, which was then stirred for overnight. After cooling to room temperature, the solution was poured into MeOH (50 mL) and the solid filtered off. The crude polymer was dissolved in CHCl₃, filtered through a 0.5-μm polytetrafluoroethylene (PTFE) filter, and then re-precipitated from MeOH. The precipitated material was purified by washing with MeOH, hexane, and acetone in a Soxhlet system. The pure polymer was collected and dried to yield **PBDTBO** (110 mg, 75%). ¹H NMR (300 MHz, CDCl₃): δ 8.17 (br, 6H), 4.12 (br, 8H), 0.96–1.56 (m, 42H), 0.68 (s, 18H). Anal. Calcd: C, 68.25; H, 7.77; N, 2.84. Found: C, 67.53; H, 7.42; N, 2.67.

Measurements and Characterization

¹H and ¹³C NMR spectra were recorded using a Varian Unity-300 NMR spectrometer. Number-average molecular weights (*M*_n) were measured through gel permeation chromatography (GPC) using a Waters chromatography unit interfaced with a Waters 2414 differential refractometer. Three 5-μm Waters styragel columns were connected

in series in decreasing order of pore size (104, 103, and 102 Å); THF was the eluent; standard polystyrene samples were used for calibration. Differential scanning calorimetry (DSC) was performed using a Perkin–Elmer Pyris DSC1 instrument operated at a heating rate of 20 °C min⁻¹ under a N₂ purge. Thermogravimetric analysis (TGA) was performed using a TA Instrument Q500 apparatus operated at a heating rate of 10 °C min⁻¹ under a N₂ atmosphere. UV–Vis spectra of the polymer in dilute 1,2-dichlorobenzene (DCB) solution (1 × 10⁻⁵ M) and in the form of a thin solid film were recorded using an HP Agilent-8453 diode array spectrophotometer. The solid film for UV–Vis spectroscopic analysis was obtained by spin-coating a DCB solution of the polymer (10 mg mL⁻¹) onto a quartz substrate. Electrochemical cyclic voltammetry (CV) was performed using a BAS 100 electrochemical analyzer and solutions in MeCN containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the electrolyte; the scan rate was 100 mV s⁻¹. A glassy disk carbon electrode coated with a thin film of polymer was used as the working electrode; a Pt wire was the counter electrode; Ag/Ag⁺ (0.01 M AgNO₃) was the reference electrode; ferrocene was the internal standard. Topographic images of the active layers were recorded using a Digital Instruments Nanoscope III atomic force microscope operated in the tapping mode under ambient conditions.

Electrochemical properties

Based on the fact that the oxidation potential of a **BDT** homopolymer with different alkyl chain length has been reported elsewhere² to be +0.44 V, we determined that the onset oxidation potential (E_{ox}) that was contributed by **BDT** and the onset reduction potential (E_{red}) that was contributed by **BO** were +0.47 and -1.64 V, respectively, versus ferrocene/ferrocenium (Fc/Fc⁺). The HOMO and LUMO energy levels can also be obtained relative to Fc/Fc⁺ as the reference electrode (4.8 eV below the vacuum level); here, the values were -5.27 and -3.16 eV respectively.

Device Fabrication and Characterization

An indium tin oxide (ITO)-coated glass substrate was cleaned sequentially with detergent, DI water, acetone, and isopropyl alcohol for 20 min and then dried in an oven. Before use, the substrate was treated with UV ozone for 30 min. A 0.45- μ m filtered of Poly(ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS, Baytron P VP AI 4083) was then spun-cast (5000 rpm, 50 s) onto the clean ITO substrates. After baking at 120 °C for 30 min in air, the substrates were transferred to a N₂-filled glove box. The active layers were prepared by dissolving the polymer and PC₆₁BM at different weight ratios, but with a fixed total concentration (40 mg mL⁻¹), in DCB with heating at 100 °C overnight, filtered through a 0.5- μ m polytetrafluoroethylene

(PTFE) filter, and spun-cast (between 600 and 2000 rpm for 60 s) onto the PEDOT:PSS layer. The substrates were then dried at room temperature under N₂ for 2 h. After thermal deposition of a 30-nm-thick film of Ca and then a 100-nm-thick Al film as the cathode at a pressure of ca. 1×10^{-6} mbar, the devices were ready for measurement. Four devices were prepared per substrate, with an active area of 10 mm² per device. The photophysical properties of the devices were measured under AM 1.5 radiation (100 mW cm^{-2}) using an Agilent 4156 semiconductor parameter analyzer. The spectral mismatch factor was calculated through comparison of the solar simulator spectrum and the AM 1.5 spectrum recorded at room temperature. External quantum efficiencies (EQEs) were measured using a system established by Optosolar, Inc. Monochromatic light was obtained from a 500-W Xe lamp source after passing through a monochromator. The theoretical short-circuit density was calculated using the equations

$$S_{\tau}(\lambda) = \frac{q\lambda}{hc} EQE(\lambda)$$

and

$$J_{sc} = \int_{\lambda_2}^{\lambda_1} E_{\text{Ref}}(\lambda) S_{\tau}(\lambda) d\lambda$$

where $S_{\tau}(\lambda)$ is the spectral responsivity of the test device, the constant term q/hc is 8.0655×10^5 , and $E_{\text{Ref}}(\lambda)$ is the reference spectral irradiance (AM1.5). Hole-only mobility measurement was performed using a device having the structure

