

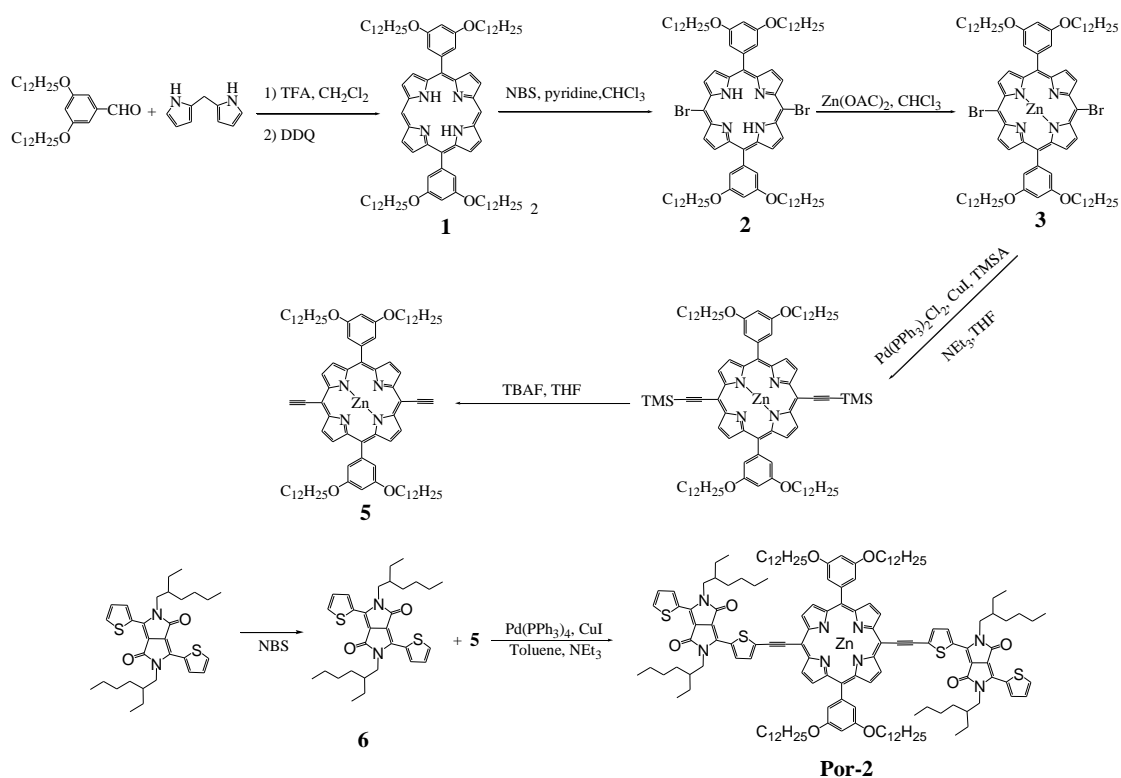
Supplementary Information

Enhanced performance for solution-processed solar cells based on porphyrin small molecules by diketopyrrolopyrrole acceptor unit and pyridine additive

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Scheme S1. Synthetic routines of Por-2.

Experimental section

Materials: All reagents, unless otherwise specified, were obtained from Aldrich, Acros, and TCI Chemical Co. and used as received. Tetrahydrofuran (THF) and toluene, and triethylamine, CH_2Cl_2 and CHCl_3 were distilled from sodium-benzophenone and CaH_2 , respectively, under nitrogen prior to use. All manipulations involving air-sensitive reagents were performed under an atmosphere of Ar or N_2 . 3,5-di(dodecyloxy)benzaldehyde, dipyrromethane and 2,5-bis-(2-ethyl-hexyl)-3,6-di-thienyl-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) were synthesized according to literature methods.¹⁻³ Por-1 and Por-2 were synthesized according to the procedures we reported.

Synthesis

5,15-Bis(3,5-di(dodecyloxy)phenyl)porphyrin 1.

