

Cathode Interlayer-Free Organic Solar Cells with Enhanced Device Performance upon Alcohol Treatment

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Experiment Details:

Materials. All reagents were purchased from commercial sources (Aldrich, Acros, Energy chemical or Suna Tech Inc.) and used as received. Tetrahydrofuran (THF) triethylamine (Et₃N) and toluene were dried over Na/benzophenoneketyl and freshly distilled prior to use.

Measurements and Instruments. ¹H NMR spectra were recorded using a Bruker Ultrashield 500 Plus NMR spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDITOF mass spectrometer. UV-vis spectra of dilute solutions (1×10^{-5} M) of samples in dichloromethane (DCM) were recorded at room temperature (ca. 25°C) using a Shimadzu UV-3600 spectrophotometer. Solid films for UV-vis spectroscopic analysis were obtained by spin-coating the molecule solutions onto a quartz substrate. Cyclic voltammetry (CV) of the molecule films was performed using a Versastat II electrochemical workstation operated at a scan rate of 50 mV s⁻¹; the solvent was anhydrous DCM, containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The potentials were measured against an Ag/Ag⁺ (0.01 M AgNO₃) reference electrode; the ferrocene/ferrocenium ion (Fc/Fc⁺) pair was used as the internal standard. The onset potentials were determined from the intersection of two tangents drawn at the rising and background currents of the cyclic voltammograms.

Synthesis.

The synthesis routes of the compounds are shown in Fig. S1 and S2, and the detailed synthesis processes are as follows.

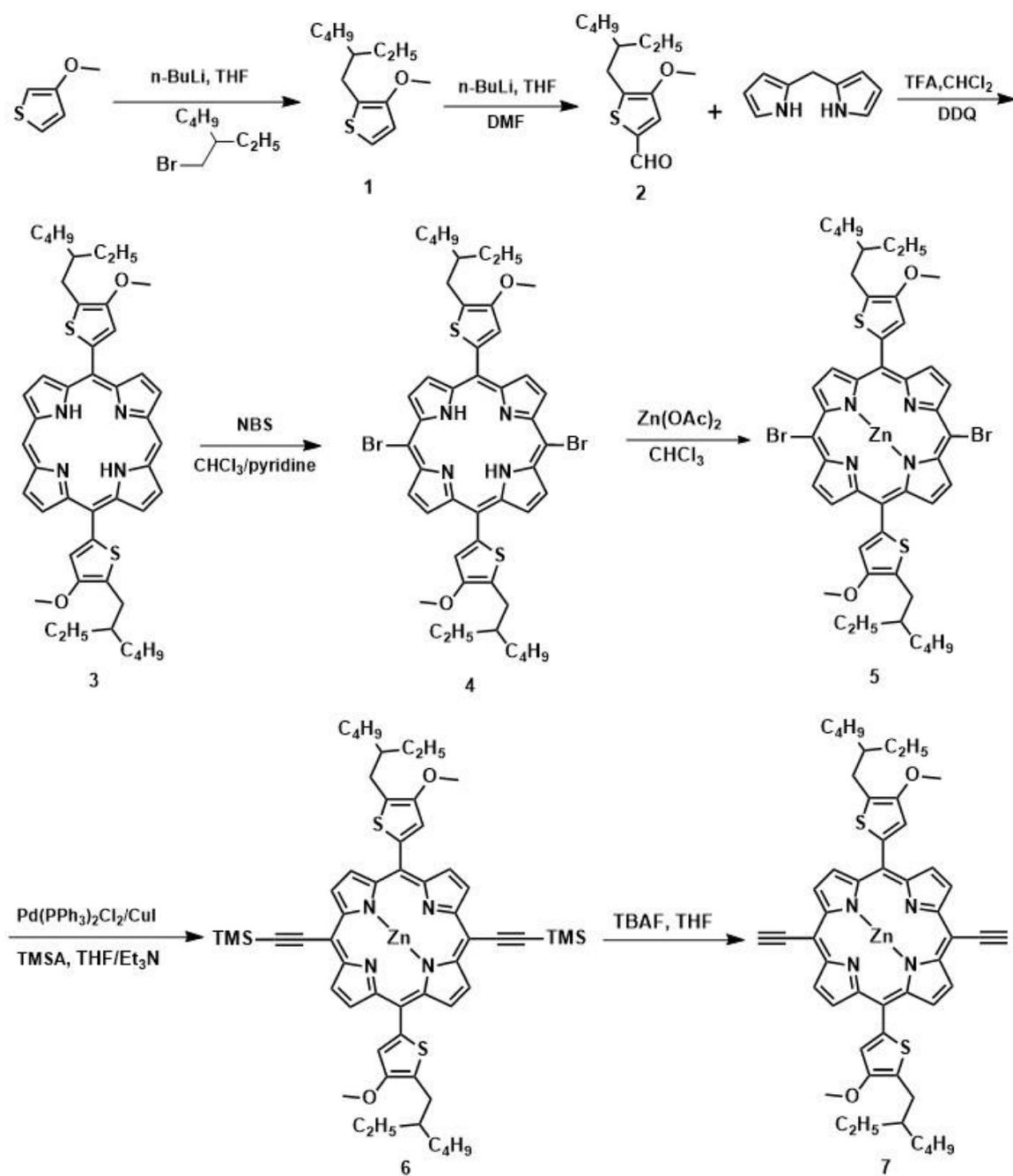


Fig. S1. Synthesis routes for the porphyrin core.

We synthesized 2-(2-ethylhexyl)-3-methoxythiophene, 5-bromo-10,20-bis[5-(2-ethylhexyl)-4-methoxythiophene-2-yl]-porphyrin(2) and 4,7-diethynylbenzo[c][1,2,5]thiadiazole according to literature procedures^{1,2,3}.

