

Electronic Supplementary Information

Low bandgap conjugated polymers based on mono-fluorinated isoindigo for efficient bulk heterojunction polymer solar cells processed with non-chlorinated solvent

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Materials and reagents. THF and toluene were distilled over sodium/benzophenone. Et₃N, acetonitrile, CH₂Cl₂ and DMSO were distilled after drying with CaH₂. Other reagents were obtained from commercial resources and used without further purification. Alkyl iodides, *N*-dodecanyl-2,8-bis(trimethylstannyl)dithieno[3,2-*b*;6,7-*b'*]carbazole and 6,6'-dibromo-7-fluoro-*N,N'*-(2-octyldodecanyl)-isoindigo was synthesized following the previous reports.¹⁻³ PC₆₁BM and PC₇₁BM are purchased from American Dye Source, Inc. (ADS). Anhydrous *o*-xylene and *o*-DCB were purchased from Sigma-Aldrich.

Instruments. ¹H and ¹³C spectra were recorded on Bruker 400-MHz in CDCl₃ or DMSO-*d*₆, all chemical shifts were reported in parts per million (ppm). Chemical shift was reported relative to an internal tetramethylsilane (TMS). UV-vis-NIR absorption spectra and photoluminescence spectra were recorded on a Shimadzu UV-3600 UV-vis-NIR spectrometer and a Perkin-Elmer LS 50B spectrofluorometer, respectively. The optical bandgap was calculated from absorption onset ($E_g^{opt} = 1240/\lambda_{onset}$ eV). High temperature GPC analysis was conducted on a PL-GPC 220 system using polystyrene as standard and 1, 2, 4-trichlorobenzene as eluent at 150 °C. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on a Perkin-Elmer TGA7 and Perkin-Elmer DSC7, respectively, under a nitrogen flow. Film CV were performed on a CHI660a electrochemical analyzer with a three-electrode cell at a scan rate of 100 mV·s⁻¹. Bu₄NPF₆ (0.1 mol·L⁻¹) and anhydrous acetonitrile were used as electrolyte and solvent, respectively. A glassy carbon electrode with a diameter of 10 mm, a Pt wire, and a saturated calomel

electrode were used as the working, counter, and reference electrodes, respectively. To obtain electronic energy levels of the polymer films, the occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated by the equations: $\text{HOMO} = - (4.80 + E_{\text{onset}}^{\text{ox}}) \text{ eV}$, $\text{LUMO} = - (4.80 + E_{\text{onset}}^{\text{re}}) \text{ eV}$, in which $E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{re}}$ are the oxidation and reduction onset potentials versus ferrocene (Fc/Fc⁺), respectively. Thin-film X-ray diffraction (XRD) were recorded on a Bruker D8 Discover thin-film diffractometer with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 40 mA. Transmission electron microscopy (TEM) of the polymers blend films were performed on JEOL JEM-1011 transmission electron microscope operated at an acceleration voltage of 100 kV.

[1] I. Meager, R. S. Ashraf, S. Mollinger, B. C. Schroeder, H. Bronstein, D. Beatrup, M. S. Vezie, T. Kirchartz, A. Salleo, J. Nelson, I. McCulloch, *J. Am. Chem. Soc.*, 2013, **135**, 11537.

[2] Y. F. Deng, J. Liu, J. T. Wang, L. H. Liu, W. L. Li, H. K. Tian, X. J. Zhang, Z. Y. Xie, Y. H. Geng, F. S. Wang, *Adv. Mater.*, 2014, **26**, 471.

[3] Y. F. Deng, Y. G. Chen, X. J. Zhang, H. K. Tian, C. Bao, D. H. Yan, Y. H. Geng, F. S. Wang, *Macromolecules*, 2012, **45**, 8621.

Experimental Section

Fabrication and characterization of OTFTs. Bottom gate and top contact device structure was used for the fabrication of OTFTs on heavily doped n-type silicon wafers with 300 nm thermally grown SiO₂ ($C_i = 10 \text{ nF/cm}^2$). The substrate was cleaned and modified with octylsilyltrichloride (OTS-C₈) according to the literature.⁴ The polymer solutions (5 mg/mL in *o*-xylene or 6 mg/mL in *o*-DCB) were deposited on the modified substrate with 1000 rpm for 2 min. Then gold electrodes were evaporated under vacuum by shadow mask with a channel width (W) of 3000 μm and a channel length (L) of 100 μm . The devices were measured in air with two Keithley 236 units.

Fabrication and characterization of BHJ PSCs. To fabricate the conventional solar cells, ITO coated glass substrate was cleaned with detergent, de-ionized water, acetone and isopropyl alcohol sequentially. After dried at 120 °C in an oven overnight, ITO surface treated with UV-ozone for 25 mins, then about 40 nm PEDOT:PSS (Baytron 4083) was deposited and baked at 120 °C for 20 min to remove the residual water. Polymer:PCBM solution (for polymer: 5 mg/mL in *o*-xylene or 6 mg/mL in *o*-DCB) was spin-coated on the substrate in N₂-filled glovebox at 600 rpm for 2 min. The film thickness was $100 \pm 5 \text{ nm}$. Finally, LiF ($\sim 1 \text{ nm}$) and Al (80 nm) were evaporated under high vacuum to serve as cathode. For the inverted solar cells, ZnO (20 nm) was spin-coated on the clean ITO substrate. The fabrication of the active layer followed the aforementioned procedure. Then MoO₃ (8 nm)/Al (80 nm) cathode was thermally deposited. The active area of the device is 12.5 mm². *J-V* curves were

recorded with computer controlled Keithley 236. An Oriel 150 W solar simulator with an AM 1.5G filter was used as light source and the light power was 100 mW/cm², which is accurately calibrated by silicon diode with KG-5 visible color filter. EQE curves were recorded on the IPCE measurement system (QE-R3011, Enli Technology Co. , Ltd) under short-circuit condition with monochromatic light obtained from Xenon lamp, chopper with the frequency of 133 Hz, a lock-in amplifier (SR830, Stanford Research Corp) and with a Si-based diode as reference cell for calibration.

Fabrication and characterization of hole-only and electron-only devices: Hole-only and electron-only devices were fabricated with the structures of glass/ITO/PEDOT:PSS (40 nm)/polymer:PC₆₁BM (180 nm)/MoO₃ (8 nm)/Al (80 nm) and glass/Al (100 nm)/polymer:PC₆₁BM (180 nm)/Al (100 nm), respectively. The devices were measured in the dark with computer controlled Keithley 236. The mobilities were calculated by fitting the dark current using the Mott–Gurney relationship.

