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Supporting Information

Novel Donor–Acceptor Polymer Containing o-Fluoro-p-alkoxyphenyl-Substituted Benzo[1,2-b:4,5-b′]dithiophene Unit for Polymer Solar Cells with Power Conversion Efficiency Exceeding 9%

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Materials

All reagents were bought from commercial sources and were used without further purification. The solvents were purified with standard methods. All air and water sensitive reactions were performed under an argon atmosphere. Silica gel (200-300 mesh) was used for column chromatography. New monomers were characterized by ^{1}H NMR, ^{13}C NMR, and Atmospheric Pressure Chemical Ionization-Time of Flight (APCI-TOF) high resolution mass spectra (HRMS).

Characterization

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-600 spectrometer. APCI-TOF HRMS were performed on Bruker Maxis UHR-TOF (both positive and negative ion reflector mode). The molecular weight and polydispersity were determined by gel permeation chromatography (GPC) analysis using an ELEOS System. Thermogravimetric analysis (TGA) measurements were performed using a TA-Q600 analyzer with a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

The ultraviolet-visible (UV-Vis) spectra were measured on a Varian Cary 50. The electrochemical behaviors of the fullerene derivatives were investigated by cyclic voltammograms (CV). The CV was performed in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) (0.1 M) in acetonitrile. A three-electrode cell consisting of a glassy carbon working electrode, a Pt counter electrode and an Ag/AgCl reference electrode was used. The scan rate was 100 mV/s. The polymer films were coated on a glassy carbon electrode by dipping the corresponding solutions onto the electrode. The potential of ferrocene/ferrocenium (Fc/Fc^+) was measured to be 0.40 V compared to the Ag/AgCl electrode under the same conditions. It is assumed that the redox potential of Fc/Fc+, has an absolute energy level of -4.8 eV to vacuum. Ultraviolet photoelectron spectroscopy (UPS) was perfromed on the Thermo Scientific ESCALab 250Xi. The gas discharge lamp was used for UPS, with helium gas admitted and the He I (21.22 eV) emission line employed. The helium pressure in the analysis chamber during analysis was about 2×10^{-8} mbar. The data were acquired with -10 V bias. Atomic force microscopy (AFM) images were obtained on an Agilent 5400 scanning probe microscope using AC mode. The blend films of conjugated polymer and $PC_{71}BM$ were prepared under the same experimental conditions as that of optimized photovoltaic devices fabrication. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-1011 at an accelerating voltage of 100 kV. The GIWAXS data were obtained at beam line BL16B1 of the Shanghai Synchrotron Radiation Facility (SSRF).

Fabrication of photovoltaic devices

Photovoltaic devices with a layered structure of ITO/PEDOT:PSS/polymers:$PC_{71}BM$ /Ca (10 nm)/Al (100 nm) were fabricated on ITO coated glass substrates (15 mm×15 mm). The ITO coated glasses were cleaned in an ultrasonic bath with detergent, ultra pure water, acetone, and isopropyl alcohol sequentially for 20 min, and then oxygen plasma treated for 20 min. The substrates were spin-coated with PEDOT:PSS at 5000 rpm, and dried at 120 ^{o}C for 20 min in air. The copolymers and $PC_{71}BM$ were dissolved in deoxygenated anhydrous *o*-dichlorobenzene in the weight ratios of 1:1, 1:1.5 and 1:2, respectively and stirred overnight in glovebox. An active layer consisting of the blend of the copolymer and $PC_{71}BM$ was then spin coated on PEDOT:PSS. A typical concentration of the polymer/$PC_{71}BM$ blending solution was 20 mg/mL. Subsequently Ca (10 nm) and Al (100 nm) were thermally evaporated in a vacuum of 2×10^{-4} Pa on top of the active layer as cathode. A shadow mask with the area of 0.1 cm^2 was used to define the device area when evaporating the cathode. Photovoltaic performance was characterized under illumination with an AM 1.5G (100 mW cm^{-2}), and the current–voltage curves were recorded using a Keithley 2400 source meter. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

Synthesis of compound 1

To the solution of 4-bromo-3-fluorophenol (9.50 g, 50 mmol), anhydrous potassium carbonate (13.80 g, 100 mmol) in dry DMF (150 ml), 7-(bromomethyl)pentadecane (15.2 g, 50 mmol) was added in one portion. The reaction mixture was stirred at 100 ^{o}C for 24 h, and then was cooled to room temperature. Thereafter, it was poured into water (100 mL) and exacted three times with hexane. The organic layers were combined and dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by silica gel flash column chromatography using petroleum ether as an eluent to afford compound **1** as colorless oil (17.60 g, 42.49 mmol) in 85% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 7.41 (t, 2H), 6.71 (dd, 2H), 6.63 (dd, 2H), 3.81 (t, 4H), 1.78 (m, 2H), 1.48–1.24 (m, 48H), 0.96–0.87 (m, 12H).