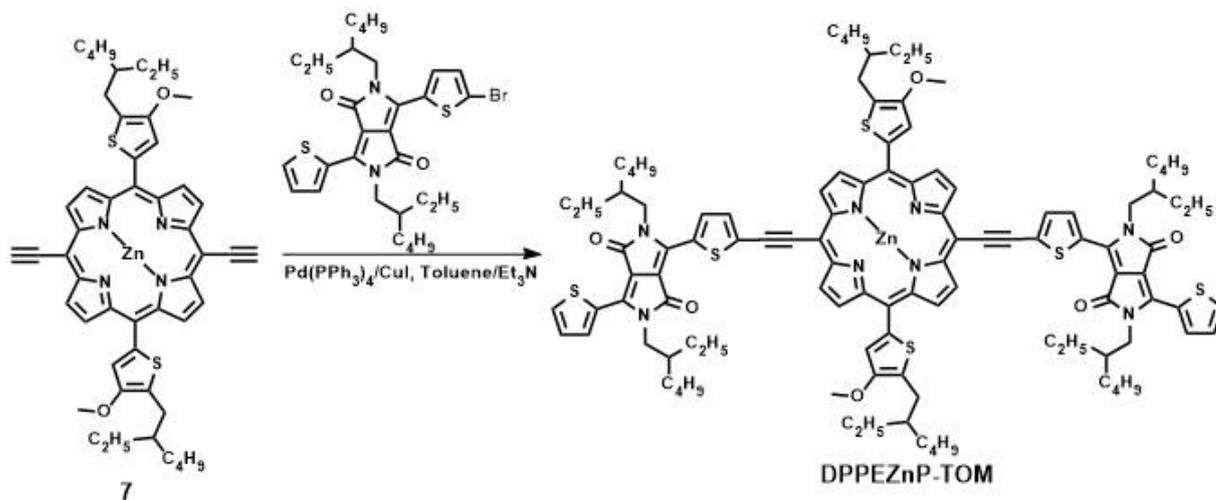


Fig. S2. The synthesis route of DPPEZnP-TOM.

5-(2-(2-Ethylhexyl)-4-methoxythiophene)-2-carbaldehyde (1): (2-(2-ethylhexyl)-3-methoxythiophene) was dissolved in dry THF. To a stirred solution of (2-(2-ethylhexyl)-3-methoxythiophene) (13.6 g, 59.4 mmol) in DMF, POCl₃ (13.0 g, 180.0 mmol) was added drop-wise at 0°C, stirring was warmed, neutralized by NaOH to neutrality. After extraction with CHCl₃, the organic phase was dried over MgSO₄. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v = 1/4) as the eluent to give 9.49 g pure product in 66.8% yield. Yellow oil; ¹H NMR(500 MHz, CDCl₃) δ (ppm): 9.72 (s, 1H), 7.46 (s, 1H), 3.87 (s, 3H), 2.69 (d, 2H), 1.56-1.67(m, 1H), 1.21-1.37 (m, 8H), 0.84-0.92 (t, 6H).

5,15-Bis-(5-(2-ethylhexyl)-4-methoxythiophene)-2-yl-porphyrin (2): A solution of 5-(2-(2-ethylhexyl)-3-methoxythiophene)-2-carbaldehyde (4.74g, 18.66 mmol) and dipyrromethane (2.72g, 18.66 mmol) in CH₂Cl₂ (1.5L) was purged with nitrogen for 30 min, and then trifluoroacetic acid (TFA) (0.22 mL) was added. The mixture was stirred for 12h at room temperature, and then 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (6.90g) was added. After the mixture was stirred at room temperature for an additional 1h, the reaction was quenched by 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 CH₂Cl₂/methanol gave **2** as a dark red solid (2.26g, 32%). ¹H NMR(500 MHz, CDCl₃) δ (ppm): 10.27 (s, 2H), 9.38 (s, 8H), 7.72 (s, 2H), 4.10 (s, 6H), 3.20 (d, 4H), 1.83-1.93(m, 2H), 1.40-1.69 (m, 16H), 0.97-1.17 (m, 12H), -2.97 (s, 2H).

5,15-Dibromo-10,20-bis-(5-(2-ethylhexyl)-4-methoxythiophene)-2-yl)-porphyrin (3): Porphyrin **2** (1.26 g, 1.66mmol) were dissolved in 600 mL chloroform and pyridine (5 mL) and then cooled to 0 °C. To the cold solution, N-bromosuccinimide (709 mg, 3.98 mmol) was added and the mixture was stirred at 0 °C for 30 min. Then the reaction was quenched by acetone, and the mixture was washed with water and dried over anhydrous Na₂SO₄. After the solvent was removed, the residue was purified by flash column chromatography on silica gel using petroleum ether/dichloromethane (2:1) as the eluent. Recrystallization from CH₂Cl₂/methanol gave **3** as a purple solid (1.29 g, 85%). ¹H NMR (500 MHz, CDCl₃) δ(ppm): 9.69(d, 4H), 9.12 (d, 4H), 7.66 (s, 2H),4.07 (s, 6H), 2.99 (d, 4H), 1.80-1.88(m, 2H), 1.37-1.66 (m, 16H), 0.96-1.09(m, 12H),-2.71 (s, 2H).