Photoluminescence (PL) measurements: The films of the pure polymers and their blends with PC₆₁BM were spin-cast on quartz substrates for measuring PL spectra. PL quenching efficiencies (ΔPL) were calculated according to the following equation:

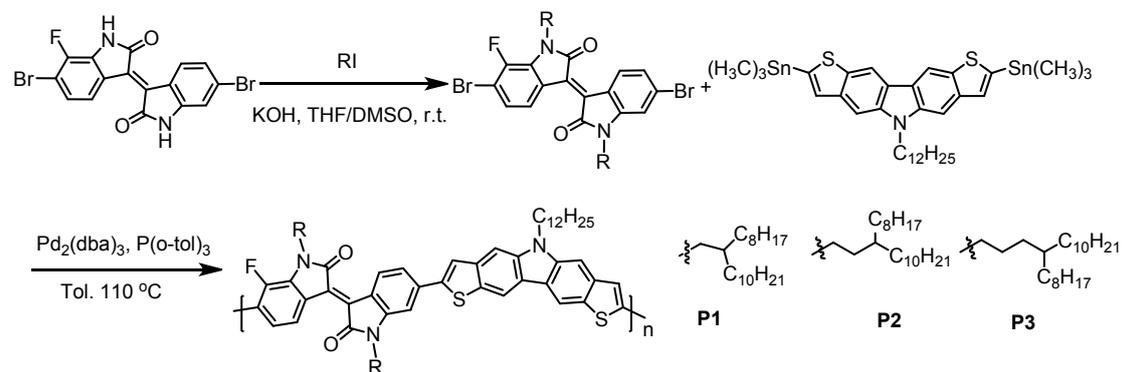
$$\Delta PL = \left(1 - \frac{PL_{Blend}}{PL_{Polymer}}\right) \times 100\%,$$

where PL_{Blend} and $PL_{Polymer}$ are the PL integrations of polymer : PC₆₁BM blends and pure polymer, respectively.

[4] Y. F. Deng, Y. G. Chen, X. J. Zhang, H. K. Tian, C. Bao, D. H. Yan, Y. H. Geng, F. S. Wang, *Macromolecules*, 2012, **45**, 8621.

Synthesis

Scheme S1. Synthesis of monomers and polymers



6,6'-Dibromo-7-fluoro-*N,N*-di(3-octyltridecyl)isoidigo

To a solution of 6,6'-dibromo-7-fluoroisoidigo (300 mg, 0.68 mmol) and KOH powder (153.7 mg, 2.72 mmol) in dimethyl sulfoxide (DMSO) (20 mL), 3-octyl-1-tridecyl iodide (1.16 g, 2.72 mmol) in THF (20 mL) was added under nitrogen. The mixture was stirred for 24 h at 25 °C before pouring into water (500 ml) for extraction with CHCl_3 . The organic extracts were washed with water, dried with MgSO_4 and concentrated under reduced pressure. The residue was purified on silica gel chromatography with PE: CH_2Cl_2 (8:1) as eluent to give the product as a deep-red solid. (242 mg, 35.1 %). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 9.06 (d, $J = 8$ Hz, 1H), 8.93 (d, $J = 8$ Hz, 1H), 7.16-7.18 (m, 2H), 6.90 (s, 1H), 3.94 (t, $J = 8$ Hz, 2H), 3.72 (t, $J = 8$ Hz, 2H), 1.60-1.72 (m, 4H), 0.98-1.44 (m, 68H), 0.86 (t, $J = 8$ Hz, 12H). ^{13}C NMR (CDCl_3 , 100, MHz, ppm): δ 167.20, 145.87, 144.71, 142.22, 132.18, 132.04, 131.40, 127.22, 126.26, 125.69, 125.20, 123.39, 120.36, 40.79, 38.46, 35.61, 33.45, 32.86, 31.93, 30.95, 30.03, 29.68, 29.35, 26.56, 22.69, 14.12. Elemental Anal.: Calcd. For $\text{C}_{58}\text{H}_{91}\text{Br}_2\text{FN}_2\text{O}_2$: C, 67.82; H, 8.93; N, 2.73. Found, C, 67.96; H, 8.75; N, 2.79.

6,6'-Dibromo-7-fluoro-*N,N'*-di(4-octyltetradecyl)isoidigo

The synthetic procedure is similar to that for 6,6'-dibromo-7-fluoro- *N,N*-di(3-octyltridecyl)isoindigo. Deep red solid, yield: 37.3%. ¹H NMR (CDCl₃, 400 MHz, ppm): ¹H NMR (CDCl₃, 400 MHz, ppm): δ 9.06 (d, *J* = 8 Hz, 1H), 8.93 (d, *J* = 8 Hz, 1H), 7.16-7.18 (m, 2H), 6.93 (s, 1H), 3.91 (t, *J* = 8 Hz, 2H), 3.71 (t, *J* = 8 Hz, 2H), 1.60-1.76 (m, 4H), 0.99-1.45 (m, 72H), 0.86 (t, *J* = 8 Hz, 12H). ¹³C NMR (CDCl₃, 100, MHz, ppm): δ 167.33, 145.95, 144.88, 142.47, 133.81, 132.32, 132.05, 131.39, 127.28, 126.29, 125.74, 125.24, 123.38, 120.32, 114.19, 111.43, 42.71, 40.66, 37.10, 33.53, 31.92, 30.80, 30.54, 30.09, 29.69, 29.35, 26.65, 26.11, 24.44, 14.12. Elemental Anal.: Calcd. For C₆₀H₉₅Br₂FN₂O₂ : C, 68.29; H, 9.07; N, 2.65. Found, C, 68.43; H, 8.78; N, 2.72.

poly[*N*-dodecyl dithieno[3,2-*b*;6,7-*b*]carbazole-*alt*-7-fluoro-*N,N*-di(2-octyldodecyl)isoindigo] (P1). 6,6'-Dibromo-7-fluoro-*N,N'*-(2-octyldodecanyl)-isoindigo (350 mg, 0.35031 mmol, 1 equiv), *N*-dodecanyl-2,8-bis(trimethylstannyl)dithieno[3,2-*b*;6,7-*b*]carbazole (276.32 mg, 0.35732 mmol, 1.02 equiv), Pd₂(dba)₃ (6.4 mg, 2 mol%), P(*o*-tol)₃ (17 mg, 16 mol%) and 35 mL toluene were added to a Schlenk Tube, and the tube was charge with argon through a freeze-pump-thaw cycle for three times. The mixture was stirred at 110 °C for 48 hrs, then end-capped with bromobenzene for 12 hrs. The polymer solution was added to CH₃OH dropwise. The precipitate was collect by filtration. The crude polymer was dissolved into dichlorobenzene and treated with sodium diethyldithiocarbamate trihydrate to remove catalyst residues. The polymer was finally purified by Soxhlet extraction with ethanol, acetone, hexane in succession (401

mg, 89.1%). Elemental Anal.: Calcd. For $(C_{84}H_{120}FN_3O_2S_2)_n$: C, 78.39; H, 9.40; N, 3.26. Found, C, 78.86; H, 8.92; N, 3.05.

poly[*N*-dodecyldithieno[3,2-*b*;6,7-*b*]carbazole-*alt*-7-fluoro-*N,N'*-di(3-octyltridecyl)isoindigo] (P2). The synthetic procedure is similar to that for **P1**. Yield: 92.1%. Elemental Anal.: Calcd. For $(C_{86}H_{124}FN_3O_2S_2)_n$: C, 78.55; H, 9.50; N, 3.20. Found, C, 78.93; H, 9.08; N, 3.01.

poly[*N*-dodecyldithieno[3,2-*b*;6,7-*b*]carbazole-*alt*-7-fluoro-*N,N'*-di(4-octyltetradecyl)isoindigo] (P3). The synthetic procedure is similar to that for **P1**. Yield: 85.9%. Elemental Anal.: Calcd. For $(C_{88}H_{128}FN_3O_2S_2)_n$: C, 78.69; H, 9.61; N, 3.13. Found, C, 80.08; H, 9.42; N, 2.95.

