Supplementary Information

Naphtho[1, 2-*b*: 5, 6-*b*’]difuran as a New Building Block towards Efficient Polymer Solar Cells

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1. Experimental section

1.1 Materials. *n*-BuLi, Pd(PPh$_3$)$_4$ and Sn(CH$_3$)$_3$Cl were obtained from Acros Organics, and they were used as received. Toluene was dried over P_2O_5 and freshly distilled prior to use. Other reagents and solvents were purchased commercially and used without further purification.4,7-Di(5-bromothiophen-2-yl)-5,6-dioctyloxybenzo-[c][1,2,5]-thiadiazole (M2) was prepared according to the reported procedures.[1,2]

1.2 Characterization. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker DMX-400 spectrometer, chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. EI-MS spectra were obtained with use of an electron impact ionization procedure. Number-average (M_n) and weight-average (M_w) molecular weights were measured by gel permeation chromatograph (GPC) method using polystyrene as a standard ($CHCl_3$ as the eluting solvent). TGA was performed on a PE TGA-7 at a heating rate of 20 K/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSCII at a heating or cooling rate of 10 K/min under N_2 . UV-vis absorption spectra were taken using a Hitachi U-3010 UV-Vis spectrophotometer. For solid state measurements, polymer solution in chloroform was cast on quartz plates. Optical bandgap was calculated from the onset of the absorption band. Cyclic voltammograms (CV) were recorded on a CHI 660C (China) Electrochemical Workstation using platinum disk coated with the polymer film, Pt wire and Ag/AgCl electrode in an anhydrous and argon-saturated solution as working electrode, counter electrode and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution at a scan rate of 50 mV/s. AFM images were obtained using a Veeco's Dimension V atomic force microscopic (AFM) in the tapping mode. Transmission electron microscope (TEM) measurements were performed in a JEM-2100F.

1.3 Fabrication of organic field-effect transistors. Organic field-effect transistors (OFETs) were fabricated with a bottom-gate top-contact configuration. Thermally oxidized (100) silicon wafers (n^{++} doped) with a SiO_2 thickness of 300 nm were sequentially cleaned with detergent, deionized water, acetone and ethanol in ultrasonic bath. Then hydrophilic treatment of these silicon wafers was performed by soaking the substrates in a mixture of deionized water, 25% ammonium hydroxide and 30 % H_2O_2 (5:1:1 by volumetric ratio) for 20 min at 80 °C followed by rinsing with deionized water and dried with nitrogen flow. Octadecyltrimethoxysilane self-assembled monolayer was selected as a dielectric modification layer in OFETs according to the reported method.[3] The conjugated polymer film was deposited from its chlorobenzene solution (6 mg/mL) on the substrate by spin-coating at 1200 rpm for 40 s. Before spin-coating, the polymer's chlorobenzene solution was let to stand on the dielectric modification layer for 20 minutes for better wetting of the surface. Finally, Au source and drain electrodes were deposited on the polymer semiconductor layer through vacuum thermal evaporation. The characteristics of OFETs were measured by a Keithley 4200 SCS semiconductor parameter analyzer under ambient conditions. The field-effect mobility (μ) was calculated by using the following equation in the saturation regime:

$$I_{\mathrm{DS}} = \frac{WC_i}{2L}\mu\left(V_{\mathrm{GS}} - V_{\mathrm{T}}\right)^2$$

where I_{DS} is the drain current, W and L are the channel width (8800 μm) and length (80 μm), respectively, C_i is the capacitance per unit area of the gate insulator (11.5 nF/cm^2), V_{GS} is the gate voltage, and V_{T} is the threshold voltage. The transfer curve was obtained at a V_{DS} value of -50 V.