Synthesis of compound 2

Compound **1** (10.35 g, 25 mmol) was dissolved in dry THF (50 mL) in the argon atmosphene, and then *n*-butyllithium solution (25 mmol, 10.00 mL, 2.5 M in hexane) was added dropwise at -78 ^{o}C. After addition, the reaction mixture was maintained at this temperature for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (2.20 g, 10 mmol) and allowed to warm to 55 ^{o}C for 2 h. The solution was cooled down to room temperature and then $SnCl_2{\cdot}2H_2O$ (18.05 g, 80 mmol) in 10% aqueous HCl (20.0 mL) was added. The solution was refluxed for 2 h and then the cooled mixture was poured into water and extracted with hexane. The combined organic phase was dried over Na_2SO_4 and evaporated to obtain the crude product as pale yellow oil, which was purified on a silica gel column, eluting with petroleum ether as eluent. Compound **2** was obtained as a pale yellow solid (3.87 g, 4.50 mmol) in 45% yield. ^{1}H NMR (600 MHz, CDCl3), δ(ppm): 7.57–7.49 (m, 2H), 7.40 (dd, 2H), 7.18–7.15 (m, 2H), 6.91–6.86 (m, 2H), 6.84 (d, 2H), 3.92 (d, 4H), 1.87–1.80 (m, 2H), 1.52–1.24 (m, 48H), 0.93–0.86 (m, 12H).

Synthesis of compound 3

Compound 2 (3.44 g, 4.0 mmol) was dissolved into 50 mL of methylene chloride in a 100 mL flask. Bromine (1.28 g, 8.0 mmol) was dissolved into 20 mL of methylene chloride in a funnel and slowly dropped into the flask under an ice-water bath, and then the reactant was stirred at 40 °C over night. Then the reaction mixture was cooled to room temperature. The solvent was removed under vacuum to afford crude product as yellow solid, which was purified on a silica gel column, eluting with petroleum ether as eluent to afford compound **3** as a pale yellow solid (2.20 g, 2.16 mmol) in 54% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ(ppm): 7.48–7.40 (m, 2H), 7.12 (t, 2H), 6.89–6.85 (m, 2H), 6.83 (d, 2H), 3.92 (d, 4H), 1.88–1.81 (m, 2H), 1.52–1.24 (m, 48H), 0.94–0.86 (m, 12H).

Synthesis of *o*-FBDTP

Compound **3** (2.03 g, 2.00 mmol) was added in a 50 mL dry flack. After purging with argon, fresh distilled THF (30 mL) was added. The reaction mixture was cooled down to -78 °C, and *n*-butyllithium (2.5 M in hexane, 1.68 mL, 4.20 mmol) was added dropwise. After 1 h of stirring at this temperature, the neat trimethylstannyl chloride (1.0 M in hexane, 4.2 mL, 4.2 mmol) was added. The solution was allowed to warm to room temperature and stirred for another 12 h, followed by dilution with hexane and washing with brine. The organic layer was collected and dried over anhydrous Na_2SO_4, then the solvent was removed in vacuo. The recrystallization of the crude product using isopropanol afforded *o*-FBDTP as pale yellow solid (1.85 g, 1.56 mmol) in 78% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) = 7.57–7.50 (m, 2H), 7.22–7.14 (m, 2H), 6.93–6.88 (m, 2H), 6.86 (d, 2H), 3.94 (d, 4H), 1.88–1.80 (m, 2H), 1.55–1.25 (m, 48H), 0.95–0.85 (m, 12H), 0.35 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$), δ(ppm): 161.23, 160.85, 160.77, 159.57, 142.94, 141.93, 137.62, 132.11, 131.97, 130.73, 122.86, 118.80, 118.69, 110.80, 102.66, 102.49, 71.32, 38.00, 31.92, 31.88, 31.40, 31.37, 30.04, 29.71, 29.61, 29.35, 29.34, 26.90, 26.87, 22.70, 22.69, 14.13, -8.35. HRMS (APCI-TOF): Calcd for: $C_{60}H_{92}F_2O_2S_2Sn_2$ ($M+H^+$): 1185.4636, found: 1185.4635.