The procedure for the model coupling reaction

6,6'-Dibromo-7-fluoro-*N,N'*-(2-octyldodecanyl)-isoindigo (134.56 mg, 0.134 mmol, 2 equiv), benzo[*b*]thiophen-2-yl-trimethyl-stannane (20 mg, 0.067 mmol, 1 equiv), $Pd_2(dba)_3$ (2.46 mg, 2 mol%), $P(o-tol)_3$ (6.55 mg, 16 mol%) and 10 mL toluene were added to a Schlenk Tube. The tube was charge with argon through a freeze-pump-thaw cycle for three times. The mixture was stirred for 48 hrs at 110 °C, poured into 100 mL water, and then extracted with CH_2Cl_2 . The organic extracts were dried with $MgSO_4$, and the solvent was removed by evaporation. The residue was purified by silica gel chromatography with PE: CH_2Cl_2 (8:1 to 4:1) as eluent to give compound **3** and **4** as a deep-red solid.

Compound **3** (14.6 mg, 20.6%). 1H NMR ($CDCl_3$, 400 MHz, ppm): δ 9.04 (d, $J = 12$ Hz, 2H), 7.81-7.87 (m, 3H), 7.32-7.38 (m, 3H), 7.17 (dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz 1H),

6.91 (d, $J = 1.76$ Hz, 1H), 3.91 (d, $J = 8$ Hz, 2H), 3.63 (d, $J = 8$ Hz, 2H), 1.89 (m, 2H),
1.14-1.46 (m, 64H), 0.82 (t, $J = 8$ Hz, 12H).

Compound **4** (31.1 mg, 43.9%). ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 9.14 (d, $J = 8$
Hz, 1H), 8.93 (d, $J = 8$ Hz, 1H), 7.79-7.85 (m, 2H), 7.65 (s, 1H), 7.35-7.40 (m, 3H),
7.18 (dd, $J_1 = 8$ Hz, $J_2 = 4$ Hz, 1H), 7.08 (d, $J = 1.76$ Hz, 1H), 3.85 (d, $J = 8$ Hz, 2H),
3.72 (d, $J = 8$ Hz, 2H), 1.91 (m, 2H), 0.98-1.47 (m, 64H), 0.83 (t, $J = 8$ Hz, 12H).

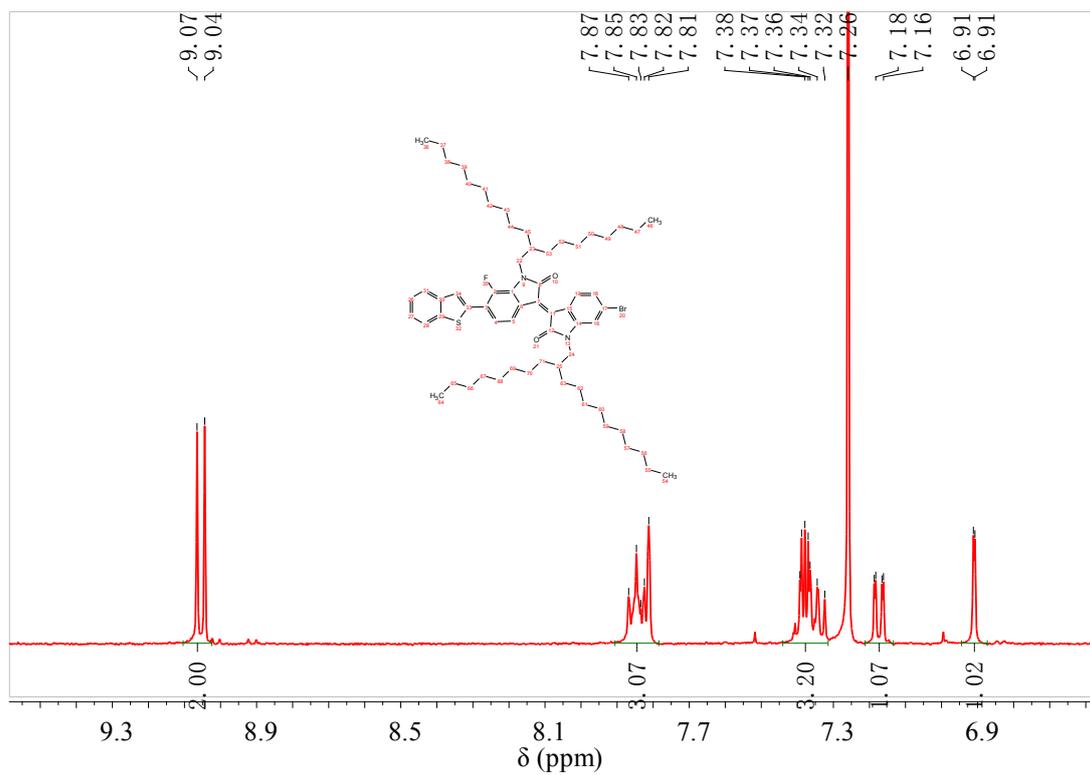


Figure S1. Aromatic region of the ¹H NMR (CDCl₃, 400 MHz) of compound **3**.

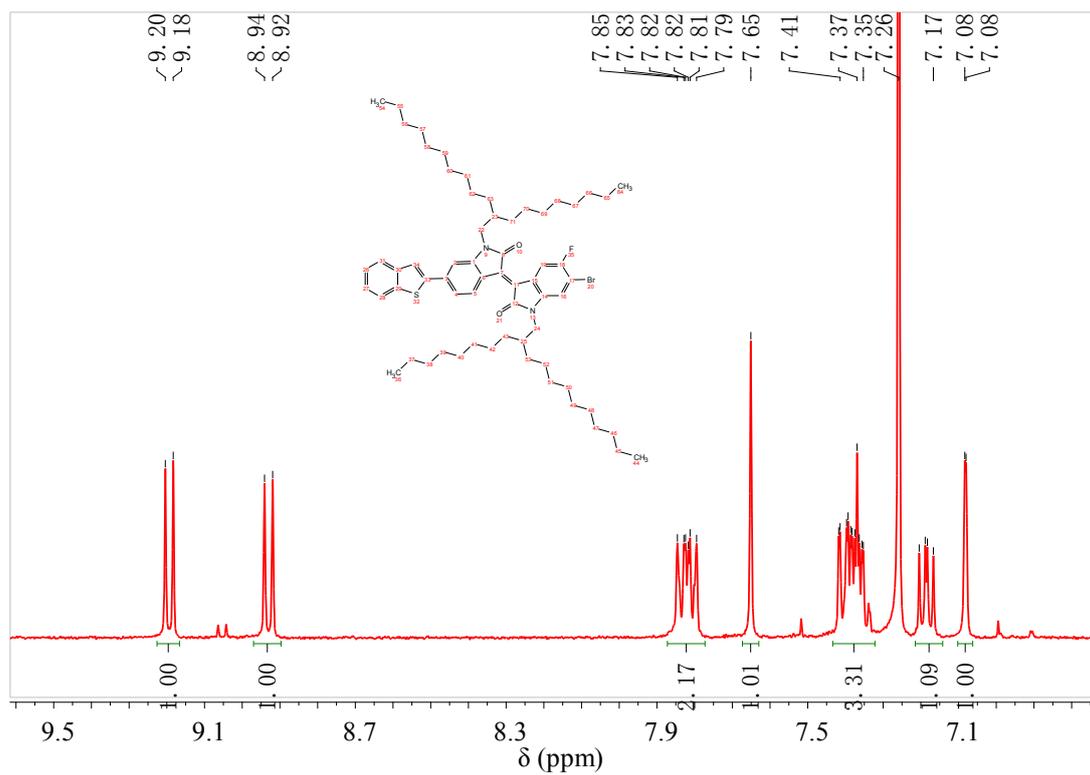


Figure S2. Aromatic region of the ^1H NMR (CDCl_3 , 400 MHz) of compound 4.