A solution of 3,5-di(dodecyloxy)benzaldehyde (2.304 g, 4.86 mmol) and dipyrromethane (700 mg, 4.86 mmol) in CH_2Cl_2 (500 mL) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (0.25 mL) was added. The mixture was stirred for 12h at room temperature, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (1.8 g) was added. After the mixture was stirred at room temperature for an additional 2h, the reaction was quenched by adding triethylamine (5 mL). Then the solvent was removed, and the residue was purified by flash column chromatography on silica gel using dichloromethane as the eluent. Recrystallization from CHCl_3 /methanol to give a purple solid. ^1H NMR (300 MHz, CDCl_3): δ 10.30 (s, 2H), 9.39 (d, $J=4.6$ Hz, 4H), 9.18 (d, $J=4.6$ Hz, 4H), 7.42 (s, 4H), 6.91 (s, 2H), 4.13 (t, $J=6.6$ Hz, 8H), 1.93 (m, 8H), 1.47 (m, 8H), 1.24 (m, 64H), 0.83 (m, 12H), -3.2 (s, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ 158.67, 147.02, 145.31, 143.16, 131.46, 131.13, 119.07, 114.64, 105.16, 101.12, 68.47, 67.94, 31.92, 29.68, 29.62, 29.47, 29.45, 29.34, 26.16, 25.60, 22.68,

14.09. Mass (MALDI-TOF): Obs. 1200.2; Calcd. for $C_{80}H_{118}N_4O_4$: 1199.8. UV-vis (CH_2Cl_2), $\lambda_{max}=406$ nm.

5,15-Dibromo-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin 2.

N-Bromosuccinimide (274 mg, 1.54 mmol) was added to a chloroform (700mL) solution containing porphyrin 1 (840 mg, 0.7 mmol) and pyridine (35 mL) at $0^\circ C$, and the mixture was stirred for 30 min. Then the mixture was allowed to warm up to room temperature and then stirred for 4h. After the reaction was quenched by addition of acetone, the mixture was washed with water and dried over anhydrous Na_2SO_4 . Then the solvent was removed, and the residue was purified by flash column chromatography on silica gel using petroleum ether/dichloromethane (3:1) as the eluent. Recrystallization from $CHCl_3$ /methanol gave **2** as a purple solid. 1H NMR (300 MHz, $CDCl_3$): δ 9.59 (d, $J=4.8$ Hz, 4H), 8.95 (d, $J=4.8$ Hz, 4H), 7.31 (s, 4H), 6.89 (s, 2H), 4.13 (t, $J=6.6$ Hz, 8H), 1.85 (m, 8H), 1.46 (m, 8H), 1.24 (m, 64H), 0.83 (m, 12H), -3.2 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.40, 143.06, 121.31, 114.46, 103.60, 101.24, 68.44, 34.04, 32.85, 31.90, 29.70, 29.66, 29.62, 29.54, 29.44, 29.37, 29.33, 28.77, 28.19, 26.11, 22.69, 14.11, 14.09. MS Mass (MALDI-TOF): Obs. 1358.1; Calcd. for $C_{80}H_{116}Br_2N_4O_4$: 1357.6. UV-vis (CH_2Cl_2), $\lambda_{max}=424$ nm.

5,15-Dibromo-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin zinc 3.