5,15-Dibromo-10,20-bis-(5-(2-ethylhexyl)-4-methoxythiophene)-2-yl)-porphyrin zinc (II) (4): To a solution of **3** (1.20 g, 1.31 mmol) in chloroform (100 mL), was added a solution of Zn(OAc)₂ (1.19 g, 6.54 mmol) in methanol (20 mL). The reaction mixture was refluxed for 4 h and then washed with water and dried over anhydrous Na₂SO₄. After the solvent was removed, the residue was purified by flash column chromatography on silica gel using CHCl₃ as the eluent to afford a dark red solid **4** (1.26 g, 98%). ¹H NMR (500 MHz, CDCl₃) δ(ppm): 9.46(d, 4H), 9.03 (d, 4H), 7.27 (s, 2H),4.07 (s, 6H), 2.71 (d, 4H), 1.67-1.75(m, 2H), 1.33-1.66 (m, 16H), 0.92-1.06(m, 12H).

5,15-Bis(trimethylsilyl ethynyl)-10,20-bis-(5-(2-ethylhexyl)-4-methoxythiophene)-2-yl)-porphyrin zinc (II) (5): Porphyrin **4** (774 mg, 0.79mmol) was dissolved in THF

(40mL) and tri-ethylamine (20mL) was added. The mixture was purged with nitrogen for 30 min. Then Pd(PPh₃)₂Cl₂ (55 mg, 0.08mmol), CuI (15 mg, 0.08 mmol), and trimethylsilylacetylene (308 mg, 3.14mmol) were added. The mixture was stirred at room temperature for 72 h under argon, the reaction was quenched with saturated brine. After the mixture was extracted with CHCl₃ a few times, the combined organic layers were dried with anhydrous Na₂SO₄ and concentrated. Finally, the residue was purified by column chromatography (silica gel, CH₂Cl₂/petroleum ether (1.5:1) to afford **5** as a purple solid. ¹H NMR (500 MHz, CDCl₃) δ (ppm): 9.66(d, 4H), 9.18 (d, 4H), 7.48 (s, 2H), 3.87 (s, 6H), 2.84 (d, 4H), 1.71-1.80 (m, 2H), 1.36-1.63 (m, 16H), 0.94-1.08 (m, 12H), 0.61 (t, 18H).

5,15-Diethynyl-10,20-bis-(5-(2-ethylhexyl)-4-methoxythiophene)-2-yl)-porphyrin zinc (II) (6): Tetrabutylammonium fluoride (0.12 mL, 1M in THF) was added to a stirred solution of porphyrin **5** (534 mg, 0.51mmol) in THF (40 mL). After the mixture was stirred for 5 min, water was added to quench the reaction. Then the solution was extracted with chloroform, washed with water and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by gel permeation chromatography (GPC) to afford **6** as a deep blue solid (399 mg, 87%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 9.68(d, 4H), 9.22 (d, 4H), 7.50 (s, 2H), 4.12 (s, 2H), 3.85 (s, 6H), 2.83 (d, 4H), 1.71-1.80 (m, 2H), 1.36-1.63 (m, 16H), 0.94-1.08 (m, 12H).

DPPEZnP-TOM: Using instead and following a similar procedure for **DPPEZnP-TOM**, the highly pure **DPPEZnP-TOM** was also obtained as a gray green solid in a yield of 62%. ¹H NMR (500 MHz, CDCl₃+Pyridine-D₅) δ (ppm): 9.42 (d, 4H), 9.18 (d, 4H), 7.76 (dd, 2H), 8.64 (s, 2H), 7.79 (s, 2H), 7.64 (dd, 2H), 7.28 (s, 2H), 7.20 (dd, 2H), 4.14 (s, 6H), 3.96 (m, 4H), 3.44 (d, 4H), 3.04 (d, 4H), 1.78-1.93 (m, 4H), 1.41-1.72 (m, 18H), 1.13-1.38 (m, 32H), 1.98-1.12 (mt, 12H), 0.79-0.94 (m, 24H). ¹³C NMR (125 MHz, CDCl₃+Pyridine-D₅) δ (ppm): 161.12, 152.96, 151.80, 150.87, 139.80, 138.70,

137.72, 135.52, 132.66, 131.79, 130.50, 129.83, 129.44, 128.79, 128.42, 124.67, 124.00, 115.86, 107.98, 107.90, 102.61, 100.96, 89.84, 59.39, 45.88, 45.40, 41.27, 39.15, 39.08, 32.85, 30.27, 30.20, 29.89, 29.08, 28.50, 28.37, 28.35, 26.06, 23.53, 23.22, 23.15, 23.09, 14.30, 14.14, 14.04, 11.09, 10.51, 10.48. (MALDI-TOF, m/z) calculated for C₁₁₀H₁₂₈N₈O₆S₆Zn: 1913.76; found 1914.56.