1.4 Fabrication and characterization of polymer solar cells. The PSCs were fabricated in the configuration of the traditional sandwich structure with an indium tin oxide (ITO) glass positive electrode and a metal negative electrode. Patterned ITO glass with a sheet resistance of 10Ω/□ was purchased from CSG HOLDING Co. LTD. (China). The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol, then treated in an ultraviolet-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. The PEDOT:PSS (poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)) (Baytron P4083, Germany) was filtered through a 0.45 μm filter and spin coated at 2000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT:PSS film was baked at 150 ºC for 15 min in the air to give a thin film with a thickness of 40 nm. A blend of the polymer and PCBM was dissolved in orth-dichlorobenzene (*o*-DCB), and spin-cast at 3000 rpm for 45 s onto the PEDOT:PSS layer. The substrates were then dried at 70 ^{o}C for 15 min. The thickness of the photoactive layer is in the range of 70-100 nm measured by Ambios Technology XP-2 profilometer. A bilayer cathode consisting of Ca (~20 nm) capped with Al (~100 nm) was thermal evaporated under a shadow mask with a base pressure of ca. 10^{-5} Pa. The active area of the PSCs is 4 mm^2. Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW/cm^2 (Oriel 67005, 500 W) calibrated by a standard silicon cell. *J-V* curves were recorded with a Keithley 236 digital source meter.

1.5 Synthesis of compound 1. Under N_2, 1,5-dihydroxynaphthalene (6.40 g, 40.0 mmol), 1-bromo- undecan-2- one (22.4 g, 90 mmol) and anhydrous K_2CO_3 (16 g, 116 mmol) were mixed in dry acetonitrile (200 mL) and heated to reflux for 4 h. The cooled reaction mixture was then poured into water and extracted three times with CH_2Cl_2. The combined organic extractions were washed with water successively, dried over $MgSO_4$ and then evaporated. The crude product was purified by chromatography on silica gel (elution with

CH_2Cl_2/hexane=10/1). Compound 1 was obtained (14.8 g, 75%) as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.93 (d, 2H), 7.74 (d, 2H), 7.54 (d, 2H), 4.62 (t, 4H), 2.78 (t, 4H), 1.77-1.27(m, 28H), 0.88 (t, 6H). GC-MS: *m/z* =497. Elemental analysis: calc. for $C_{32}H_{48}O_4$(%): C, 77.38; H, 9.47; O, 12.88; found: C, 77.27; H, 9.60; O, 13.03.

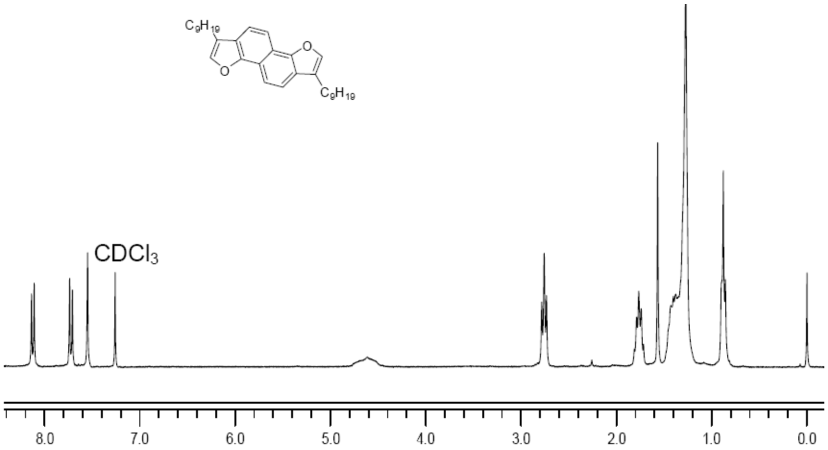
1.6 Synthesis of compound 2. Compound 1 (4.96 g, 10 mmol) in methylene chloride (50 mL) was added CH_3SO_3H (9.6 g, 100 mmol) to give a deep blue solution. The reaction mixture was stirred for 4 h under reflux and then poured into ice, the extractions were washed with water, dried over $MgSO_4$ and then evaporated. The crude product was purified by chromatography on silica gel (elution with hexane). Compound 2 was obtained (2.85 g, 62%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.14 (d, 2H), 7.74 (d, 2H), 7.55 (d, 2H), 2.78 (t, 4H), 1.76-1.26 (m, 28H), 0.88 (t, 6H). ^{13}C NMR(100 MHz, $CDCl_3$, ppm):151.41, 140.10, 123.35, 122.01, 119.05, 118.72, 114.99, 31.89, 31.30, 29.85，29.58, 29.49, 29.34, 23.71, 22.68, 14.12. GC-MS: *m/z* =461. Elemental analysis: calc. for $C_{32}H_{44}O_2$(%): C, 83.43; H, 9.63; O, 6.95; found: C, 83.37; H, 9.60; O, 6.83.