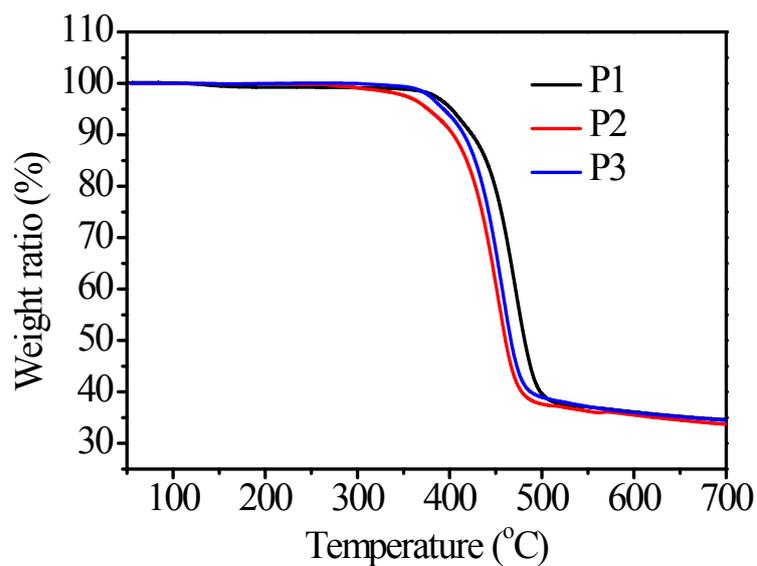


Figure S3. TGA plots of the polymers under N₂ flow with a heating rate of 10 °C/min.

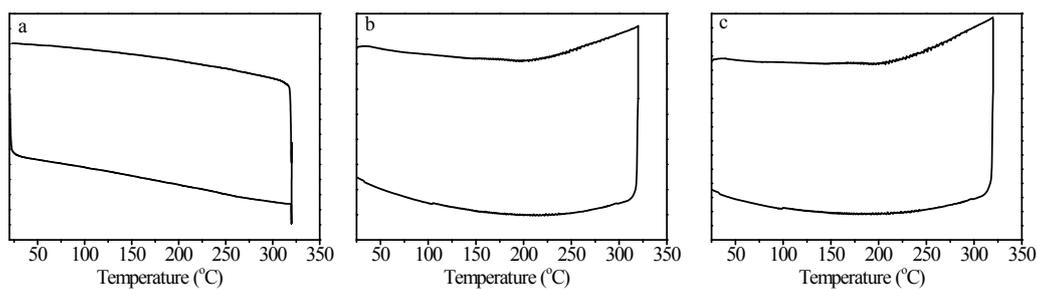


Figure S4. DSC curves of the polymer (a) **P1**; (b) **P2**; (c) **P3** under N₂ flow with a heating/cooling rate of ± 10 °C/min.

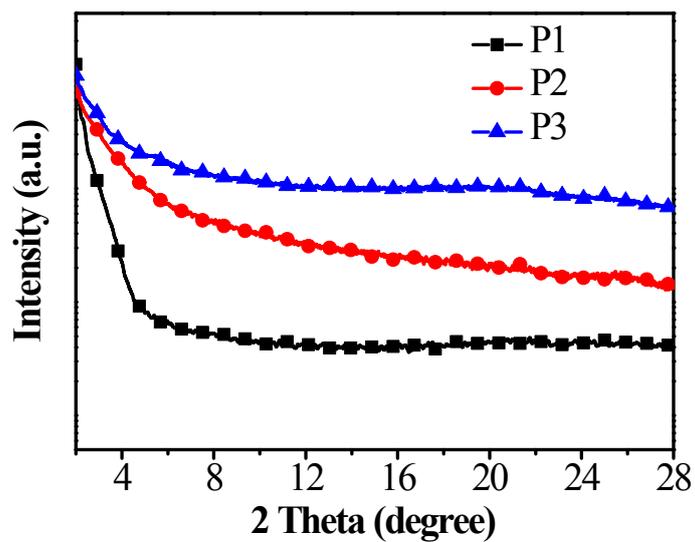


Figure S5. Film XRD of the polymers.

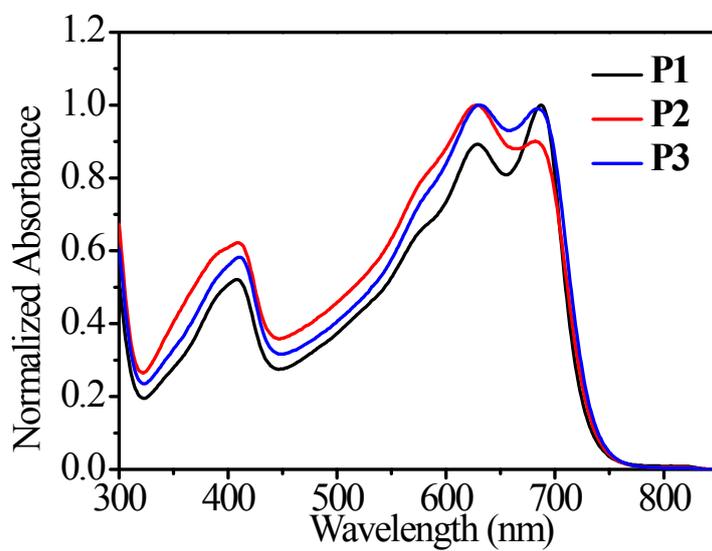


Figure S6. Absorption spectra of the polymers in *o*-xylene.

