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Electronic Supplementary Information

High-performance Inverted Polymer Solar Cells without Electron Extract Layer via One-step Coating of Cathode Buffer and Active Layer

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EXPERIMENTAL SECTION

Materials: PTB7-Th was purchased from 1-Material Inc., $PC_{71}BM$, PBDB-T and ITIC was purchased from Solenne BV, N2200 was synthesized in our laboratory.

PSCs Fabrication and Characterization. The two-step coating device structure was ITO/POF-N/Donor:Acceptor/MoO_3/Ag, and the one-step coating device structure was ITO/Donor:x%POF-N:Acceptor/MoO3/Ag. The ITO glass substrates were cleaned sequentially under sonication with acetone, detergent, deionized water, and isopropyl alcohol and then dried at 80°C in a baking oven overnight, followed by a 4-min oxygen plasma treatment. All substrates were transferred to a glovebox under nitrogen (N2). For two-step coating device, POF-N solution was prepared in methanol with a concentration of 0.5mg/ml. PTB7-Th:$PC_{71}BM$ binary solution were prepared in chlorobenzene with 3% DIO by volume, PBDB-T:ITIC binary solution were prepared in chlorobenzene with 0.5% DIO by volume and PtzBI:N2200 were prepared in 2-methyltetrahydrofuran (MeTHF) . The thickness of POF-N and active layer were about 10 nm and 100 nm. For one-step coating device, POF-N were prepared in same solvent with binary solution, then added to the binary solution by mass fraction. PTB7-Th: X% POF-N: $PC_{71}BM$ solutions were stirred on a hot plate at 70°C overnight to ensure complete dissolution. The active layer films were vacuumed 5 hours to remove the residual DIO additive for blend films. PBDB-T: x% POF-N: ITIC solutions were stirred on a hot plate at 40°C overnight to ensure complete dissolution. The active layer films were thermal annealed at 120°for 15 minutes . PtzBI:x%POF-N:N2200 solutions were stirred on a hot plate at 120°C for 1h to ensure complete

dissolution , The active layer films were thermal annealed at 100°for 30 minutes .Then the samples were transferred to the vacuum chamber. At a vacuum level of 1×10^{-7} Torr, a thin layer (10 nm) of MoO_3 was then thermally deposited as the anode interlayer, followed by thermal deposition of 100 nm of Ag as the top electrode through a shadow mask. The active area of all devices was 5.16 mm^2. The J-V curves were measured on a computer-controlled Keithley 2400 source meter under 1 sun with AM 1.5 G spectra from AAA class solar simulator (Enlitech, Taiwan), and the light intensity was 100 mW cm^{-2} as calibrated by a China General Certification Center-certified reference monocrystal silicon cell (Enlitech). Before the J-V test, a physical mask with precise area of 4 mm^2 was used to define the device area. The EQE spectra measurements were performed on a commercial QE measurement system (QE-R3011, Enlitech).

Fabrication and Characterization of Hole-only and electron-only Devices: Devices were fabricated to measure electron and hole mobility by using the space-charge-limited current (SCLC) method. The hole-only device structure was ITO/PEDOT:PSS/PTB7-Th:x%POF-N:$PC_{71}BM/MoO_3$/Ag. The electron-only device structure was ITO/Al/ PTB7-Th:x%POF-N:PC71BM/Al. The mobility was determined by fitting the dark current to the model of a single-carrier SCLC, which is described by the equation,

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$$

where J is the current, μ 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 layers, and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole mobility can be calculated from the slope of the $J^{1/2}$~V curves.

Tapping-mode AFM images were obtained using a Nano Scope NS3A system (Digital Instruments, Inc.). TEM images were obtained using a JEM-2100F instrument. Energy-dispersive X-ray spectroscopy was performed with an atomic-resolution analytical electron microscope (Titan Themis 200, FEI). All film samples were spin-cast on ITO substrates. The WF of ITO substrate with different modification was measured by Kelvin probe SKP5050. The surface energy of films was

obtained by VCA15 surface contact angle analyzer (Data physics). XPS was measured on a Thermo Electron ESCALAB 250 spectrometer equipped with a monochromatic Al X-ray source (1486.6 eV). The characterization of bulk heterojunction photoactive layer sample comprising of PTB7-Th: POF-N:$PC_{71}BM$(1:1%:1.5 in wt:wt:wt) with different depth was carried out through etching by argon reactive ion etch (Ar-RIE) at a power of 200 eV and etching layer is 0-30, respectively. The thickness was estimated to be about 95 nm after the etching layer of 30 layers.

Table S1. Photovoltaic performance of devices with structure of ITO/PTB7-Th:X%POF-N:$PC_{71}BM$/MoO_3/Ag under AM 1.5G, 100 mW cm^{-2} illumination.