Synthesis of compound 4

1-Bromo-4-(2-hexylhexadecyloxy)benzene (9.91 g, 25 mmol) was dissolved in dry THF (50 mL) in the argon atmosphene, and then *n*-butyllithium solution (25 mmol, 10.00 mL, 2.5 M in hexane) was added dropwise at -78 °C. After addition, the reaction mixture was maintained at this temperature for 2 h, followed by the addition of benzo[1,2-b:4,5-b′]dithiophene-4,8-dione (2.20 g, 10 mmol) and allowed to warm to 55 °C for 2 h. The solution was cooled down to room temperature and then $SnCl_2 \cdot 2H_2O$ (18.05 g, 80 mmol) in 10% aqueous HCl (20.0 mL) was added. The solution was refluxed for 2 h and then the cooled mixture was poured into water and extracted with hexane. The combined organic phase was dried over Na_2SO_4 and evaporated to obtain the crude product as pale yellow oil, which was purified on a silica gel column, eluting with petroleum ether as eluent. Compound **4** was obtained as a white solid (5.10 g, 6.20 mmol) in 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) = 7.62 (d, 4H), 7.38 (d, 2H), 7.34 (d, 2H), 7.08 (d, 4H), 3.94 (d, 4H), 1.88–1.80 (m, 2H), 1.55–1.22 (m, 48H), 0.95–0.84 (m, 12H).

Synthesis of BDTP

Compound **4** (1.65 g, 2.00 mmol) was added in a 50 mL dry flack. After purging with argon, fresh distilled THF (30 mL) was added. The reaction mixture was cooled down to 0 °C, and *n*-butyllithium (2.5 M in hexane, 1.68 mL, 4.20 mmol) was added dropwise. After 1 h of stirring at this temperature, the neat trimethylstannyl chloride (1.0 M in hexane, 4.2 mL, 4.2 mmol) was added. The solution was allowed to warm to room temperature and stirred for another 12 h, followed by dilution with hexane and washing with brine. The organic layer was collected and dried over anhydrous Na_2SO_4, then the solvent was removed in vacuo. The recrystallization of the crude product using isopropanol afforded BDTP as yellow solid (1.86 g, 1.62 mmol) in 81% yield. ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm) = 7.64 (d, 4H), 7.38 (s, 2H), 7.10 (d, 4H), 3.95 (d, 4H), 1.88–1.81 (m, 2H), 1.52–1.24 (m, 48H), 0.94–0.86 (m, 12H), 0.35 (s, 18H). ^{13}C NMR (150 MHz, $CDCl_3$), δ(ppm): 159.08, 142.61, 141.62, 137.09, 132.06, 130.88, 130.58, 128.47, 114.66, 70.93, 38.12, 31.94, 31.91, 31.48, 31.42, 30.08, 29.75, 29.64, 29.37, 29.32, 26.94, 26.92, 22.73, 22.71, 14.15, -8.36. HRMS (APCI-TOF): Calcd for: $C_{60}H_{94}O_2S_2Sn_2$ (M+H$^+$): 1149.4825, found: 1149.4778.

General polymerization procedure

All the polymers were synthesized by applying Stille polymerization. The representative procedure for the synthesis of polymer P1 is as following: To a 25 mL flask, compound BDTP (172.42 mg, 0.15 mmol), and C8DTBTff (107.79 mg, 0.15 mmol), $Pd_2(dba)_3$ (2.75 mg, 2 mol%), and $P(o\text{-tol})_3$ (5.50 mg, 12 mol%) were dissolved in anhydrous toluene (5 mL). After being purged with argon for another 30 min, the reaction mixture was heated to 110 °C, and stirred for 12 h under an argon atmosphere. Then the mixture was cooled down to ambient temperature and the polymer was precipitated by the addition of 150 mL methanol. The crude polymer product was then subjected to Soxhlet extraction with methanol, hexane, and chlorobenzene. The polymer recovered from chlorobenzene was precipitated by addition of 150 mL methanol. Then the product was dried under vacuum for 1 day to give the target polymer **P1** as a dark solid.

Table S1. The yield, GPC results and thermal stability of the polymers.

polymer	Yield (%)	M_n (Kda)	PDI	Td (°C)	Solubility (mg/ml)		
					chloroform	chlorobenzene	*o*-dichlorobenzene
P1	62	16.1	1.4	334	15	45	79
P2	66	17.0	1.6	337	26	68	95
P3	70	16.0	1.8	336	20	60	85

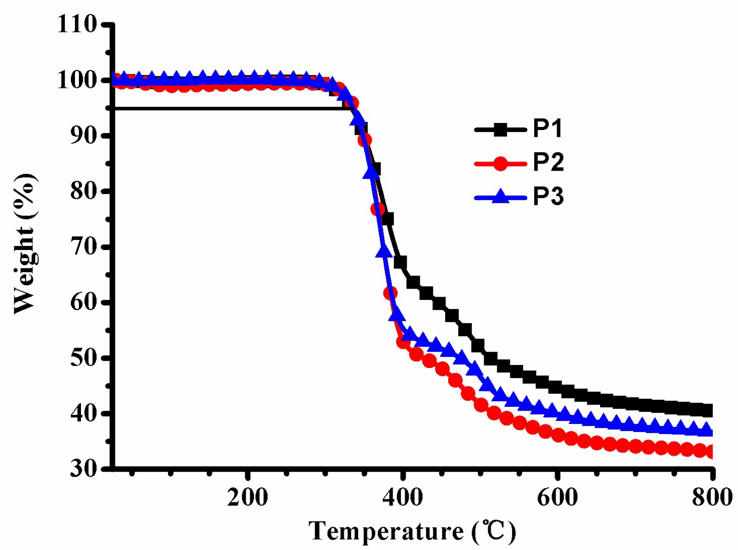


Figure S1. Thermal stability of the polymers.