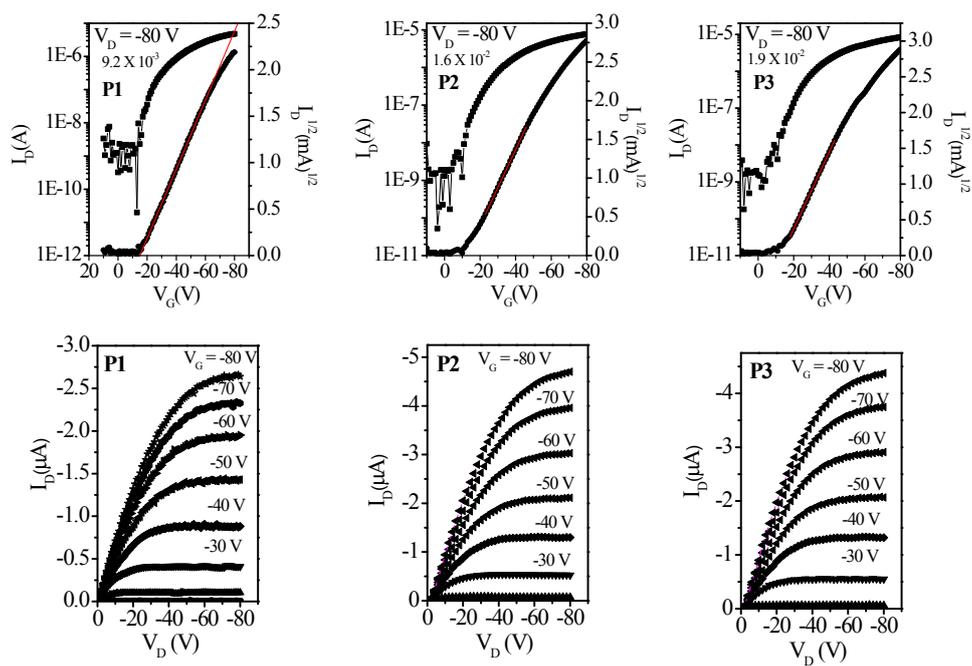


Figure S7. Transfer and output characteristics of OTFTs fabricated with *o*-xylene as solvent.

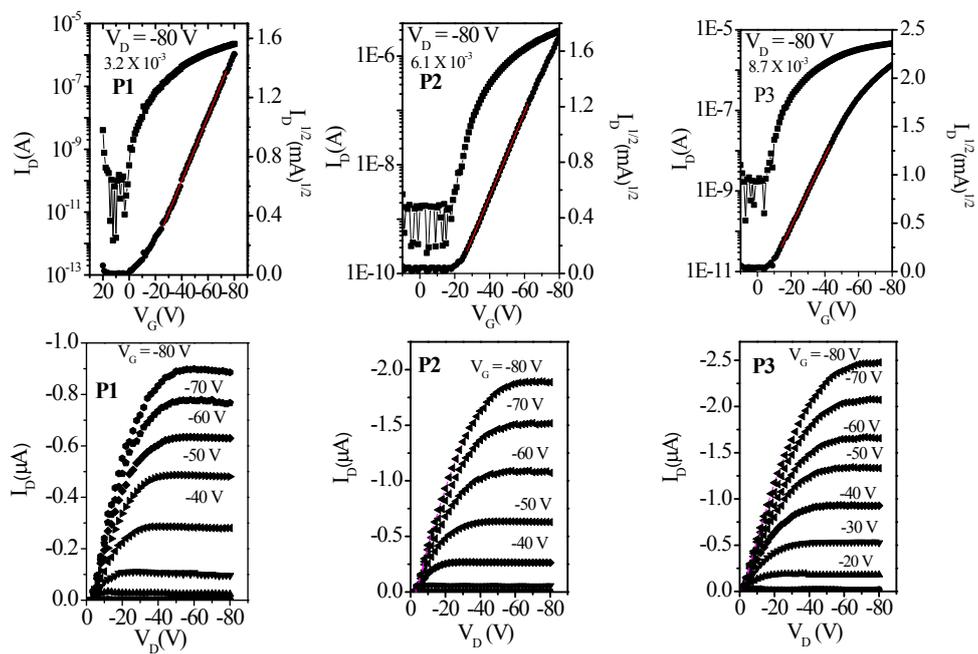


Figure S8. Transfer and output characteristics of OTFTs fabricated with *o*-DCB as solvent.

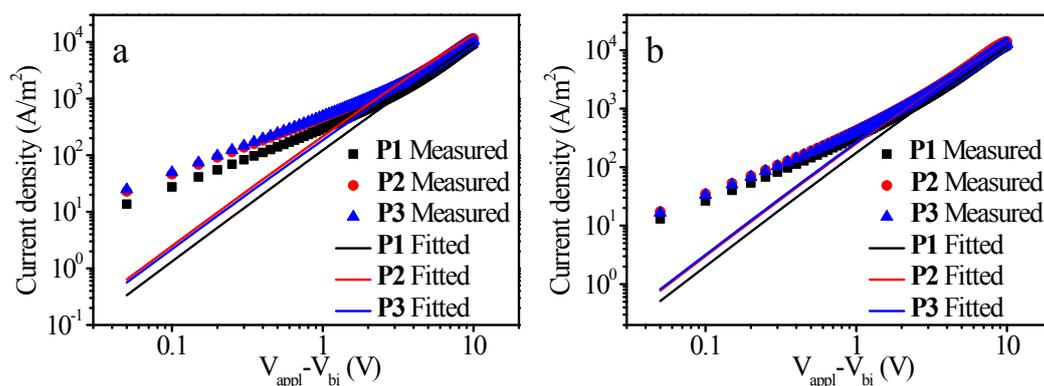


Figure S9. J - V characteristics of hole-only devices of the polymers measured under dark processed with *o*-xylene (a) and *o*-DCB (b). Lines represent the fitting results using a model of single-carrier space-charge-limited current with field-dependent mobility.

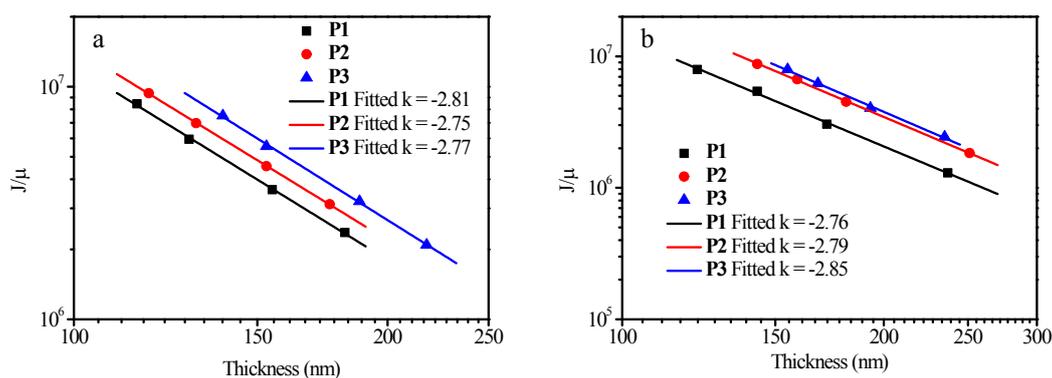


Figure S10. The double-logarithmic plots of current density relative to mobility (J/μ) as a function of active layer thickness (L) for the hole-only devices of pure polymers processed with *o*-xylene (a) and *o*-DCB (b). The solid lines represent the fitting according to power law $J_{SC} \propto L^{-3}$.