1.7 Synthesis of M1. Compound 2 (0.92 g, 2 mmol) and 50 mL of dry THF were added into a flask under an inert atmosphere. The solution was cooled down to -78 °C and 3.0 mL of n-butyllithium (7.0 mmol, 2.4 mol/L) was added dropwisely. After being stirred at -78 °C for 1 h, then 8 mL of trimethyltin chloride (8.0 mmol, 1 mol/L) was added in one portion. The cooling bath was removed and the reactant was stirred at ambient temperature overnight. Finally it was poured into 100 mL of iced water and extracted by CH_2Cl_2. The organic layer was washed by water two times, then dried by anhydrous $MgSO_4$, and evaporated to give a yellow solid. The residue was recrystallized from isopropanol to afford the target monomer M1 as yellow needles (1.01 g, 64%). ^{1}H NMR

(400 MHz, $CDCl_3$, ppm): 8.11 (d, 2H), 7.66 (d, 2H), 2.74 (d, 4H), 1.59-1.29 (m, 28H), 0.88 (t, 6H), 0.47 (s, 18H). ^{13}C NMR(100 MHz, $CDCl_3$, ppm): 158.71, 155.29, 132.92, 123.47, 118.62, 118.18, 114.80, 31.91, 31.32, 29.81, 29.59, 29.49, 29.34, 25.24, 22.69, 14.13, -8.71. GC-MS: *m*/*z* =786. Elemental analysis: calc. for $C_{32}H_{44}O_2$(%): C, 58.04; H, 7.69; O, 4.07; found: C, 58.11; H, 7.60; O, 4.13.

1.8 Synthesis of PNDFDTBT. M1 (0.157 g, 0.2 mmol), M2 (0.142 g, 0.2 mmol) and 10 mL of dry toluene were put into a two-necked flask. The solution was flushed with N_2 for 10 min, then $Pd(PPh_3)_4$ (10 mg) was added into the flask. The solution was flushed with N_2 again for 20 min. The oil bath was heated to 110 °C, and the reactant was stirred for 24 h at this temperature under N_2 atmosphere. Then the reaction mixture was cooled to room temperature, and the polymer was precipitated by the addition of 100 mL of methanol and filtered through a Soxhlet thimble, which was then subjected to Soxhlet extractions with methanol, hexanes and chloroform. The polymer was recovered as a solid from the chloroform fractions by rotary evaporation. Finally, the blue solid was obtained (0.087 g, yield: 42%). ^1H NMR (400 MHz, $CDCl_3$, ppm): 8.80-7.27（br, 8H）, 4.41-4.10(br, 4H), 3.20-2.90(br, 4H), 2.10-0.80(br, 64H). Anal. Calcd for $(C_{62}H_{80}N_2O_4S_3)_n$ (%): C, 73.66; H, 8.31; N, 2.68. Found (%): C, 73.62; H, 8.17; N, 2.71.