To a solution of **2** (745 mg, 0.55 mmol) in chloroform (50 mL) was added a solution of $Zn(OAc)_2$ (243 mg, 1.2 mmol) in methanol (12 mL). The reaction mixture was refluxed for 2h, and then washed with water and dried over anhydrous Na_2SO_4 . The solvent was removed, and the residue was recrystallization from $CHCl_3$ /methanol gave a reddish solid. 1H NMR (300 MHz, $CDCl_3$): δ 9.70 (d, $J=4.8$ Hz, 4H), 9.06 (d, $J=4.8$ Hz, 4H), 7.30 (s, 4H), 6.86 (s, 2H), 4.12 (t, $J=6.55$ Hz, 8H), 1.88 (m, 8H), 1.46 (m, 8H), 1.25 (m, 64H), 0.85 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.18, 150.60, 150.15, 143.65, 133.60, 133.04, 122.11, 114.53, 105.06, 101.16, 68.45, 31.90, 29.61, 29.60, 29.43, 29.33, 26.08, 22.65, 14.10, 14.06. Mass (MALDI-TOF): Obs. 1421.0; Calcd. for $C_{80}H_{114}Br_2N_4O_4Zn$: 1421.0. UV-vis (CH_2Cl_2), $\lambda_{max}=425$ nm.

5,15-Bis(trimethylsilyethynyl)-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin zinc 4.

3 (710 mg, 0.5 mmol) was dissolved in THF (25mL) and triethylamine (12.5 mL) was added. The mixture was purged with nitrogen for 30 min. Then Pd(PPh₃)₂Cl₂ (17.5 mg, 0.025 mmol), CuI (5 mg, 0.025 mmol), and trimethylsilylacetylene (200 mg, 2 mmol) were added. After the mixture was stirred at room temperature for 3 days under nitrogen, the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether (1:1) to afford **4** as a green solid. ¹H NMR (300 MHz, CDCl₃): δ 9.68 (d, *J*=4.6 Hz, 4H), 9.04 (d, *J*=4.6 Hz, 4H), 7.33 (s, 4H), 6.89 (s, 2H), 4.10 (t, *J*=6.4 Hz, 8H), 1.82 (m, 8H), 1.50 (m, 8H), 1.23 (m, 64H), 0.83 (m, 12H), 0.60 (s, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 158.28, 150.04, 143.75, 132.84, 131.19, 122.57, 114.37, 107.40, 101.89, 101.34, 101.15, 68.43, 31.90, 29.66, 29.63, 29.60, 29.45, 29.38, 29.33, 26.11, 22.67, 14.10. Mass (MALDI-TOF): Obs. 1455.2; Calcd. for C₉₀H₁₃₂N₄O₄Si₂Zn: 1455.6. UV-vis (CH₂Cl₂), λ_{max}=436 nm.

5,15-Diethynyl-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin zinc 5.

Tetrabutylammonium fluoride (0.72 mL, 1M in THF) was added to a stirred solution of porphyrin **4** (509 mg, 0.35 mmol) in THF (20 mL). After the mixture was stirred for 5 min, water was added to quench the reaction. The solution was extracted with chloroform, washed with water and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether (1/1)) to give **5** as a green solid. ¹H NMR (300MHz, CDCl₃): δ 9.74 (d, *J*=4.68 Hz, 4H), 9.07 (d, *J*=4.65 Hz, 4H), 7.34 (s, 4H), 6.89 (s, 2H), 4.14 (m, 10H), 1.83 (m, 8H), 1.45 (m, 8H), 1.24 (m, 64H), 0.83 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 158.35, 152.37, 150.20, 133.04, 131.19, 114.30, 68.42, 31.88, 29.63, 29.58, 29.43, 29.38, 29.30, 26.11, 22.64, 14.05. Mass (MALDI-TOF): Obs. 1311.2; Calcd. for C₈₄H₁₁₆N₄O₄Zn: 1311.2. UV-vis (CH₂Cl₂), λ_{max}=430 nm.