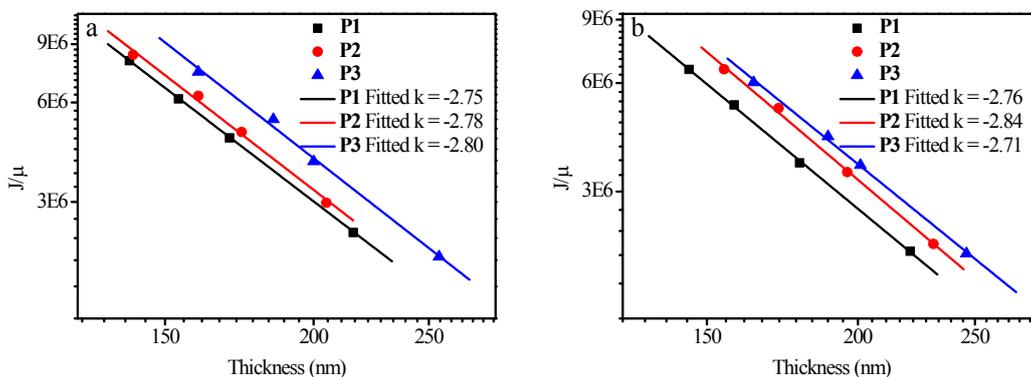


Figure S11. The double-logarithmic plots of current density relative to mobility (J/μ) as a function of active layer thickness (L) for the hole-only devices of polymer:PC₆₁BM = 1:1.5 (w/w) processed with *o*-xylene (a) and *o*-DCB (b). The solid lines represent the fitting according to power law $J_{SC} \propto L^{-3}$.

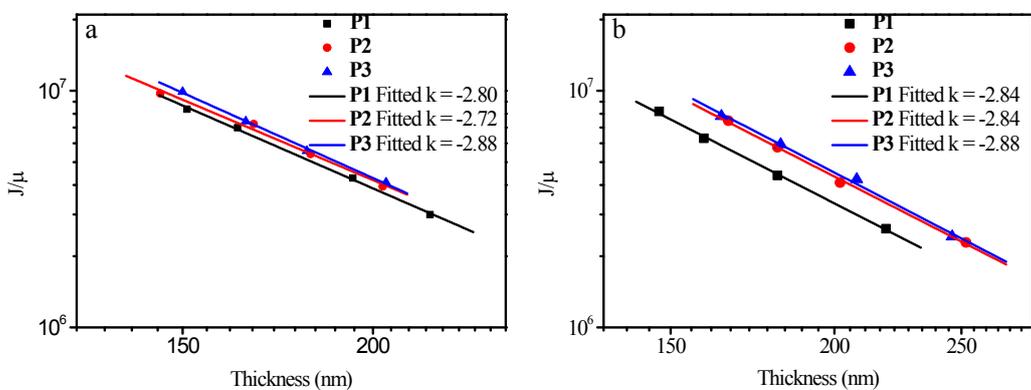


Figure S12. The double-logarithmic plots of current density relative to mobility (J/μ) as a function of active layer thickness (L) for the electron-only devices of polymer:PC₆₁BM = 1:1.5 (w/w) processed with *o*-xylene (a) and *o*-DCB (b). The solid lines represent the fitting according to power law $J_{SC} \propto L^{-3}$.

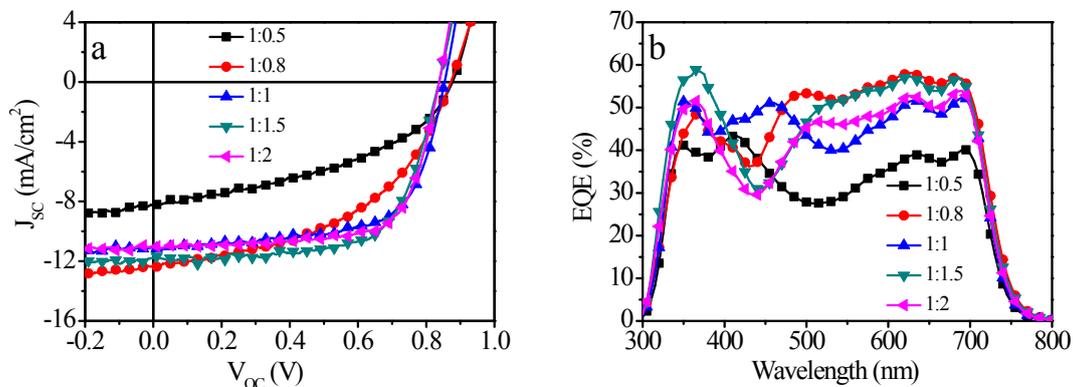


Figure S13. J - V curves (a) and EQE (b) of the devices based on **P1:PC₆₁BM** with different D/A ratios.

Table S1. Photovoltaic characteristics of the devices based on **P1:PC₆₁BM** with different D/A ratios under the illumination of AM 1.5G 100 mW cm⁻².

Ratios	V _O c (V)	J _{SC} (mA/cm ²)		FF	PCE(%)		
		Measured	Calculate		Best	Average	Calculate
			d				d
1:0.5	0.88	8.2	8.0	0.44	3.2	3.0	3.1
1:0.8	0.87	12.1	11.8	0.48	5.1	4.7	4.9
1:1	0.85	11.1	10.6	0.66	6.2	6.1	5.9
1:1.5	0.84	11.9	11.6	0.68	6.8	6.4	6.6
1:2	0.84	11.0	10.4	0.71	6.6	6.5	6.2

Table S2. Photovoltaic parameters of the inverted devices based on the three polymers with PC₆₁BM as acceptor material (polymer : PC₆₁BM = 1:1.5) under the illumination of AM 1.5G 100 mW cm⁻².

Polymer	V _{OC} (V)	J _{SC} (mA/cm ²)	FF	PCE(%)
P1	0.84	12.4	0.68	7.1%
P2	0.84	12.1	0.72	7.3%
P3	0.85	12.2	0.70	7.3%