1. J. Bouffard, T.M. Swager. *Macromolecules.* 2008, **41**, 5559.
2. P. Ding, C. Chu, B. Liu, B. Peng, Y. Zou, Y. He, K.Zhou, C.Hsu. *Macromol. Chem. Phys*. 2010, **211**, 2555.
3. Y. Ito, A.A. Virkar, S.Mannsfeld, J. Oh, M.Toney, J. Locklin, Z. Bao, *J. Am. Chem. Soc.*, 2009, **131**, 9396.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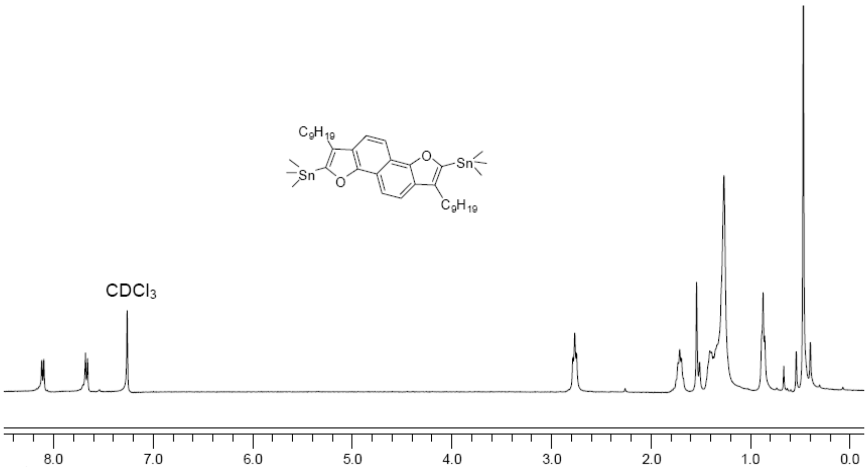
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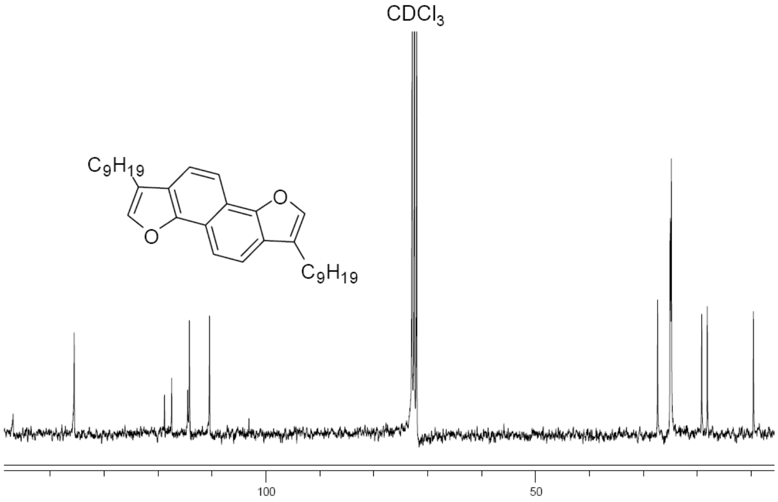
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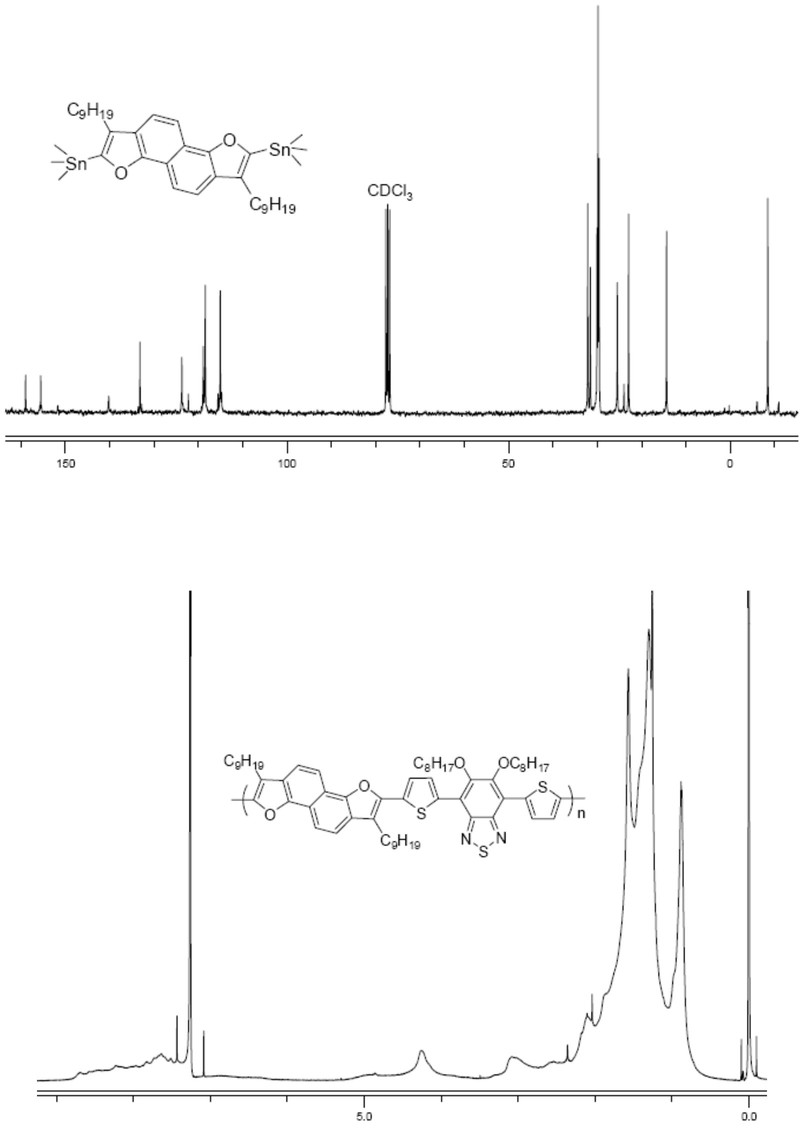