3-(5-Bromo-thiophen-2-yl)-2,5-bis-(2-ethyl-hexyl)-6-thiophen-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (6)

To a 250mL flask containing 2,5-bis-(2-ethyl-hexyl)-3,6-di-thienyl-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione (1.57g, 3.0 mmol) in 100 mL CHCl₃, was added NBS (587.4mg, 3.3mmol), and the result mixture was stirred for 9 h at room temperature, then the reaction was quenched with water. After a serial route procedures, the product was purified first by column chromatography and then by recrystallization in CH₂Cl₂/CH₃OH to provide **6** as purple solid. ¹H NMR (300MHz, CDCl₃), δ 8.89 (m, 1H), 8.62 (d, *J*=4.17Hz, 1H), 7.64 (m, 1H), 7.27 (t, *J*=4.47Hz, 1H), 7.22 (d, *J*=4.2Hz, 1H), 4.02 (m, 4H), 1.84 (m, 2H), 1.36-1.26 (m, 16H), 0.86 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): δ 161.65, 140.89, 138.94, 135.53, 135.09, 131.37, 131.25, 130.82, 129.75, 128.48, 118.62, 108.15, 45.93, 39.11, 39.06, 30.19, 28.33, 23.56, 23.02, 14.00, 10.46.

5,15-Bis(2,5-bis-(2-ethyl-hexyl)-3,6-di-thienyl-2-yl-2,5-dihydro-pyrrolo[3,4-c]pyrrole-1,4-dione-5'-yl-ethynyl)-10,20-bis(3,5-di(dodecyloxy)phenyl)-porphyrin zinc (Por-2).

To a 50 mL two necked round-bottom flask were added 5,15-diethynyl-10,20-bis(3,5-di(dodecyloxy)phenyl)porphyrin zinc (262 mg, 0.2 mmol), **6** (361mg, 0.6 mmol), anhydrous toluene (10 mL), and triethylamine (5 mL). The mixture was deoxygenated with N₂ for 30 min. Pd (PPh₃)₄ (48 mg, 0.04 mmol) and CuI (8 mg, 0.04 mmol) were added. The mixture was stirred at 80°C for 3 days. After cooling to room temperature, the mixture was washed with water and dried over anhydrous Na₂SO₄. The solvent was removed, and the residue was purified by GPC HPLC to give a dark green solid Por-2. Mass (MALDI-TOF): Obs. 2356.28; Calcd. for C₁₄₄H₁₉₂N₈O₈S₂Zn, 2356.76.

Instruments: The ¹H and ¹³C NMR spectra were measured on a Bruker AVANCE Digital 300 MHz spectrometer in deuterated CHCl₃ using tetramethylsilane as an

internal standard. Mass spectrometry (MS) data were obtained on a Bruker Daltonics BIFLEX III MALDI-TOF Analyzer using MALDI mode. Thermogravimetric analysis (TGA) measurements were performed on a NETZSCH TG 209 under a nitrogen flow at heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Cyclic voltammetry (CV) was carried out on a CHI660C electrochemical workstation at scan rate of 50 mV s^{-1} in the nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). A platinum electrode coated with a thin porphyrin film, a Pt wire and a calomel electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. UV-Vis-NIR absorption spectra were measured using a HP 8453 spectrophotometer. The atomic force microscopy (AFM) measurement of the surface morphology of samples was conducted on NanoScope NS3A system (Digital Instrument). Films of the molecule/ PC_{61}BM (PC_{71}BM) blends were cast from solutions with or without pyridine additive, followed by spin-coating on the top surface of a PEDOT:PSS substrate. The thickness of the active layer was verified by a surface profilometer (Tencor, Alpha-500).

The X-ray diffraction measurements were performed using a Panalytical Xper PRO instrument with $\text{Cu K}\alpha$ ($\lambda = 1.5418\text{ \AA}$) as the incident beam (operating conditions: 40 kV and 40 mA). Data were obtained from 2° to 5° (2θ). To obtain an identical surface of the blend layers in OPV devices, 40 nm PEDOT:PSS was spin-cast onto silicon wafers, followed by baking at $130\text{ }^{\circ}\text{C}$ for 20 minutes, and then the blend films prepared at different conditions were spin-coated on PEDOT:PSS layer. For Por-2,

both pristine and treated films were annealing at 70 °C for 20 min.