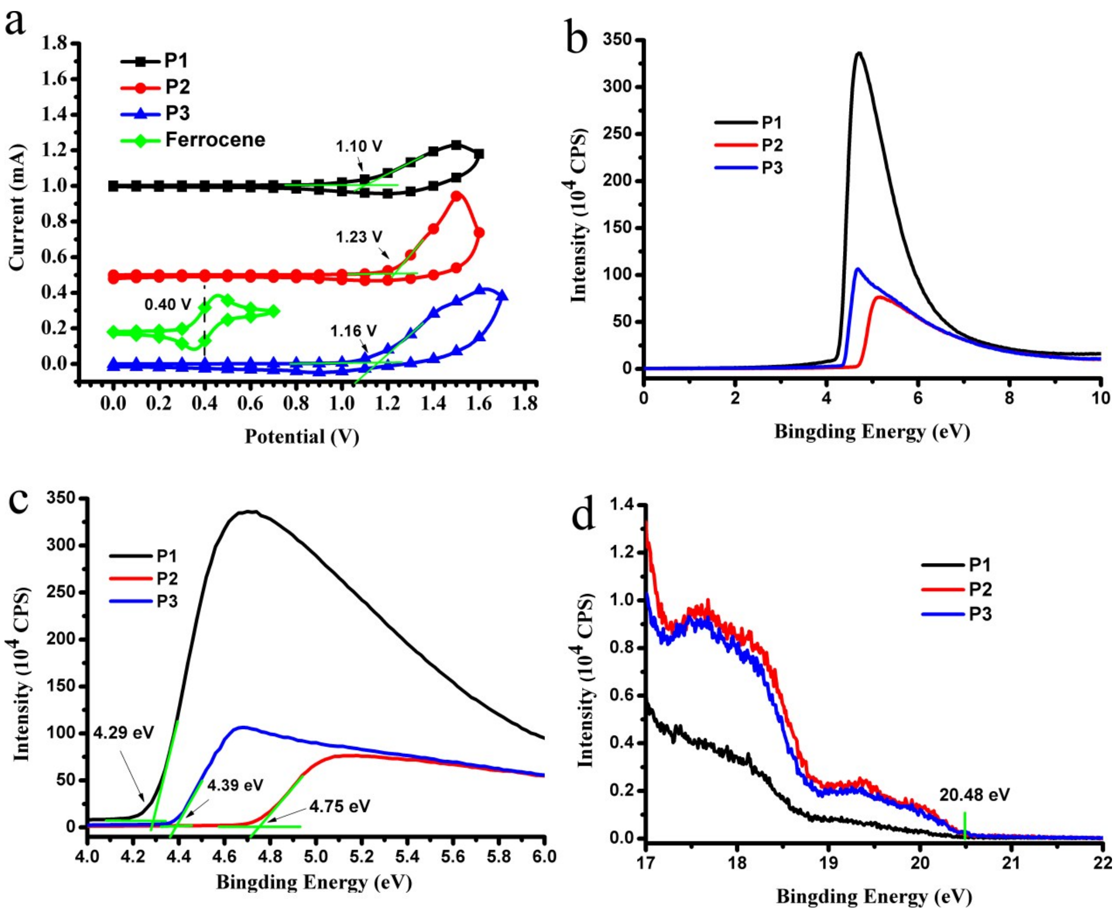


Figure S2. Cyclic voltammogram (a), UPS spectrum of the onset (b), amplified spectrum of the onset (c), and the secondary edge region (d) of the polymers P1, P2 and P3.