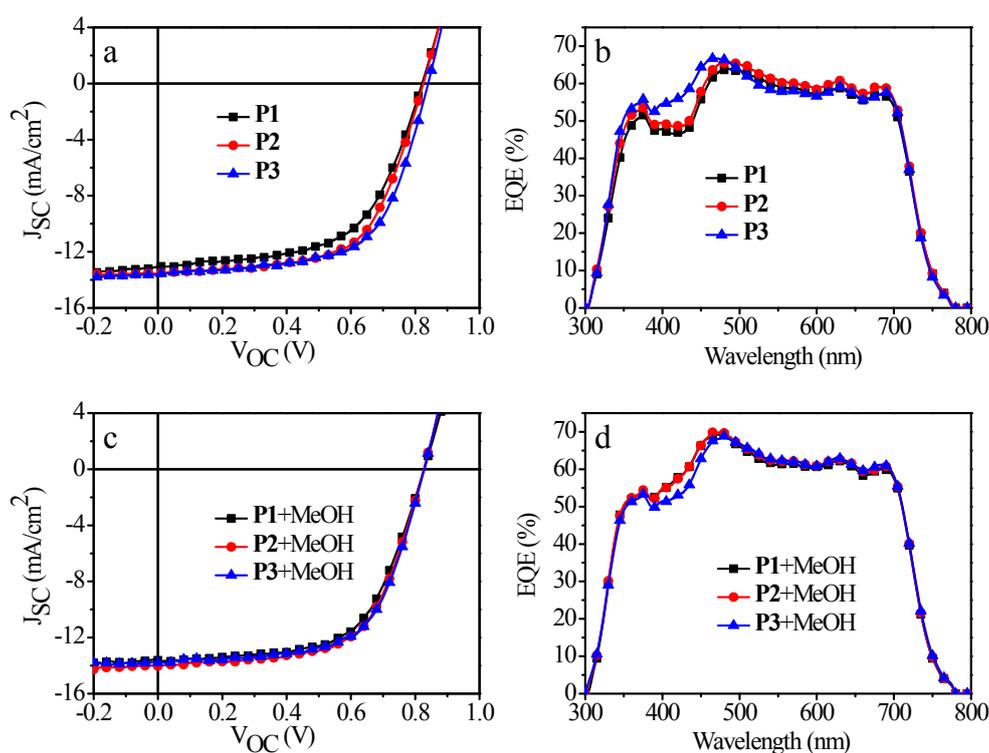


Figure S14. $J-V$ (a, c) and EQE (b, d) curves of the PSCs based on polymer:PC₇₁BM =1:1.5 with or without methanol treatment .

Table S3. Photovoltaic parameters of the PSCs based on polymer:PC₇₁BM =1:1.5.

Polymer	Solvent	V _{OC} (V)	J _{SC} (mA/cm ²)		FF	PCE(%)		
			Measured	Calculated		Best	Average	Calculated
P1	<i>o</i> -xylene+2%ODT	0.83	13.1	12.9	0.59	6.4	6.2	6.3
	<i>o</i> -DCB+1%DIO	0.83	12.9	12.5	0.57	6.1	5.8	5.9
	<i>o</i> -xylene+2%ODT / MeOH	0.84	13.6	13.3	0.61	7.0	6.9	6.8
P2	<i>o</i> -xylene+2%ODT	0.84	13.8	13.2	0.62	7.2	7.0	6.9
	<i>o</i> -DCB+1%DIO	0.83	13.5	12.9	0.60	6.7	6.6	6.4
	<i>o</i> -xylene+2%ODT / MeOH	0.84	14.2	13.8	0.63	7.6	7.5	7.3
P3	<i>o</i> -xylene+2%ODT	0.84	13.6	13.1	0.63	7.2	6.9	6.9
	<i>o</i> -DCB+1%DIO	0.83	13.2	12.7	0.60	6.6	6.4	6.3
	<i>o</i> -xylene+2%ODT / MeOH	0.84	13.9	13.5	0.63	7.4	7.3	7.1

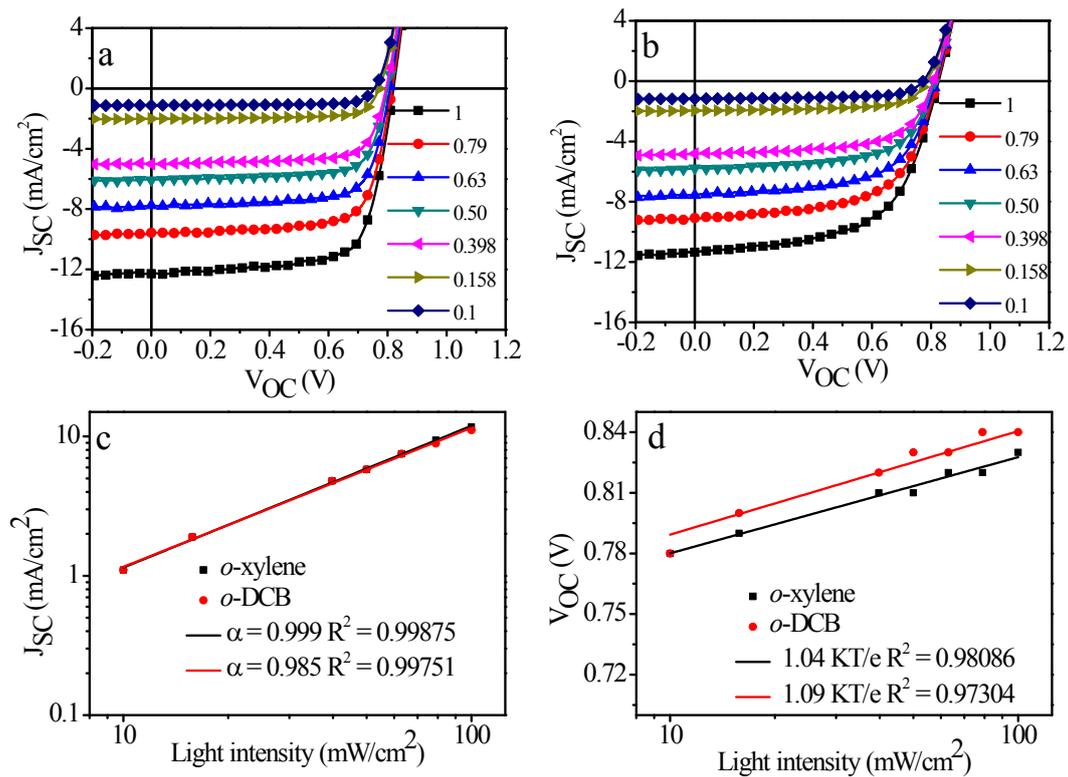


Figure S15. J - V curves of BHJ PSCs based on $\text{P2:PC}_{61}\text{BM} = 1:1.5$ (w/w) processed with *o*-xylene (a) and *o*-DCB (b) under different light intensities; (c) the double-logarithmic plot of J_{SC} as a function of the light intensity and fitting line according to power law (solid lines); (d) V_{OC} as a function of light intensity together with linear fit to the data (solid lines).