OPV fabrication: The solar cells devices were fabricated as following: ITO-coated glass substrates were cleaned prior to device fabrication by sonication in acetone, detergent, distilled water, and isopropyl alcohol. After treated with an oxygen plasma for 5 min, 40 nm thick PEDOT:PSS (Bayer Baytron 4083) layer was spin-coated on the ITO-coated glass substrates at 3000 rpm for 30s, subsequently the substrates were dried at 130°C for 20 min in air and then transferred to a N₂-glovebox for spin-casting the blend layers. For the devices based on Por-1, the active layers were fabricated as reported previously, except for different amount of pyridine additive was added into host solvent. While, for the devices based on Por-2, the mixed solution was prepared by dissolving the molecule with PC₆₁BM at various blend weight ratios of 2:1 to 1:1.5 (w/w, Por-2:PC₆₁BM=24 mg/ml) in the CB/DCB (3:1 v/v) solution, and the optimal conditions (1:1 w/w) were further investigated with different composition of pyridine and CB/DCB. The thicknesses of the blend layers were average 85 nm measured by profilometer. The active layers were allowed to dry under inert atmosphere over night and then heated to 70° C for 20 minutes. Subsequently, an ultra-thin PFN layer was subsequently deposited by spin-casting from 0.02% (w/v) solution in methanol (2000 rpm for 30 s). Finally, 80 nm Al was thermally evaporated onto the active layer in a high-vacuum chamber with base pressure $<3 \times 10^{-6}$ mbar. The effective area was measured to be 0.16 cm². The J-V characteristics of the OPVs were measured with a Keithley 236 digital source meter under AM 1.5 solar simulator (Oriel model 91192) at 100 mW cm⁻². The spectral response was measured with a commercial photo

modulation spectroscopic setup (Oriel). A calibrated Si photodiode was used as a reference before each measurement.

Hole and electron Mobilities Measurement: The mobilities of the blend layers with and without pyridine additive were determined by fitting the dark current to the model of the space charge limited current (SCLC). Hole-only devices were in configuration of ITO/PEDOT:PSS(40 nm)/active layers/MoO₃(10 nm)/Al(80 nm) and electron-only devices were in configuration of ITO/Al(40 nm)/active layers/Ca(3 nm)/Al(80 nm). Films were prepared by dissolving donor and acceptor in DCB/CB with and without pyridine as additive, followed by spin-coating on the top surface of a PEDOT:PSS or Al substrate. For Por-2, both pristine and treated films were annealing at 70 °C for 20 min. The electric-field dependent SCLC mobility was estimated using Equation (1).

$$J = \frac{9}{8} \epsilon_r \epsilon_0 \frac{E^2}{d} \mu_0 \exp(\beta \sqrt{E}) \quad (1)$$

Where J is the current, μ_0 is the zero-field mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layer, β is the field activation factor and E is the effective electric field.

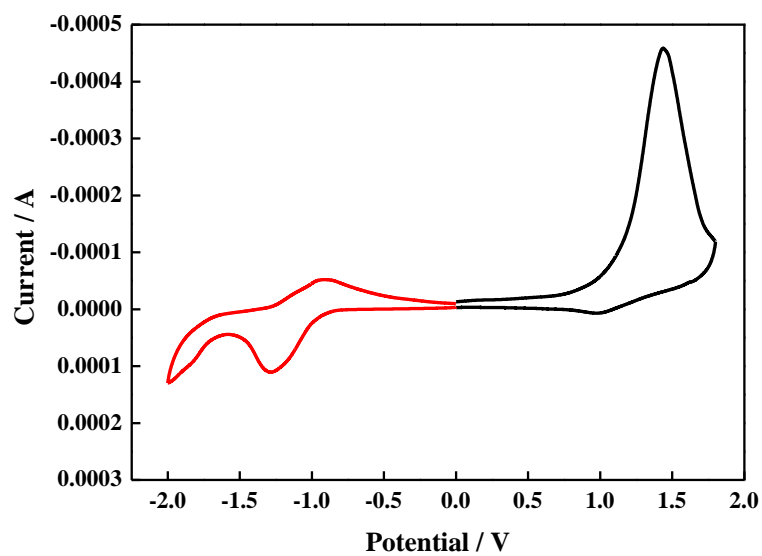


Figure S1. Cyclic voltammogram of a Por-2 film coated on a platinum electrode.