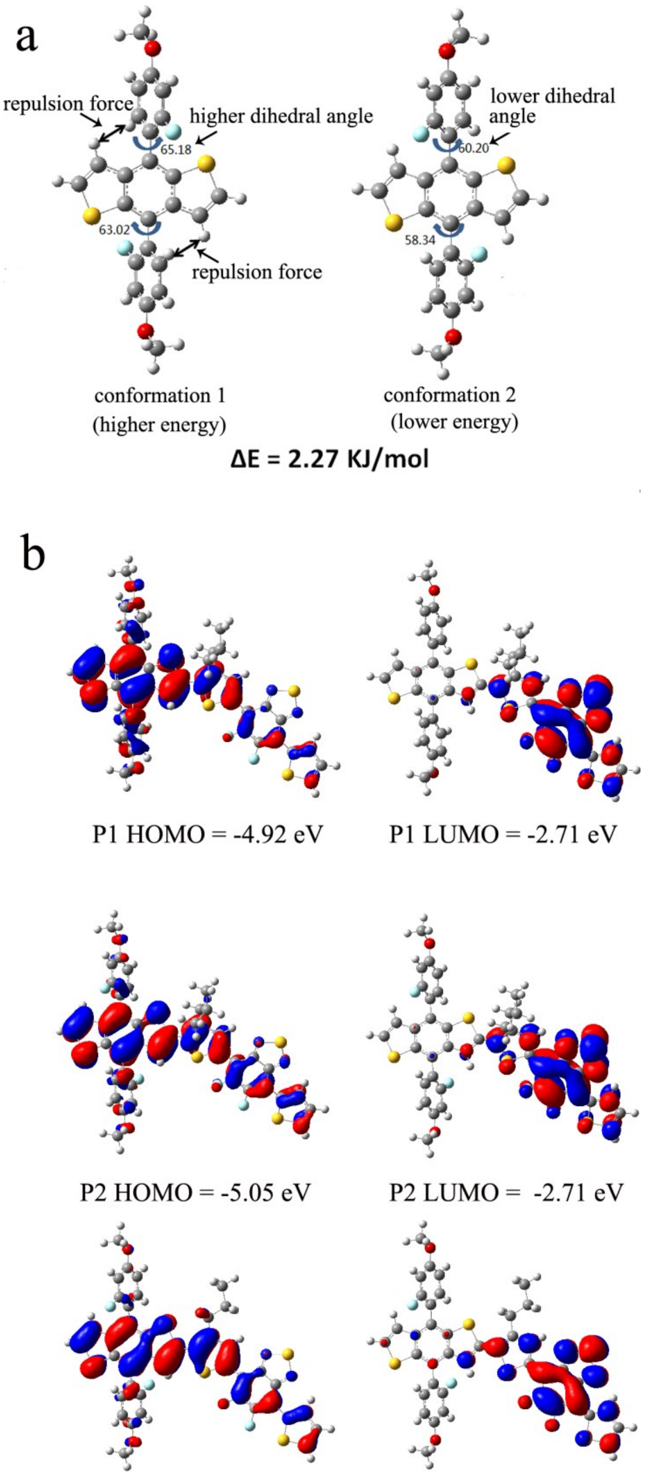
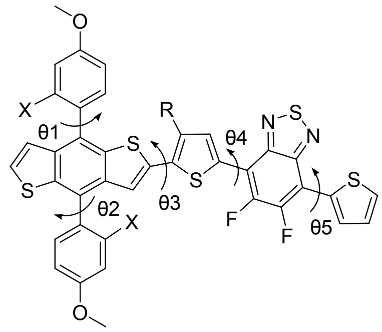


Figure S3. (a) the two possible conformations of the compound **2** and the totle energy difference, (b) the calculated distributions of the frontier molecular orbitals, and the HOMO and LUMO energy levels of the polymers.

Table S2. Calculated Bond Angles of the Repeat Units of the Copolymers[a]



polymer	X	R	θ_1 (deg)	θ_2 (deg)	θ_3 (deg)	θ_4 (deg)	θ_5 (deg)
P1	H	2-ethyl-hexyl	58.69	57.41	37.73	0.66	0.53
P2	F	2-ethyl-hexyl	59.31	60.39	42.46	0.99	0.51
P3	F	hexyl	59.74	59.20	4.18	0.71	0.09

[a] illustration of θ_1, θ_2, θ_3, θ_4, and θ_5 is given in graphic.