POF-N content	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{max} (%)	PCE_{ave}[a]. （%）
0	0.31	16.4	46	2.6	2.2
0.2%	0.77	16.9	72	9.4	9.4
0.5%	0.77	17.5	72	9.6	9.5
0.7%	0.77	17.9	72	9.9	9.8
1%	0.76	18.3	72	10.0	9.9
3%	0.77	17.6	71	9.5	9.3
5%	0.77	17.4	70	9.4	9.2
7%	0.77	17.1	72	9.3	9.2
10%	0.76	17.2	70	9.3	9.1
15%	0.76	16.5	71	8.9	8.7

[a] average data were obtained from 8 independent devices

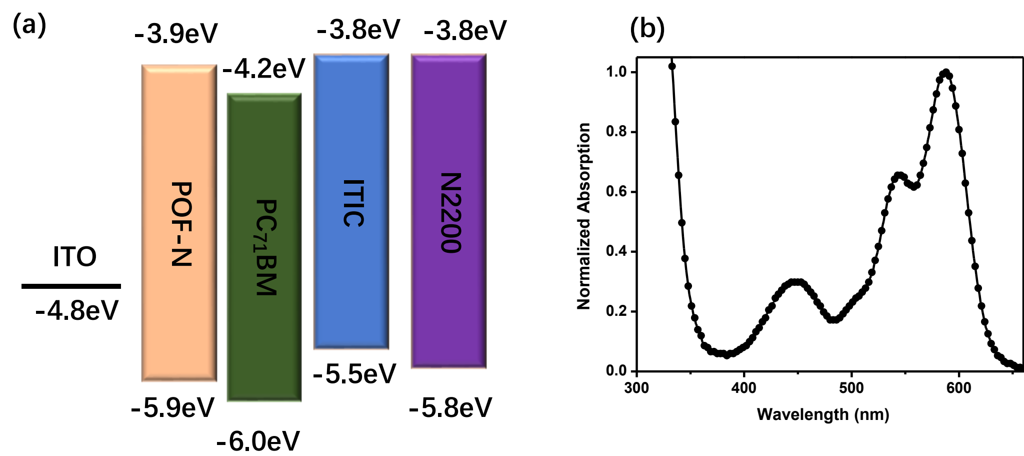

Figure S1. (a) Energy level of active layer, interlayer, and electrode. (b) UV-vis absorption spectra of POF-N films

Table S2. Photovoltaic performance of devices with structure of ITO/PTB7-Th:1%ETL:$PC_{71}BM$/MoO_3/Ag under AM 1.5G, 100 mW cm^{-2} illumination.

Sample Name	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE_{max} (%)	PCE_{ave}[a]. (%)
1%PFN:PTB7-Th:$PC_{71}BM$	0.77	16.6	70	9.0	8.9
1%PNDI-2T:PTB7-Th:$PC_{71}BM$	0.77	17.1	70	9.3	9.2
1%POF-N:PTB7-Th:$PC_{71}BM$	0.76	18.3	72	10.0	9.9

[a] average data were obtained from 8 independent devices

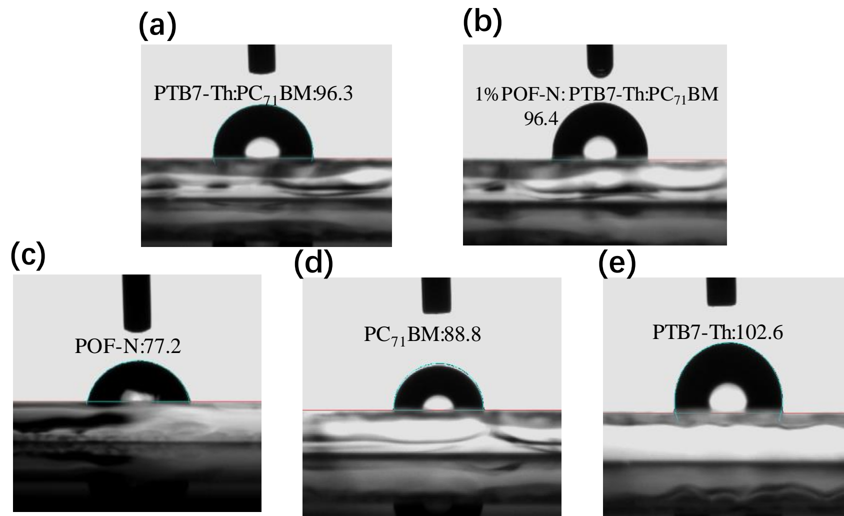

Figure S2. Contact angle measurements (DI water) of (a) PTB7-Th:$PC_{71}BM$, (b) 1%POF-N: PTB7-Th:$PC_{71}BM$, (c) POF-N, (d) $PC_{71}BM$, (e) PTB7-Th films on ITO substrates.