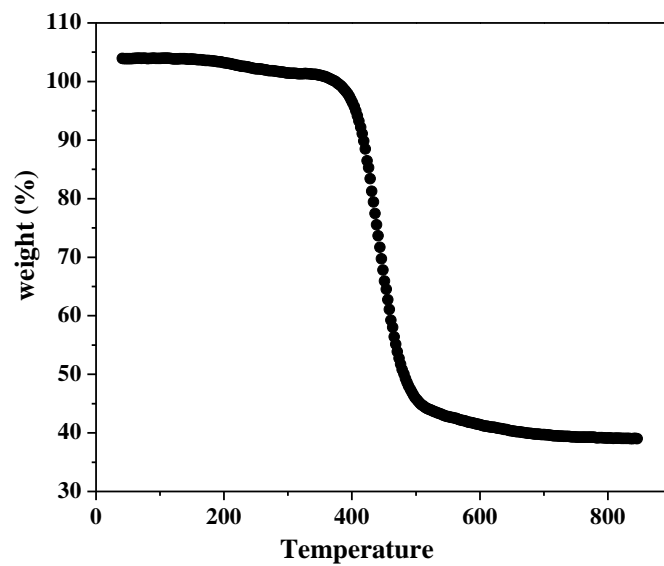


Figure S2. TGA plot of Por-2.

Table S1. Photovoltaic Properties of the OPVs Based on Por-2 blend with PC₆₁BM at different ratio (w/w). The devices were tested under the Illumination of AM1.5 G, 100 mW cm⁻².

solvent	blend ratio	J _{SC} (mA cm ⁻²)	V _{OC} (V)	FF (%)	PCE (%)
	2:1	8.92	0.78	42.1	2.93
	3:2	8.02	0.78	47.8	2.99
CB/DCB only	1:1	9.75	0.76	50.0	3.71
	1:1.5	8.01	0.76	56.3	3.42

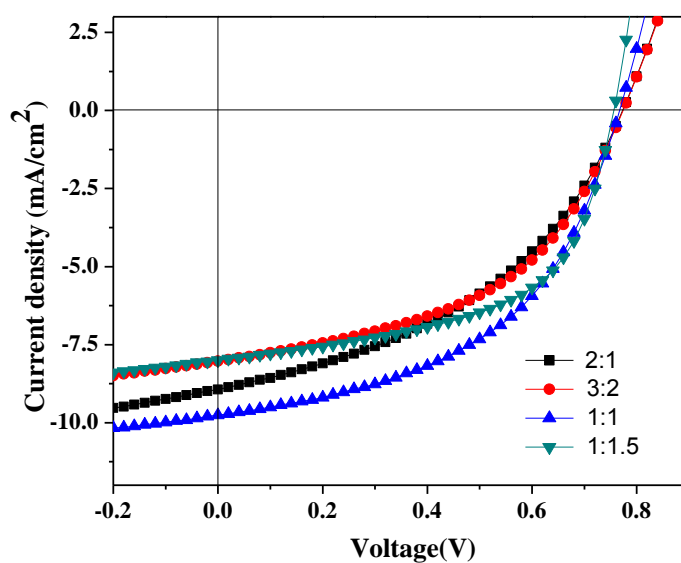


Figure S3. J-V characteristics of the solar cells based on the Por-2 blend with PC₆₁BM at different ratio (w/w)