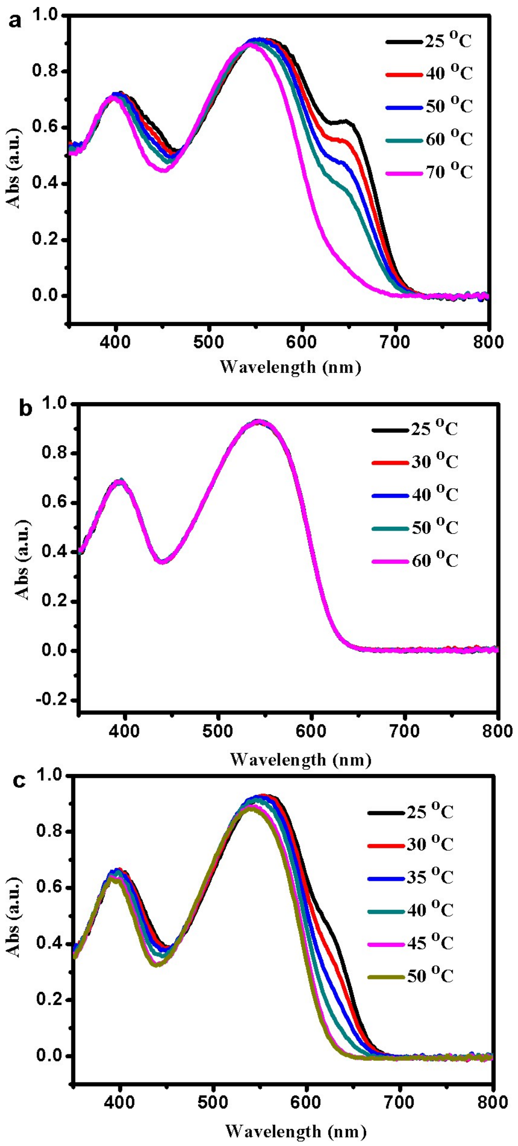


Figure S4. UV-vis absorption spectra of P1 (a), P2 (b), P3 (c) in chlorobenzene solution at different temperature.

Table S3. the performance of the devices with different raito and amount of DIO.

Polymer	Ratio[a]/Adddditive	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE$_{max}$ (PCE$_{ave}$)[b] (%)
P1	1:1/0% DIO	0.89	9.10	53.44	4.33 (4.21)
	1:1.5/0% DIO	0.88	11.27	46.96	4.67 (4.50)
	1:2/0% DIO	0.88	9.64	43.67	3.69 (3.52)
	1:1.5/1% DIO	0.84	11.17	49.24	4.64 (4.54)
	1:1.5/2% DIO	0.84	11.81	49.43	4.91 (4.72)
	1:1.5/3% DIO	0.84	10.92	48.91	4.49 (4.14)
P2	1:1/0% DIO	1.02	6.19	41.76	2.64 (2.61)
	1:1.5/0% DIO	1.03	7.30	43.76	3.29 (3.15)
	1:2/0% DIO	1.01	6.84	42.29	2.94 (2.90)
	1:1.5/1% DIO	0.94	7.92	56.82	4.24 (4.01)
	1:1.5/2% DIO	0.94	12.48	69.03	8.10 (8.05)
	1:1.5/3% DIO	0.94	12.12	64.32	7.30 (7.12)
P3	1:1/0% DIO	0.93	11.29	66.75	7.01 (6.98)
	1:1.5/0% DIO	0.93	12.97	74.49	9.02 (8.96)
	1:2/0% DIO	0.93	11.49	67.76	7.25 (7.11)
	1:1.5/1% DIO	0.90	12.86	71.20	8.23 (8.01)
	1:1.5/2% DIO	0.89	12.43	57.61	6.39 (6.22)
	1:1.5/3% DIO	0.88	12.40	48.81	5.31 (5.10)

a) The weight ratio of polymer to PC$_{71}$BM; b)The average PCE is obtained from 20 devices.