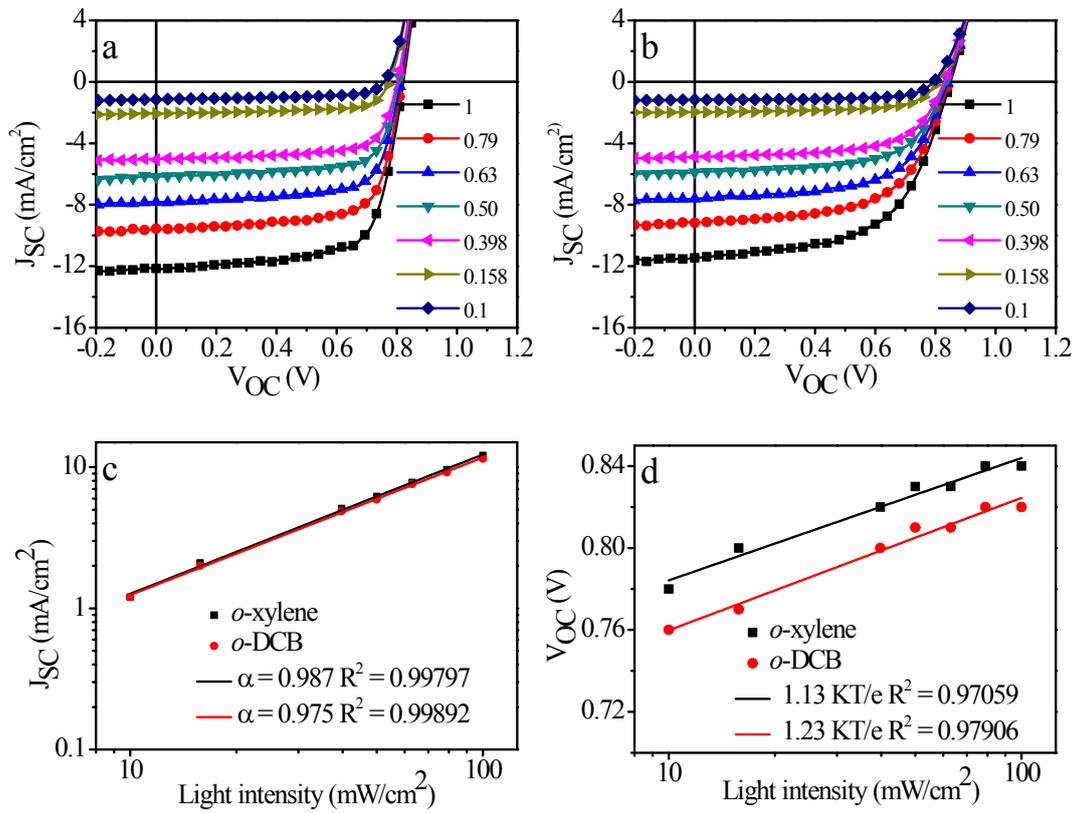


Figure S16. J - V curves of BHJ PSCs based on **P3**:PC₆₁BM = 1:1.5 (w/w) processed with *o*-xylene (a) and *o*-DCB (b) under different light intensities; (c) the double-logarithmic plot of J_{SC} as a function of the light intensity and fitting line according to power law (solid lines); (d) V_{OC} as a function of light intensity together with linear fit to the data (solid lines)

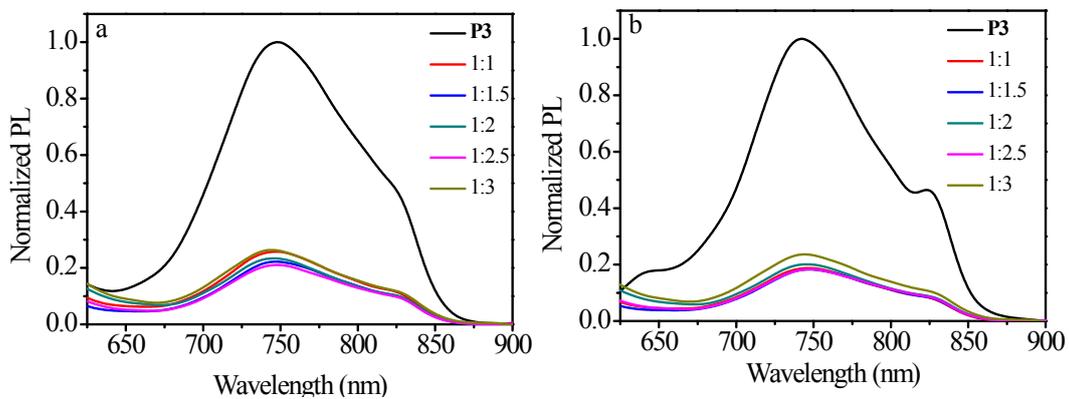


Figure S17. Normalized PL spectra of **P3** and blend films with PC₆₁BM prepared with *o*-DCB (a) and *o*-xylene (b).

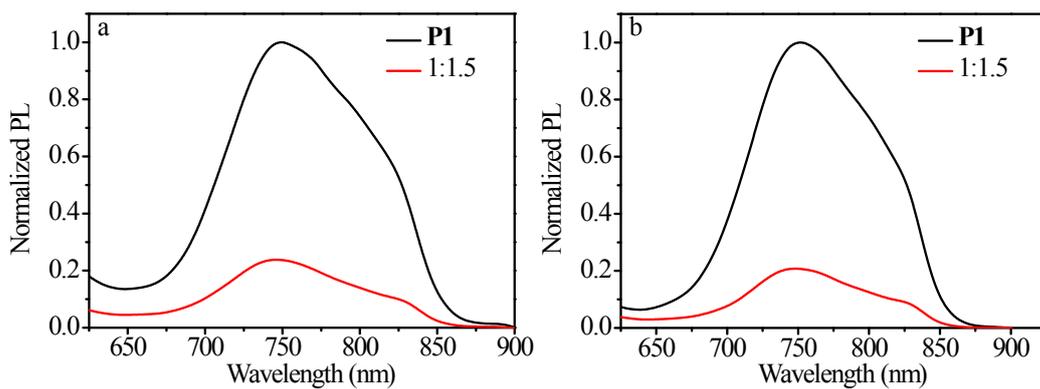


Figure S18. Normalized PL spectra of **P1** and **P1:PC₆₁BM = 1:1.5 (w/w)** prepared with *o*-DCB solutions (a) and *o*-xylene (b).

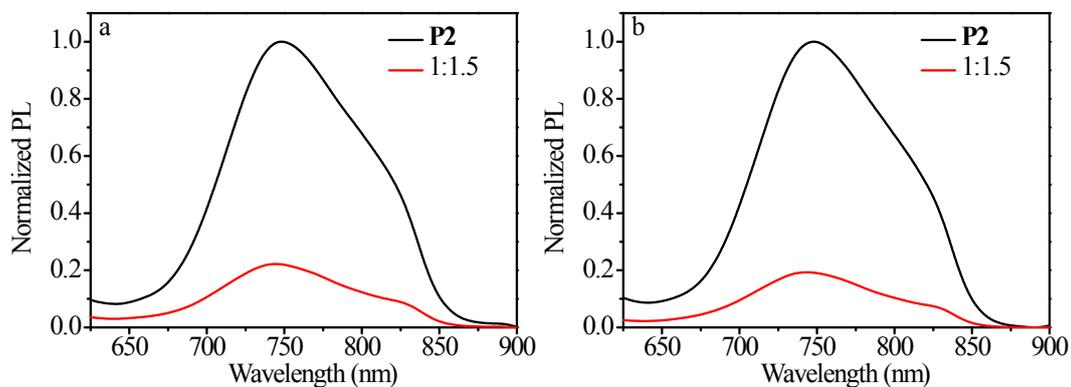


Figure S19. Normalized PL spectra of **P2** and **P2:PC₆₁BM = 1:1.5 (w/w)** prepared with *o*-DCB solutions (a) and *o*-xylene (b).

Table S4. The value of PL quenching efficiencies (ΔPL).

Polymer	ratio	solvent	ΔPL
P1	1:1.5	<i>o</i> -DCB	77%
		<i>o</i> -xylene	81%
P2	1:1.5	<i>o</i> -DCB	78%
		<i>o</i> -xylene	82%
P3	1:1	<i>o</i> -DCB	75%
		<i>o</i> -xylene	83%
	1:1.5	<i>o</i> -DCB	78%
		<i>o</i> -xylene	83%
	1:2	<i>o</i> -DCB	77%
		<i>o</i> -xylene	81%
	1:2.5	<i>o</i> -DCB	79%
		<i>o</i> -xylene	83%
1:3	<i>o</i> -DCB	74%	
	<i>o</i> -xylene	77%	