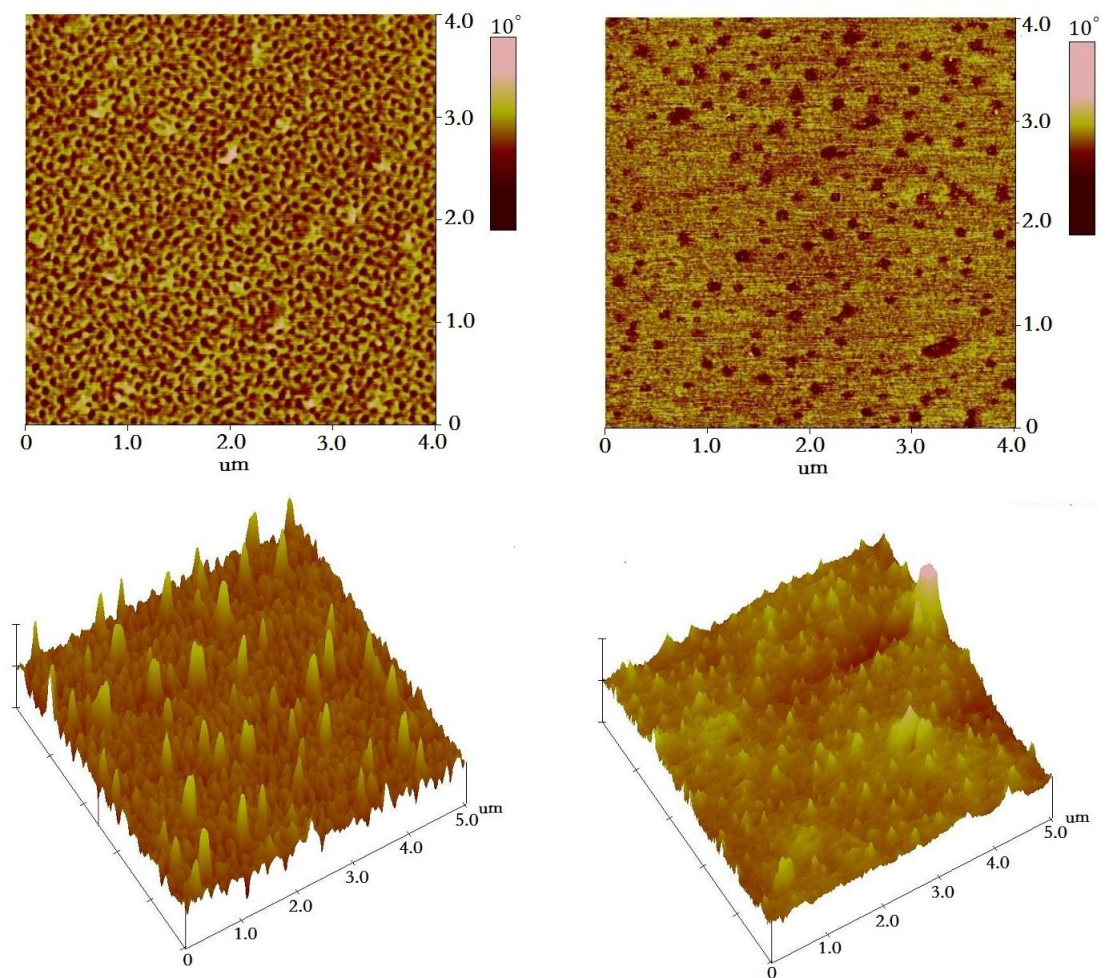


Figure S4. Tapping-mode AFM phase and height images of the surface of Por-1/PC₇₁BM (1:3, w/w) blend films (left top and left bottom) without pyridine and (right top and right bottom) with 1 vol% pyridine. The date scale of the height image is 10 nm.