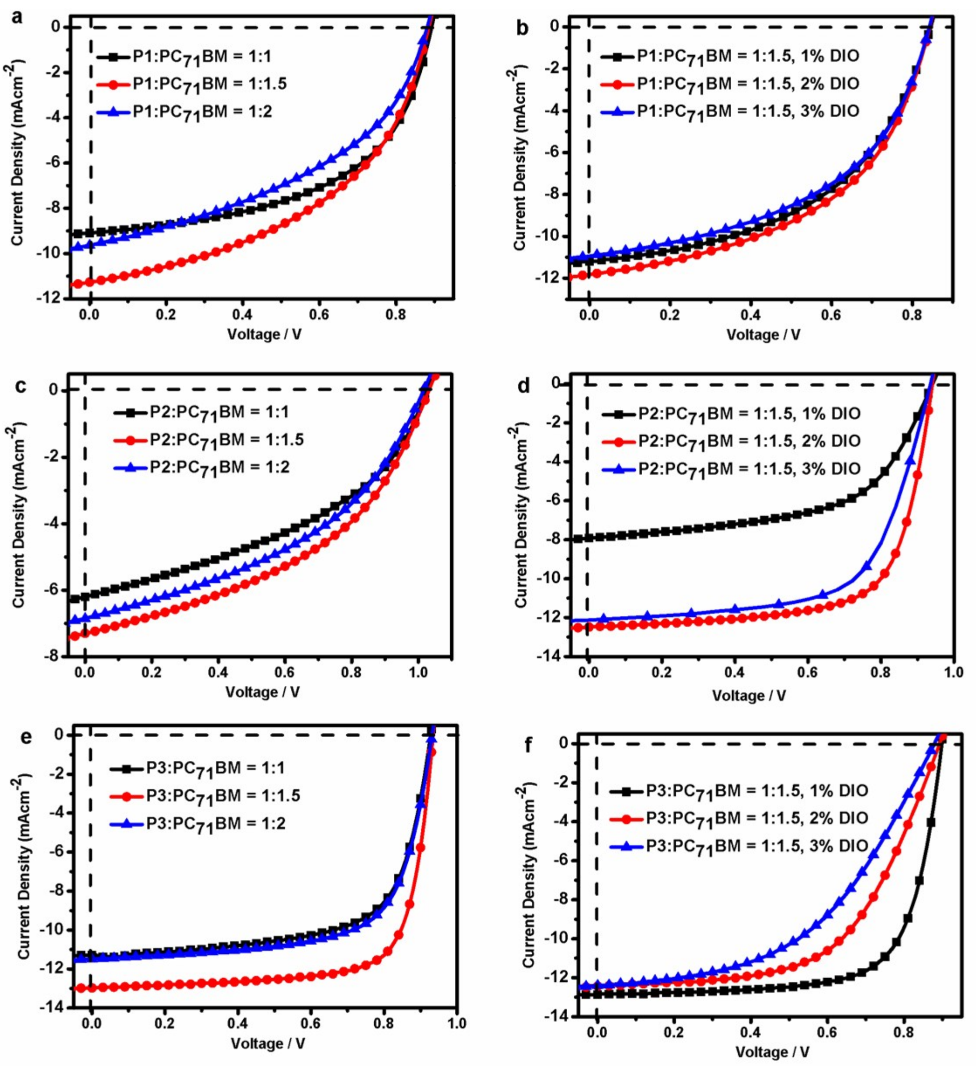


Figure S5. the *J*-V curves of polymer P1, P2, P3 with different weight ratio to $PC_{71}BM$ (a, c, e), and different amount of DIO (b, d, f) as additive.

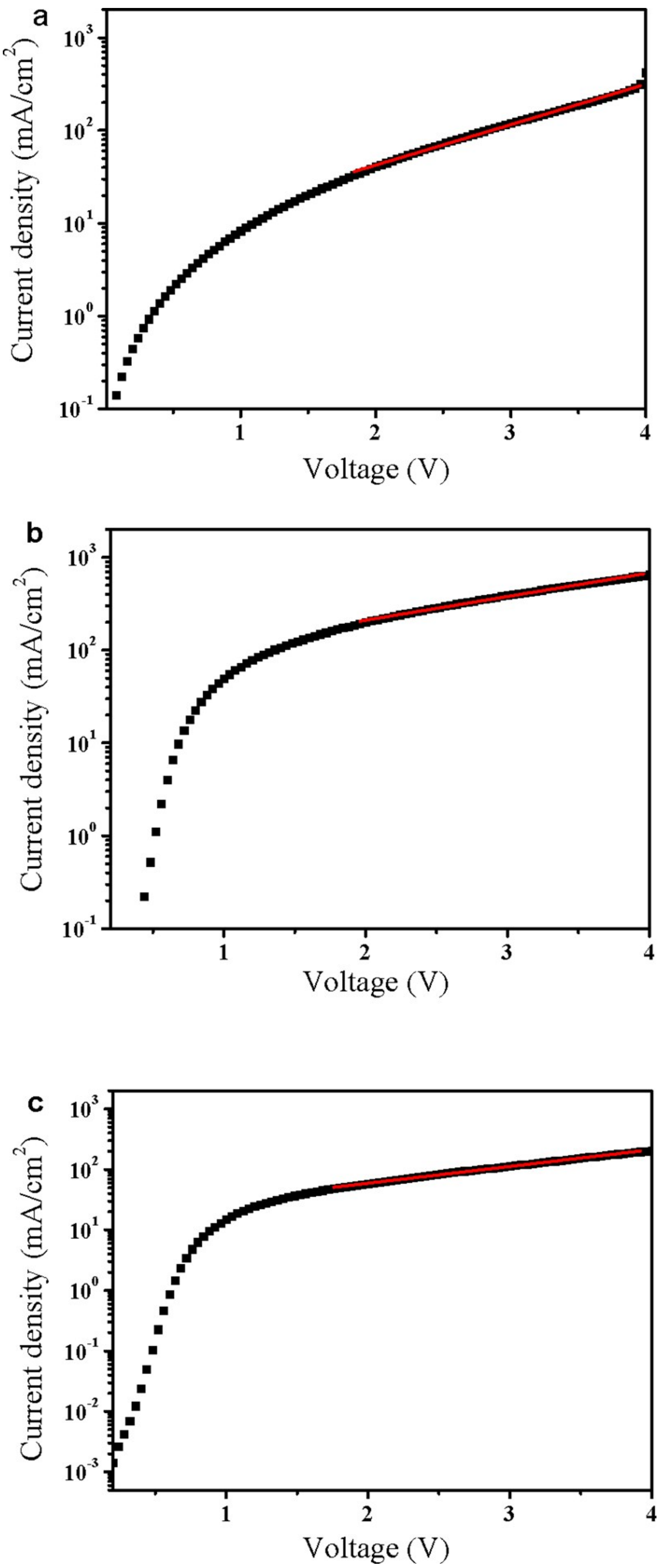


Figure S6. *J*-*V* plots for the devices ITO/PEDOT:PSS/polymer:$PC_{71}BM$/Au. The solid line is the fittig of the data points (the thicknesses of the polymer films were 100 nm). The graphs a, b, c represent P1, P2, P3, respectively.