ITO/PEDOT:PSS/**PBDTBO**:PC₆₁BM/Au. The hole mobility was determined by fitting the dark J - V curve into the space-charge-limited current (SCLC) model, based on the equation

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_h \frac{V^2}{L^3}$$

where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the material, μ_h is the hole mobility, V is the voltage drop across the device, and L is the thickness of the active layer.

Fig.S5 show transmission electron microscopy (TEM) images of **PBDTBO**/PC₆₁BM films at weight ratios of (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4. Because the electron scattering density of PC₆₁BM is higher than that of the conjugated polymer, the **PBDTBO** domains appear as bright regions whereas the dark regions can attributed to PC₆₁BM domains. These images show that the size of the aggregated PC₆₁BM domains remain about the same while the number of aggregated PC₆₁BM domains increases when the weight ratio of PC₆₁BM to **PBDTBO** increases. This phenomenon is consistent with the fact that the surface of the **PBDTBO**/PC₆₁BM films becomes rougher when the PC₆₁BM weight ratio increases in the AFM study (see Fig.S4).

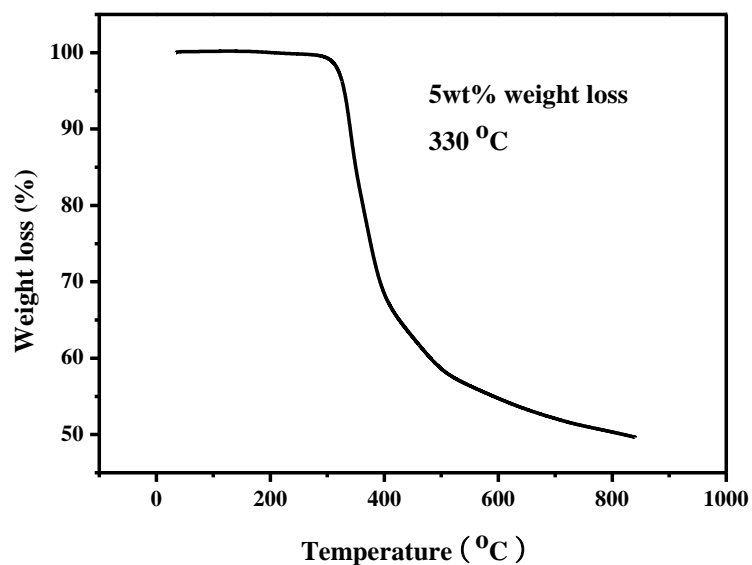


Fig. S1 TGA thermogram of **PBDTBO**, recorded at a heating rate of 10 °C min^{-1} under a N_2 atmosphere.

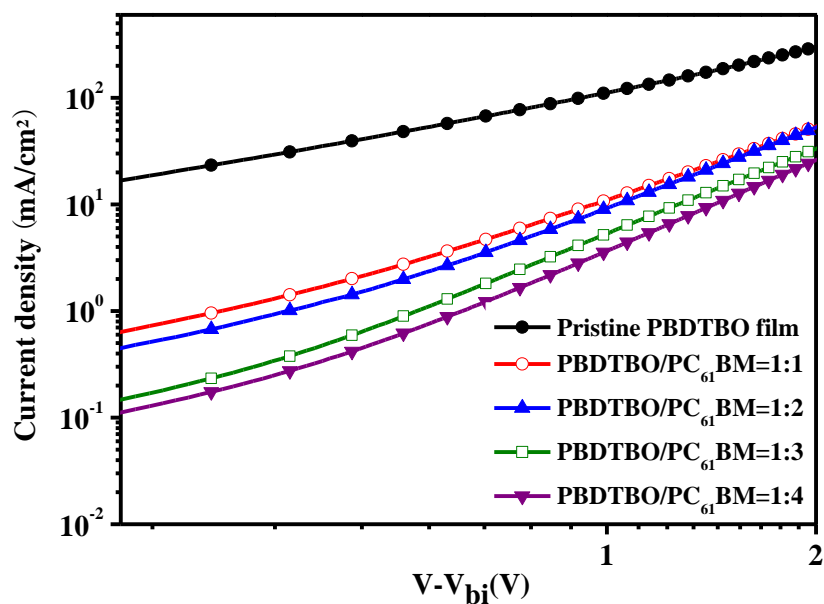


Fig. S2 Dark $J-V$ curves for hole-dominated carrier devices incorporating the pristine and blend films at various blend weight ratios.