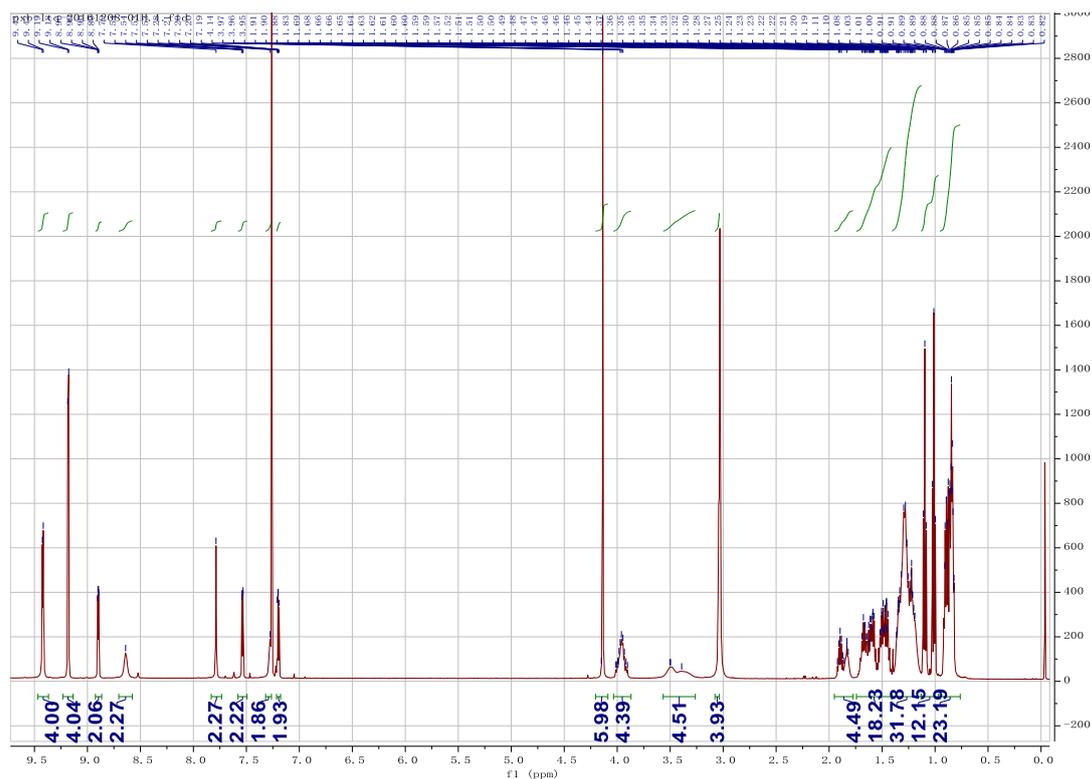


Fig. S3. The ¹H (500 MHz) spectrum of DPPEZnP-TOM in CDCl₃ with 5% pyridine-D₅.

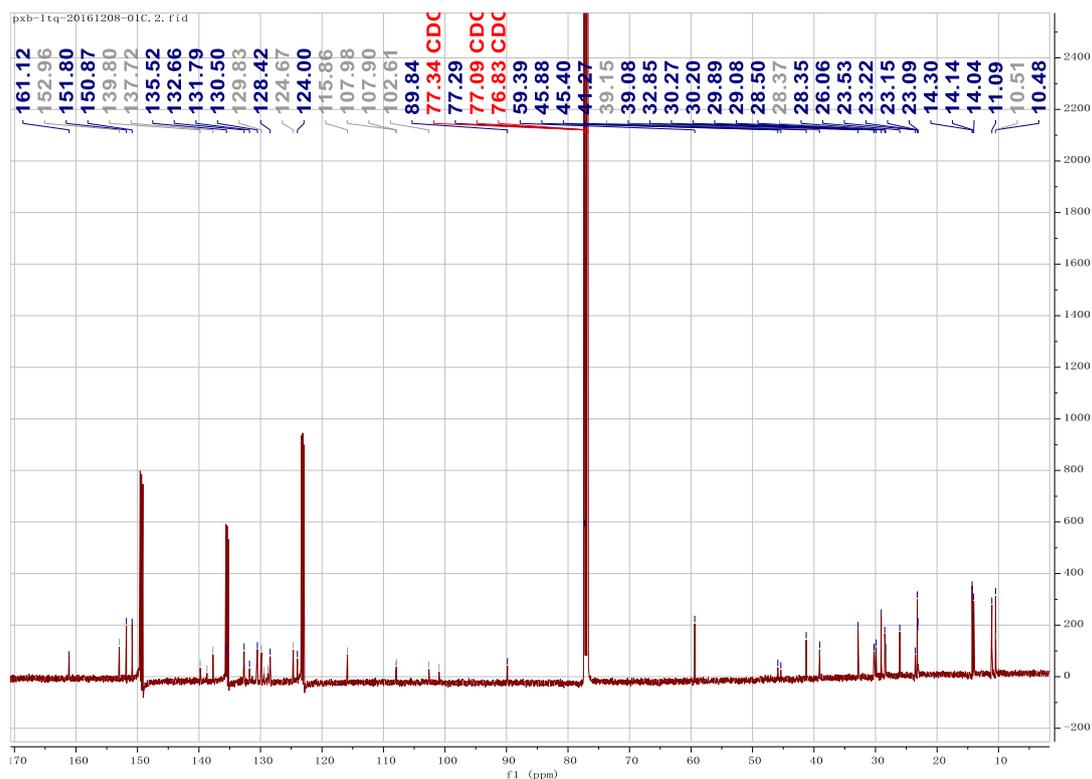


Fig. S4. The ^{13}C (125 MHz) spectrum of DPPEZnP-TOM in CDCl_3 with 5% pyridine- D_5 .

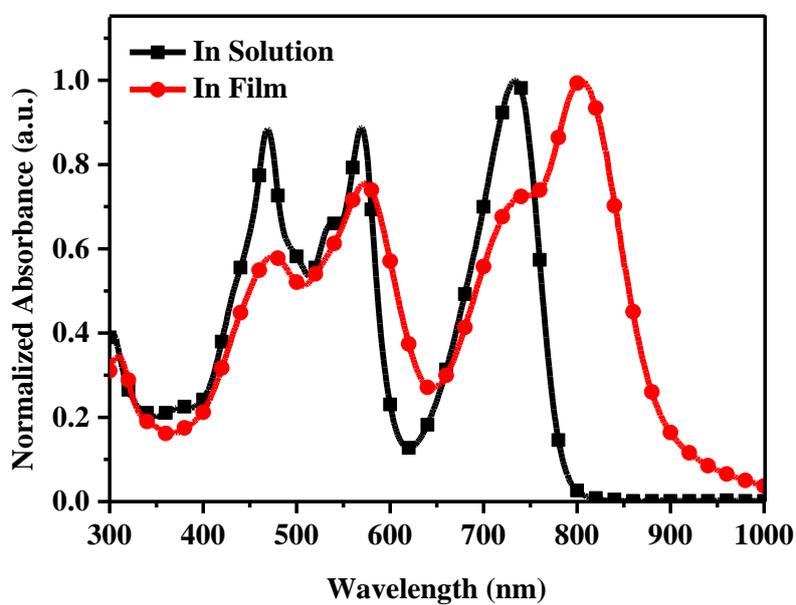


Fig. S5. UV-vis-NIR absorption spectrum of DPPEZnP-TOM in THF solution and in film.