Fig. S1 ^{1}H NMR and ^{13}C NMR spectra of the new compounds, ^{1}H NMR spectrum of **PNDFDTBT** in $CDCl_3$.

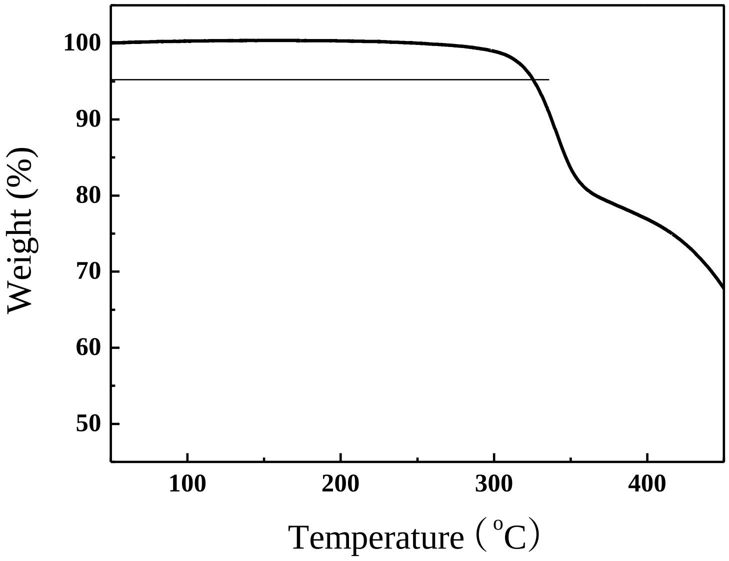

Fig. S2. TGA thermogram of **PNDFDTBT** with a heating rate of 20 K/min.

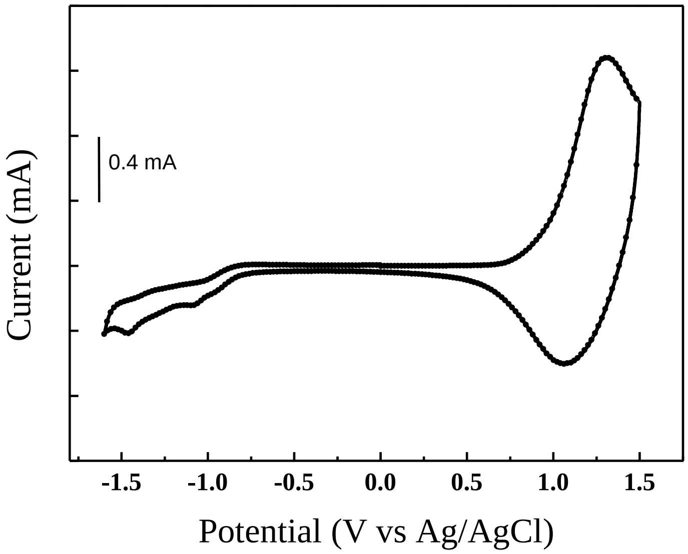

Fig. S3. Cyclic voltammogram of **PNDFDTBT** film cast on platinum disk in 0.1 M Bu_4NPF_6 /CH_3CN solution at 50 mV/s.