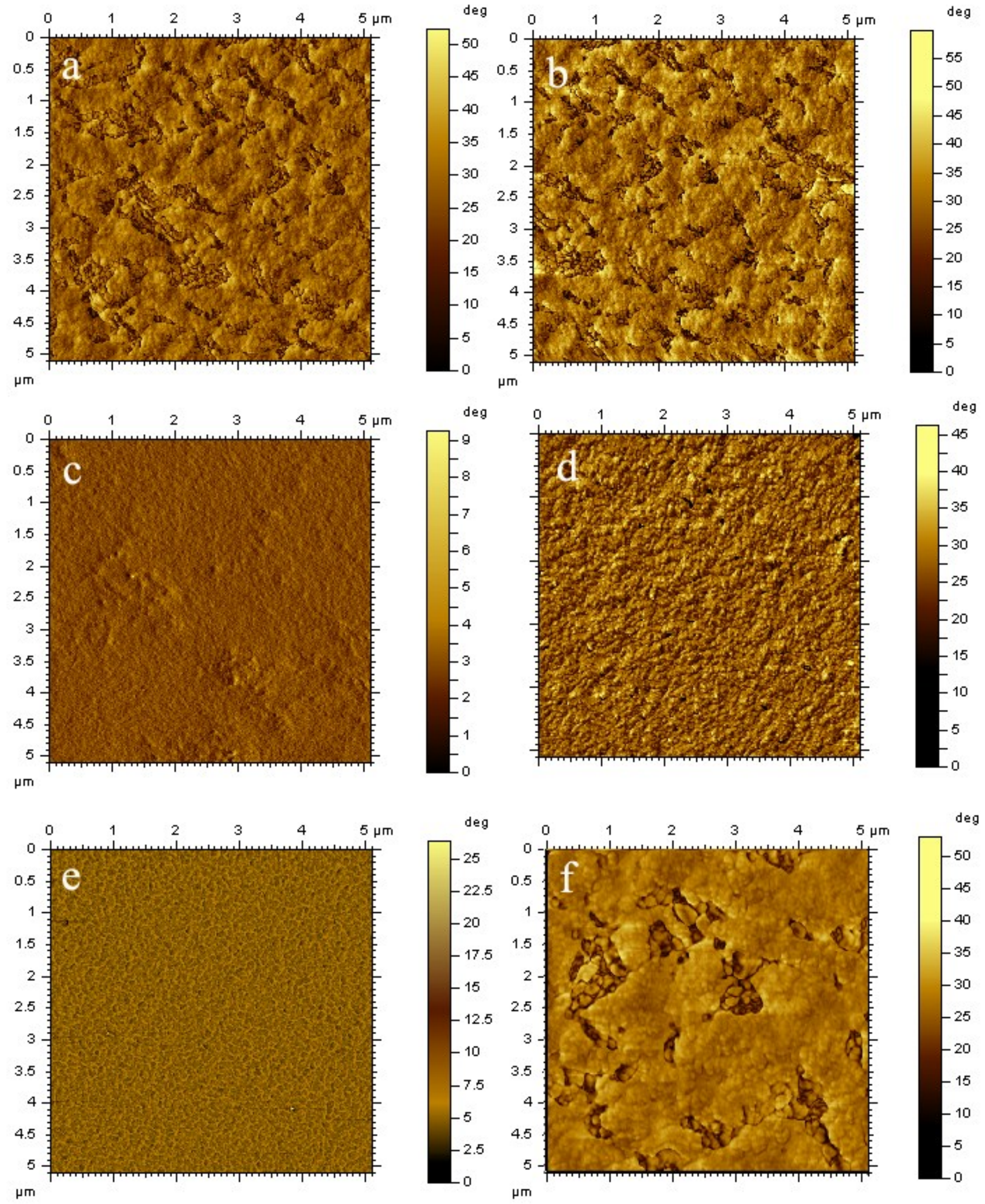


Figure S7. AFM phase images of the active layers of P1/PC$_{71}$BM (a), P1/PC$_{71}$BM with 2% DIO (b), P2/PC$_{71}$BM (c), P2/PC$_{71}$BM with 2% DIO (d), P3/PC$_{71}$BM (e), and P3/PC$_{71}$BM with 2% DIO (f).