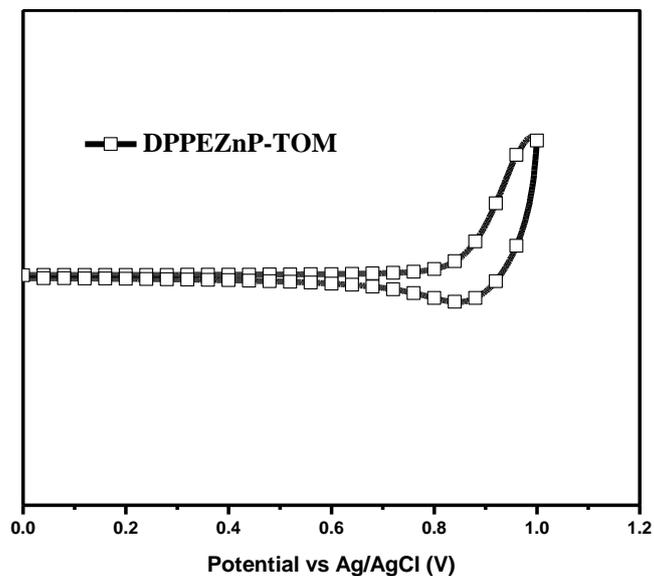


Fig. S6. Cyclic voltammogram of DPPEZnP-TOM film in acetonitrile containing 0.10 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as the supporting electrolyte and an Ag/AgCl electrode as the reference electrode at a speed of 50 mV s⁻¹.

Table S1. Absorption characteristics of DPPEZnP-TOM.

Molecules	$\lambda_{\text{abs}}(\text{nm})$		$\lambda_{\text{onset}}^{\text{a}}$ (nm)	E_{g}^{b} (eV)	HOMO ^c (eV)	LUMO ^d (eV)
	solution	film				
DPPEZnP-TOM	732	804	912	1.36	-5.23	-3.87

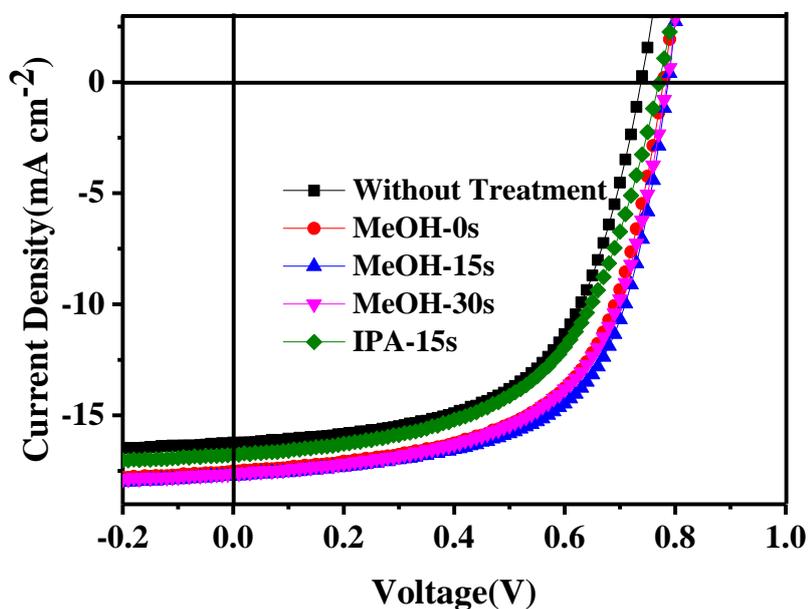


Fig. S7. J-V curves of DPPEZnP-TOM:PC₆₁BM devices with different MeOH soaking time and IPA treatment.

Table S2. Photovoltaic parameters of DPPEZnP-TOM:PC₆₁BM OSCs for the active layers without any treatment, with MeOH treatment and with IPA treatment.

treatment	Soaking time	Voc(V)	Jsc(mA cm ⁻²)	FF(%)	PCE(%)
Without		0.75	16.22	59.05	7.18(7.55)
MeOH	0 s	0.78	17.50	60.51	8.26(8.46)
	15 s	0.78	17.74	62.14	8.59(8.96)
	30 s	0.78	17.62	59.62	8.19(8.69)
IPA	15 s	0.77	16.75	56.60	7.29 (7.85)

Table S3. Photovoltaic parameters of DPPEZnP-TEH:PC₆₁BM OSCs for the active layers without any treatment, with MeOH treatment and with IPA treatment.

	Voc(V)	Jsc (mA cm ⁻²)	FF(%)	PCE(%)	Rs(ohm cm ²)
Without treatment	0.73	16.32 (16.16) ^a	55.03	6.55±0.08 (6.63)	11.29
MeOH Treatment	0.75	18.83 (17.26) ^a	59.54	8.38±0.16 (8.54)	4.48
IPA Treatment	0.73	17.31 (16.99) ^a	55.91	6.92±0.10 (7.07)	9.68

^a Calculated J_{SC} values from EQE curves.