Weight ratio of active layer	Thickness (nm)	μ_h ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
Pristine PBDTBO film	80	4.6×10^{-4}
PBDTBO / PC_{61}BM = 1:1	135	1.7×10^{-4}
PBDTBO / PC_{61}BM = 1:2	122	1.1×10^{-4}
PBDTBO / PC_{61}BM = 1:3	125	7.7×10^{-5}
PBDTBO / PC_{61}BM = 1:4	120	4.9×10^{-5}

Table S1 Hole mobilities in the pristine and blend films at various blend weight ratios.

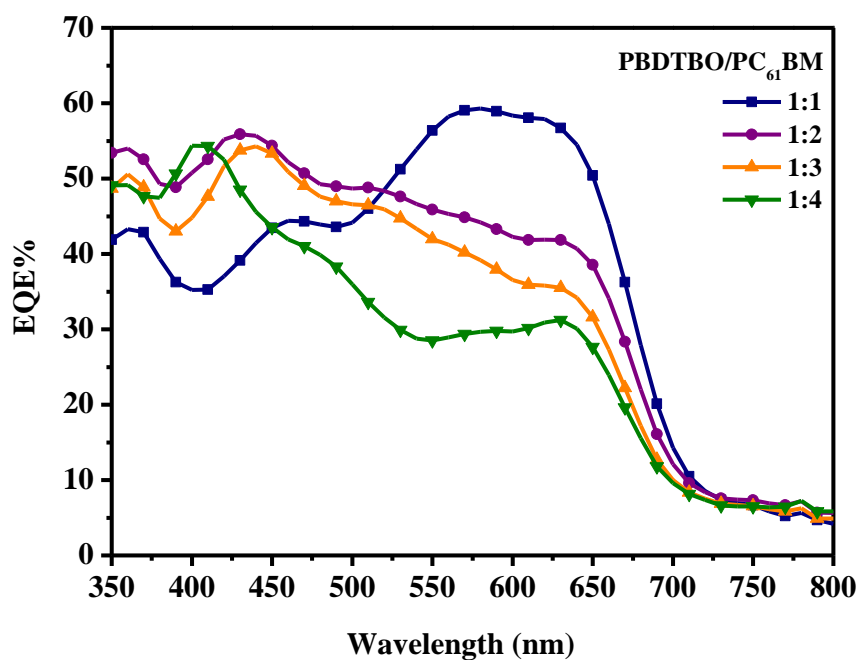


Fig. S3 EQE spectra of BHJ solar cells incorporating **PBDTBO**/ PC_{61}BM blends at various weight ratios.