X-ray Diffraction:

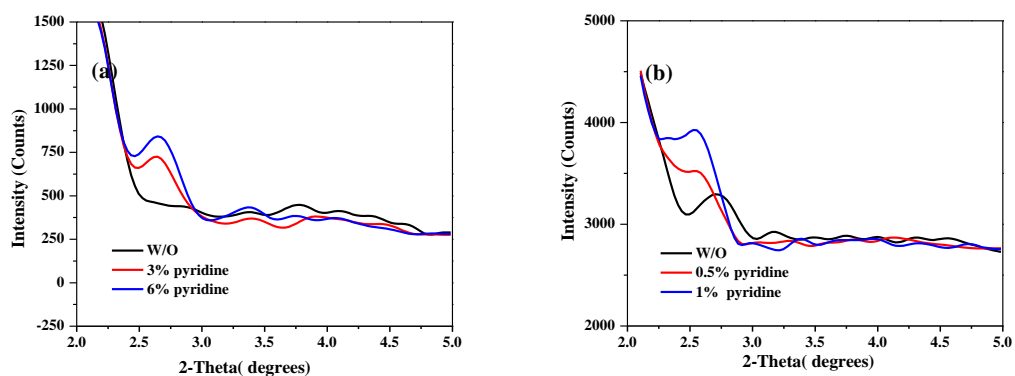


Figure S5. X-ray diffraction of the films processed with or without pyridine additive
(a) Por-2/PC₆₁BM (1:1, w/w) blend films, (b) Por-1/PC₇₁BM (1:3, w/w) blend films.

Table S2. Hole and electron mobilities obtained from SCLC.

Devices	Additive	Hole mobility (cm ² V ⁻¹ s ⁻¹)	Electron mobility (cm ² V ⁻¹ s ⁻¹)
Por-2/PC ₆₁ BM (1:1 w/w)	W/O	4.6×10 ⁻⁵	1.9×10 ⁻⁴
	With 3% pyridine	1.6×10 ⁻⁴	9.4×10 ⁻⁵
Por-1/PC ₇₁ BM (1:3 w/w)	W/O	2.2×10 ⁻⁷	1.7×10 ⁻⁴
	With 1% pyridine	7.6×10 ⁻⁶	3.3×10 ⁻⁵

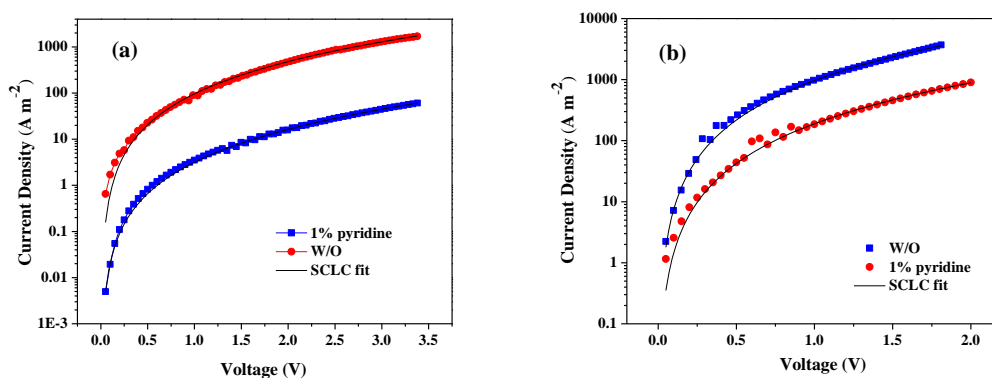


Figure S6. J-V characteristics of the hole-only (a) and electron-only (b) devices of Por-1/PC₇₁BM (1:3, w/w) blends processed with and without pyridine in the configuration of ITO/PEDOT:PSS/active layer(~70 nm)/MoO₃/Al and ITO/Al/active layer(~87 nm)/Ca/Al, respectively.

Reference

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2. E. Zhou, Q. Wei, S. Yamakawa, Y. Zhang, K. Tajima, C. Yang and K. Hashimoto, *Macromolecules*, 2010, 43, 821-826.
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