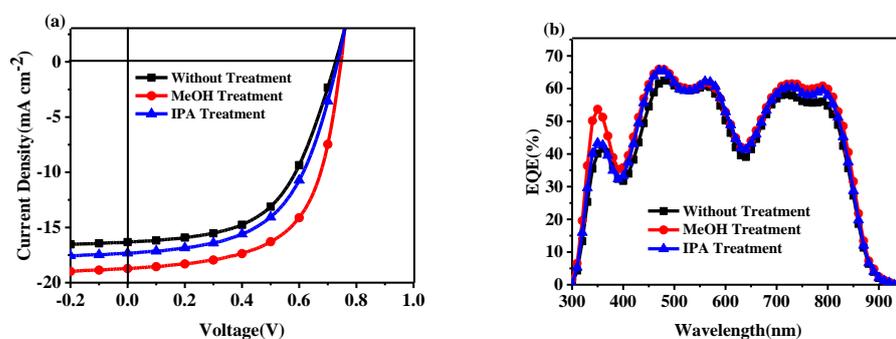


Fig. S8. (a) J - V curves and (b) EQE curves of DPPEZnP-TEH: PC₆₁BM devices for the active layers without any treatment, with MeOH treatment and with IPA treatment.

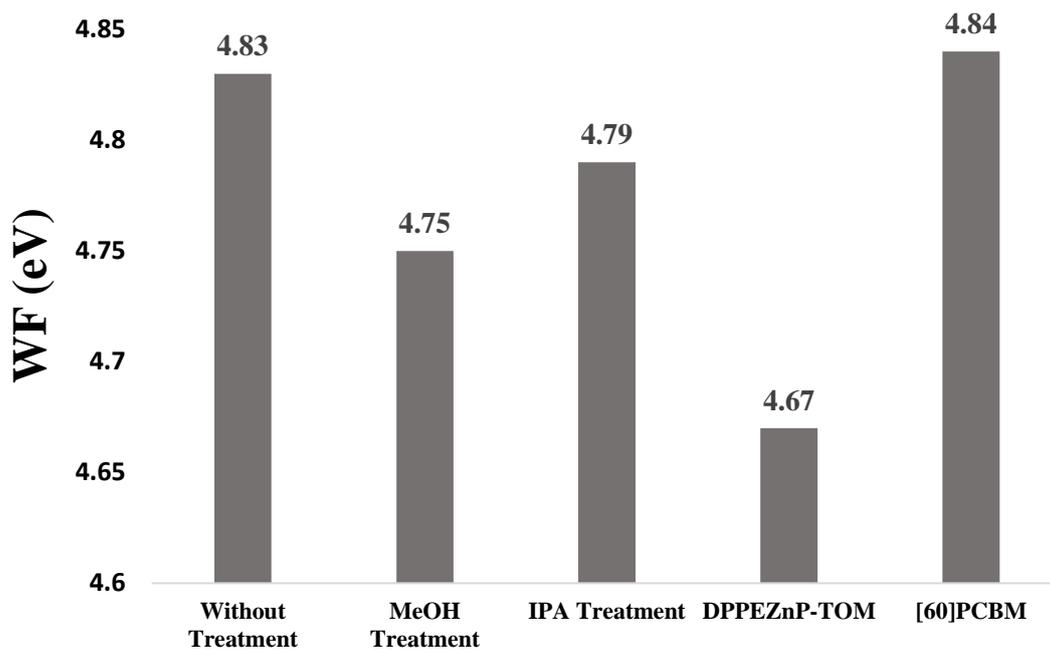


Fig. S9. WFs of pure DPPEZnP-TOM and PC₆₁BM films and the blend films of DPPEZnP-TOM:PC₆₁BM without and with alcohol treatment.

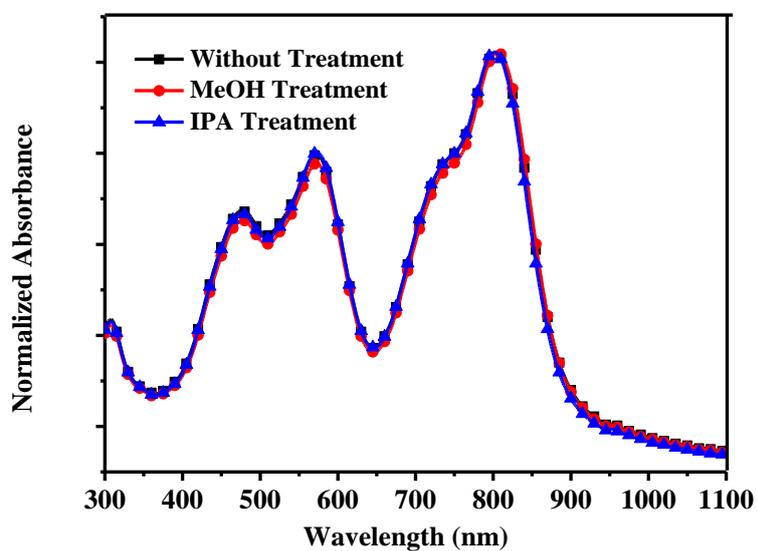


Fig. S10. Absorption spectra of DPPEZnP-TOM pure films without and with MeOH or IPA treatment.