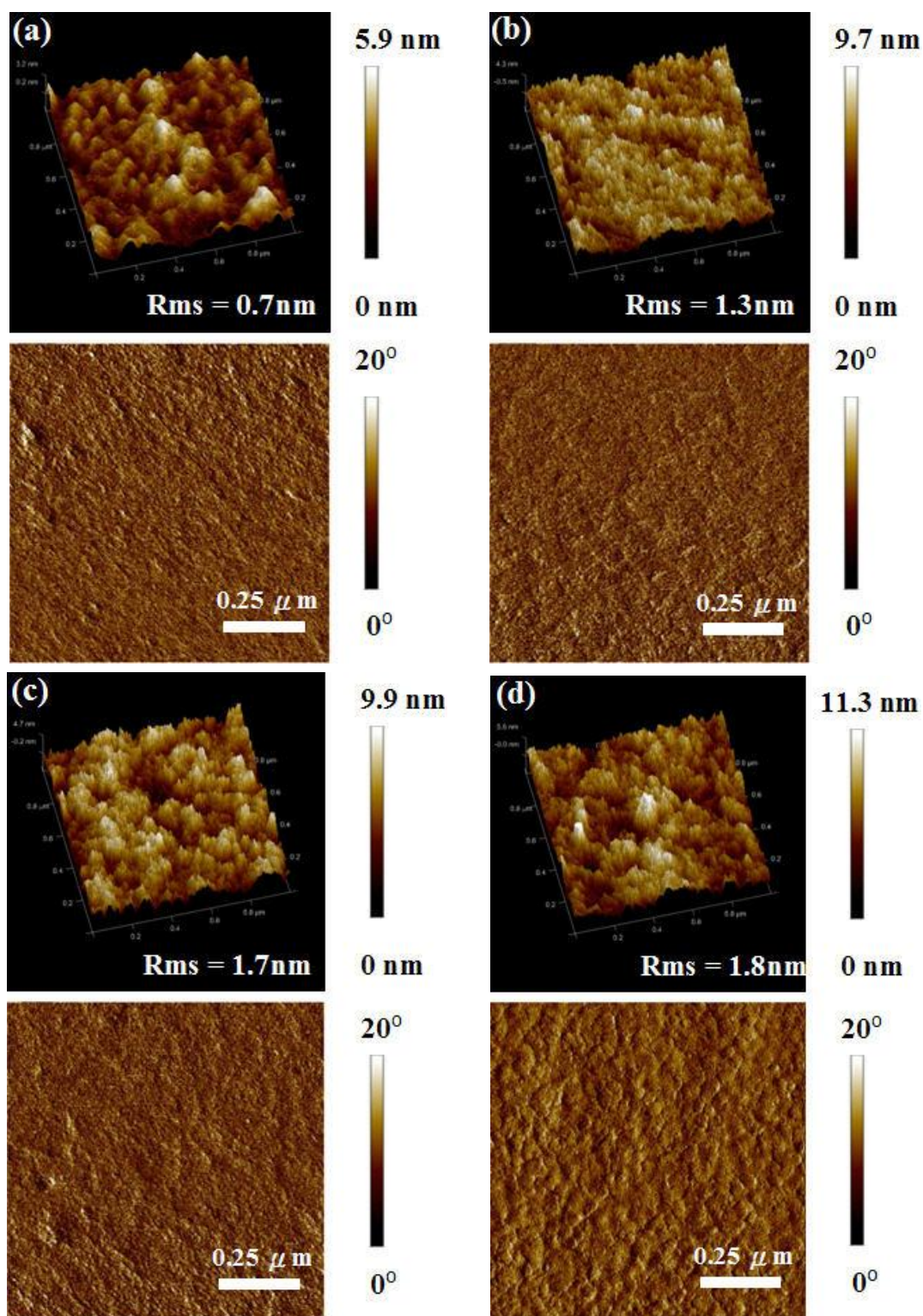


Fig. S4 Height and phase images of PBDTBO/PC₆₁BM films at blend weight ratios of (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4.

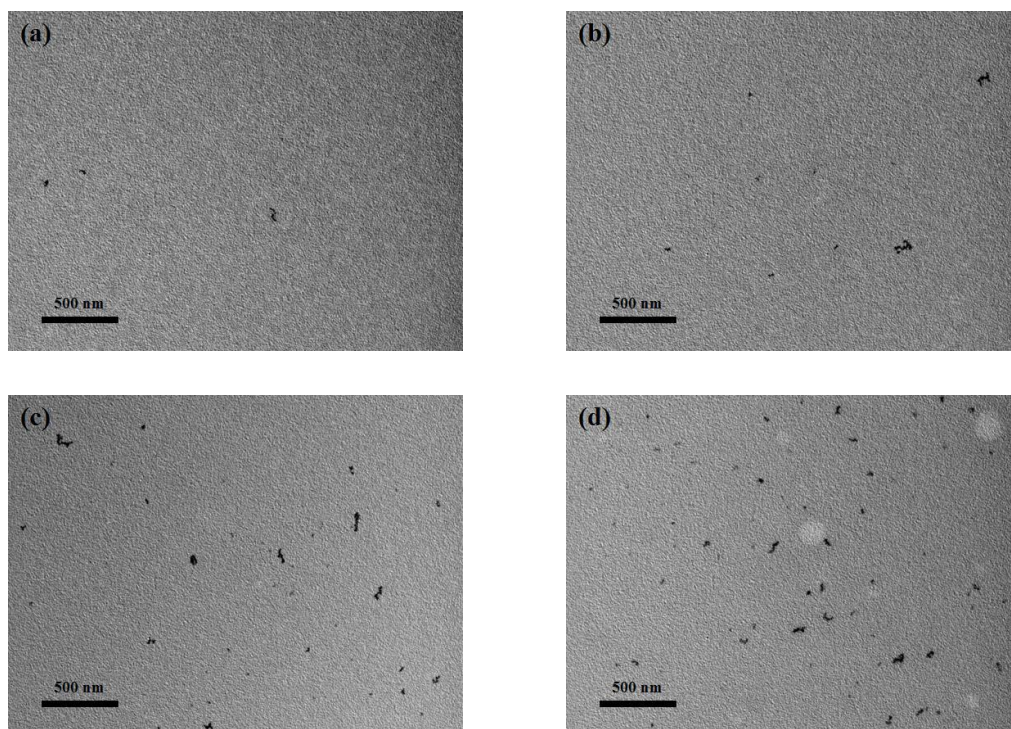


Fig. S5 TEM image of **PBDTBO/PC₆₁BM** films at blend weight ratios of (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:4.

References

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