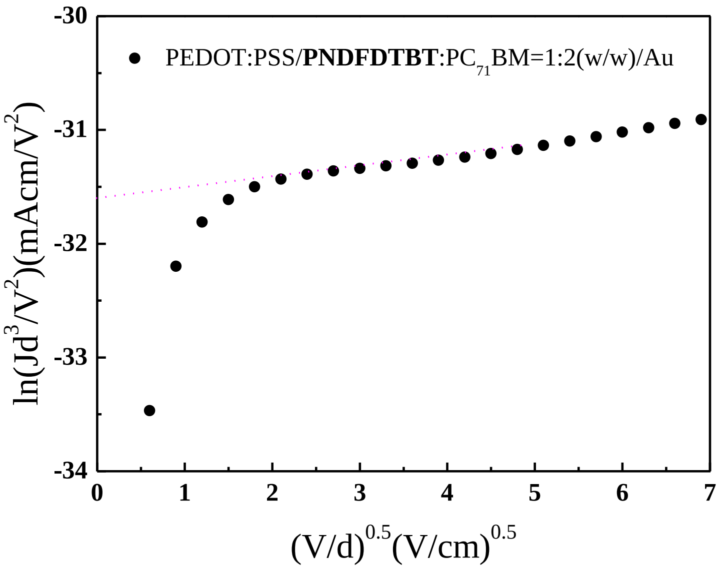

Fig. S4. $\ln(Jd^3/V^2)\,\mathrm{Vs}\,(V/d)^{0.5}$ plots of the blends of **PNDFDTBT** and PC$_{71}$BM for the measurement of the hole mobility by SCLC method.

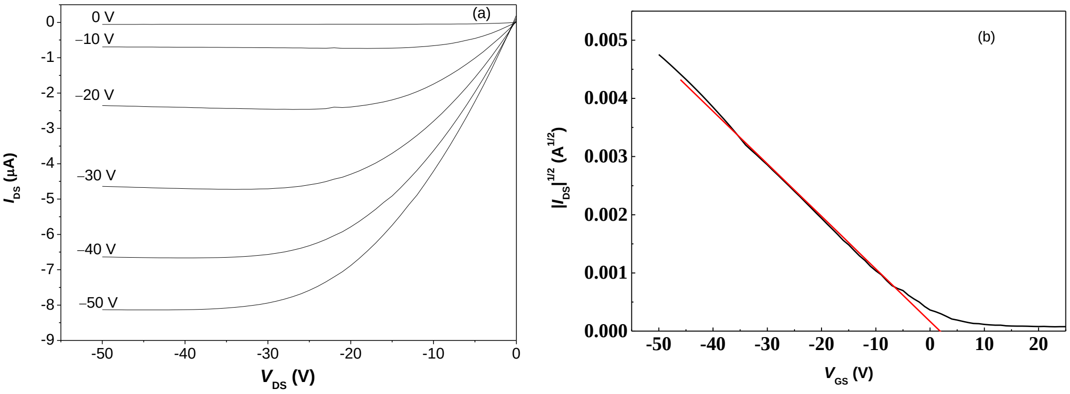

Fig. S5. Output and transfer characteristics of **PNDFDTBT** (a) output; (b) transfer.