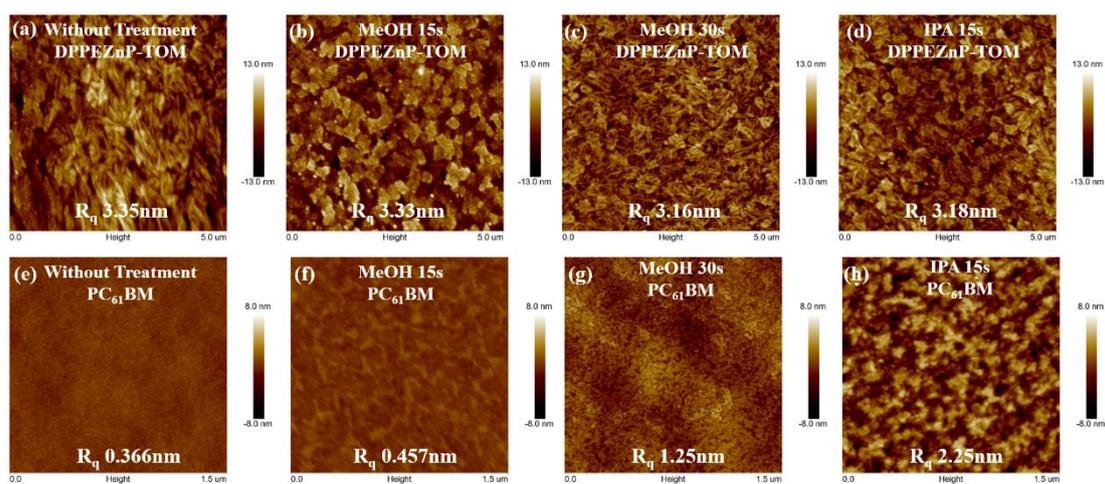


Fig. S11. AFM height images of the DPPEZnP-TOM films (a) without alcohol treatment and with (b) MeOH treatment for 15s (c) MeOH treatment for 30s and (d) IPA treatment for 15s; AFM height images of PC₆₁BM films (e) without alcohol treatment and with (f) MeOH treatment for 15s (g) MeOH treatment for 30s and (h) IPA treatment for 15s

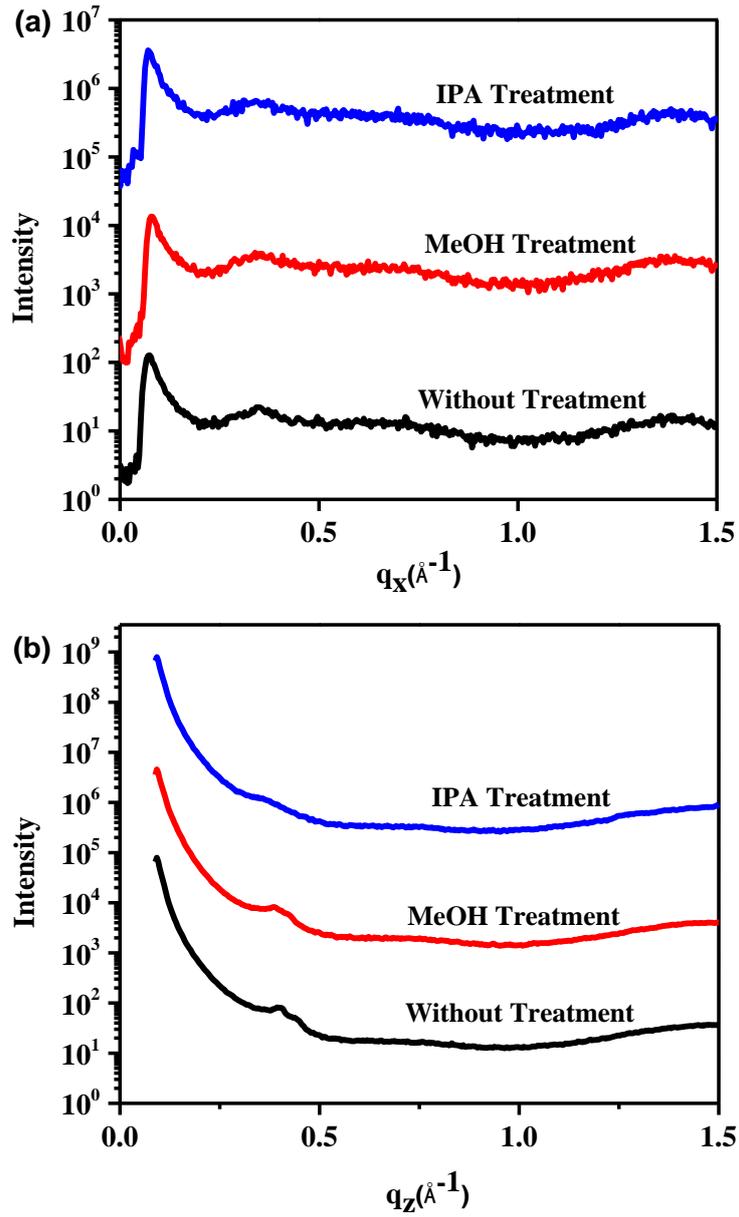


Fig. S12 GIWAX spectra of (a) in-plane (IP) and (b) out-of-plane (OOP) for DPPEZnP-TOM: PC₆₁BM blend films without any treatment, with MeOH treatment and with IPA treatment.

Table S4. Measured and simulated performance parameters of the DPPEZnP-TOM:PC₆₁BM devices upon different treatments.

	nkT/q	n	J_D (mA cm ⁻²)
Without Treatment	0.0443	1.71	9.94×10^{-8}
MeOH Treatment	0.0388	1.49	9.51×10^{-9}
IPA Treatment	0.0619	1.84	2.59×10^{-7}

The dark injected current J versus applied voltage for DPPEZnP-TOM:PC₆₁BM devices was exponentially fitted according to the equation of $J=J_D \exp(qV/nkT)$, therefore to determine reverse saturation current density J_D .⁴

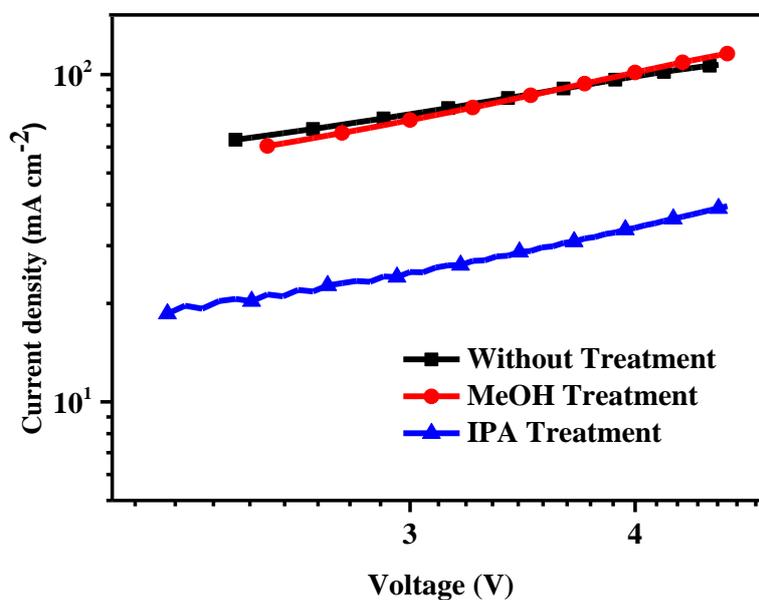


Fig. S13. The J-V curves of the electron-only devices based on DPPEZnP-TOM:PC₆₁BM without alcohol treatment and with MeOH treatment and with IPA treatment for 15 s.

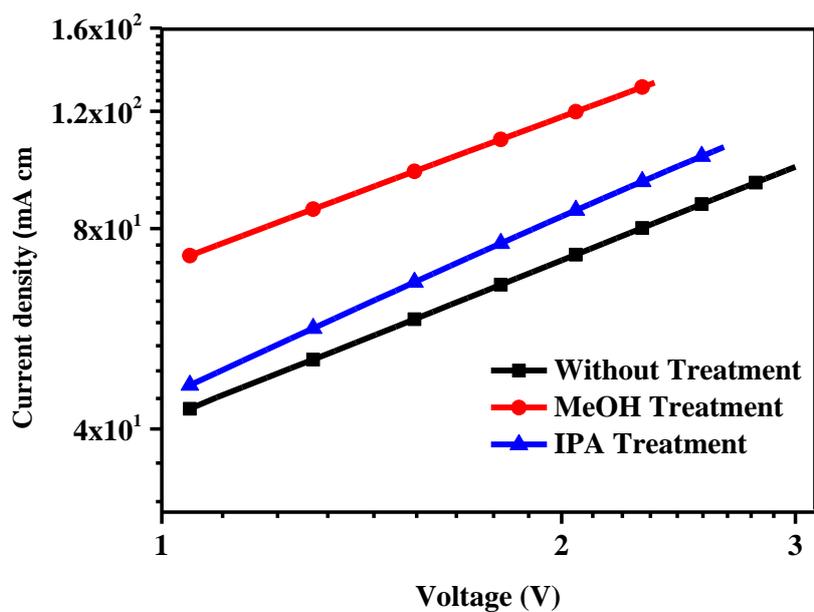


Fig. S14. The J - V curves of the hole-only devices based on DPPEZnP-TOM:PC₆₁BM without alcohol treatment and with MeOH treatment and with IPA treatment.

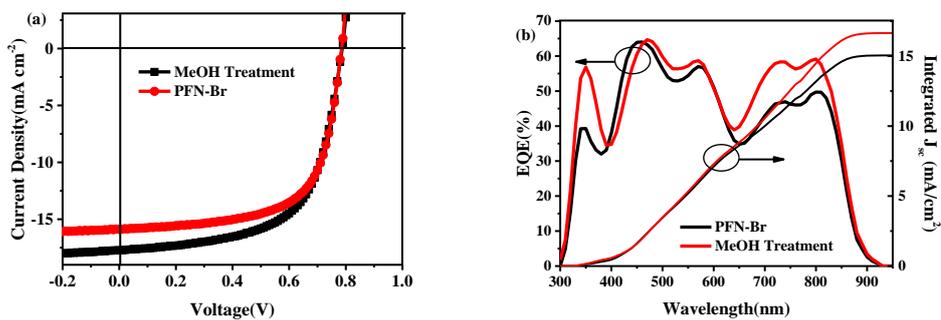


Fig. S15. (a) J - V and (b) EQE spectra of DPPEZnP-TOM:PC₆₁BM devices with PFN-Br CILs and upon MeOH treatment for 15 s.

Table S5. The photovoltaic parameters of the DPPEZnP-TOM:PC₆₁BM OSCs with PFN-Br CILs and upon MeOH treatment.

	Voc(V)	Jsc(mA cm ⁻²)	FF(%)	PCE(%)
Without	0.75±0.01	16.22±0.47 (15.78)	59.05±0.48	7.18±0.04 (7.55)
PFN-Br	0.79±0.01	15.88±0.32 (15.04) ^a	65.59±0.40	8.23±0.32 (8.55) ^b
MeOH	0.78±0.01	17.74±0.34 (16.64) ^a	62.14±0.63	8.59±0.37 (8.96) ^b

^a Calculated J_{SC} values from EQE curves, ^b The maximum PCE.

References:

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