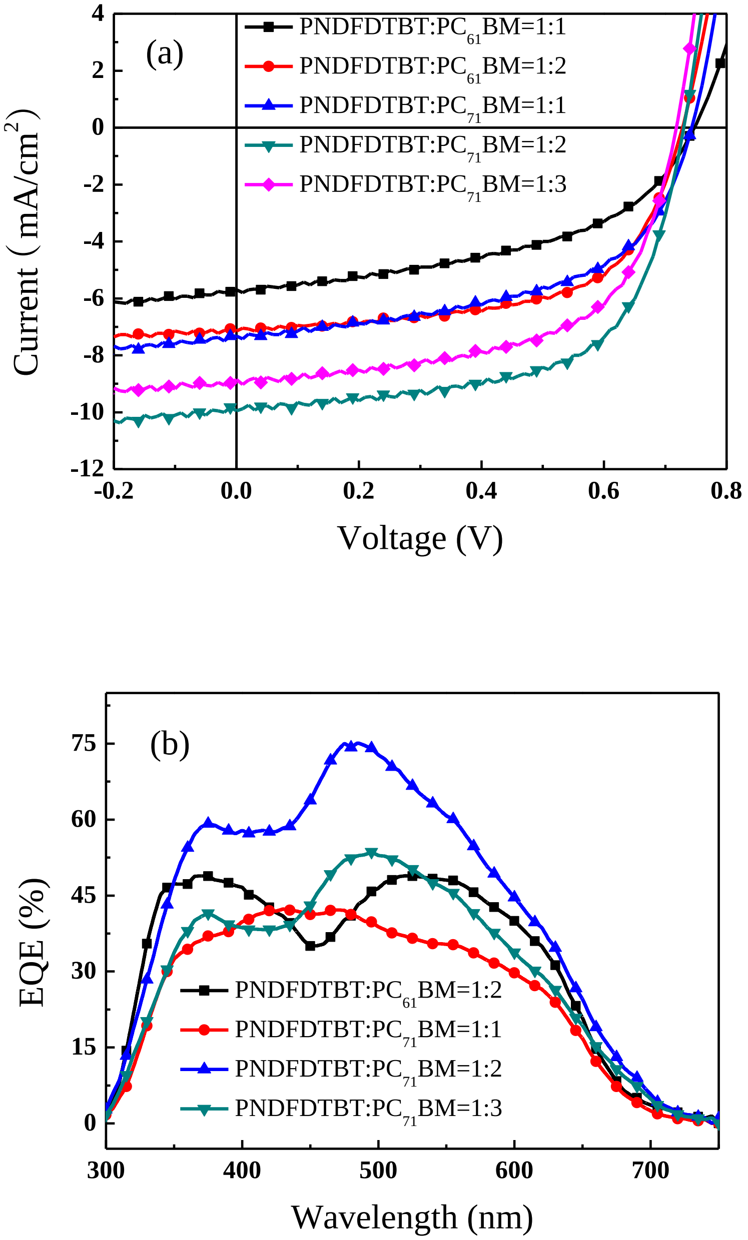

Fig. S6. Typical *J*-*V* curves (a) and *EQE* spectra (b) of the polymer solar cells based on **PNDFDTBT**:PCBM.

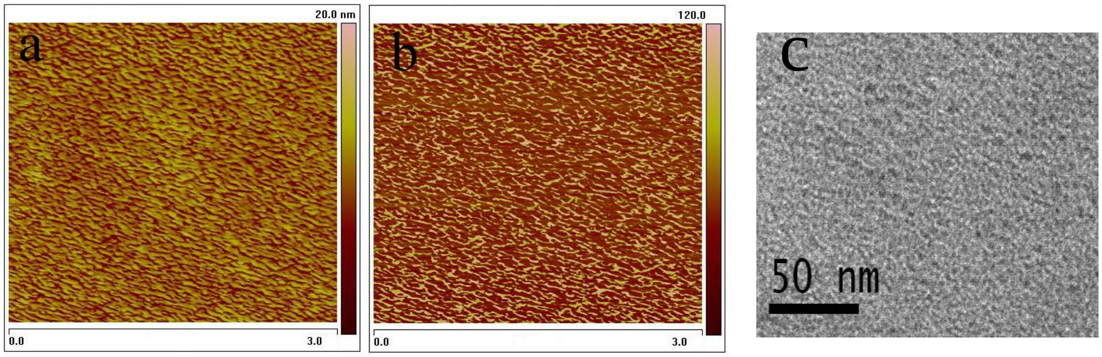

Fig. S7. AFM and TEM images of **PNDFDTBT**:PC$_{71}$BM (1:2) in *o*-DCB: (a) height image; (b) phase image; (c) TEM image.

Table S1 Photovoltaic properties of PSCs based on **PNDFDTBT**:PCBM with different weight ratios.

Active layer	V_{oc}	J_{sc}	*FF*	*PCE*
PNDFDTBT:PC$_{61}$BM=1:1	0.75	5.71	48.2	2.06
PNDFDTBT:PC$_{61}$BM=1:2	0.73	7.15	60.4	3.15
PNDFDTBT:PC$_{71}$BM=1:1	0.74	7.33	54.5	2.95
PNDFDTBT:PC$_{71}$BM=1:2	0.73	9.96	61.8	4.50
PNDFDTBT:PC$_{71}$BM=1:3	0.72	8.85	59.9	3.81