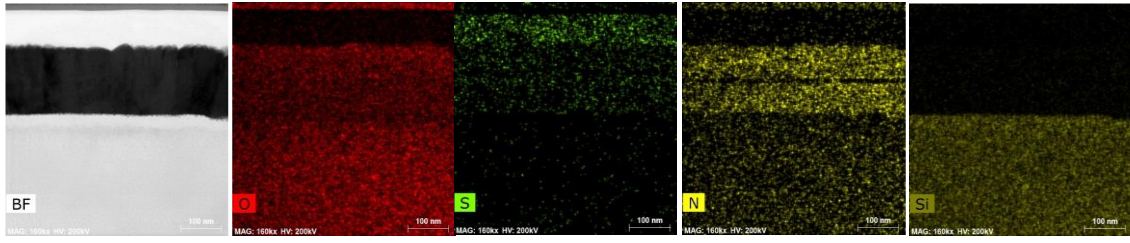

Figure S3. TEM-EDX element mapping of ITO/5%POF-N:PTB7-Th:$PC_{71}BM$.

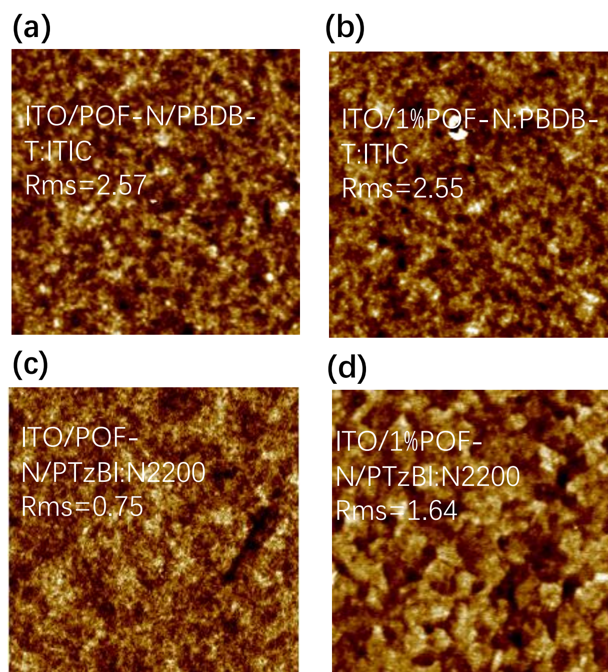

Figure S4. AFM height images of PBDB-T:ITIC and PTzBI:N2200 blend films (a, c) 100 nm one-step coating films; (b, d) 100 nm two-step coating films.

Table S3. Energy level of ITO coated with 10 nm PTB7-Th:$PC_{71}BM$ (with different ratio of POF-N) by UPS measurement, the ratio of POF-N increases from 1 wt% to 15 wt%.

Simple	E_{cutoff} (Ev)	WF (Ev)
0% POF-N	16.33	4.89
1% POF-N	16.40	4.82
3% POF-N	16.48	4.74
5% POF-N	16.58	4.64
7% POF-N	16.61	4.61
10% POF-N	16.65	4.57
15% POF-N	16.79	4.43

Table S4. Electron mobility of the active layers doped with or without 1% POF-N.

Simple	Electron mobility
PTB7-Th:$PC_{71}BM$	3.0×10^{-4}
1% POF-N:PTB7-Th:$PC_{71}B$	7.3×10^{-4}
PBDB-T:ITIC	4.4×10^{-4}
1%POF-N:PBDB-T:ITIC	4.6×10^{-4}
PTzBI:N2200	5.6×10^{-5}
1%POF-N:PTzBI:N2200	7.2×10^{-6}

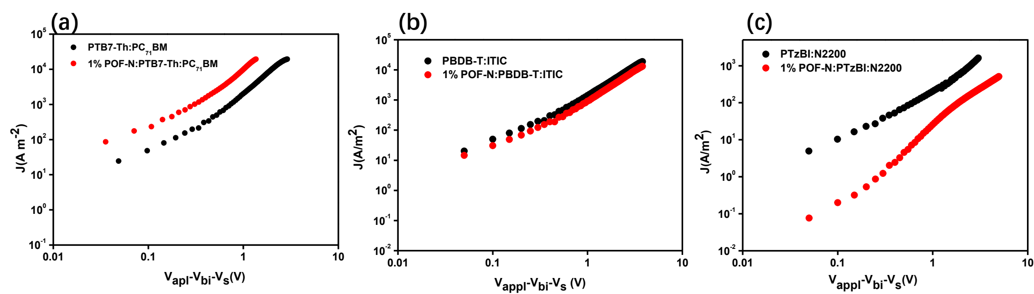

Figure S5. J versus V_{appl}-V_{bi}-V_s characteristic in SCLC regions of electron-only devices. (a) PTB7-Th:1% POF-N:$PC_{71}BM$; (b)PBDB-T: 1% POF-N:ITIC; (c) PTzBI: 1% POF-N:N2200.

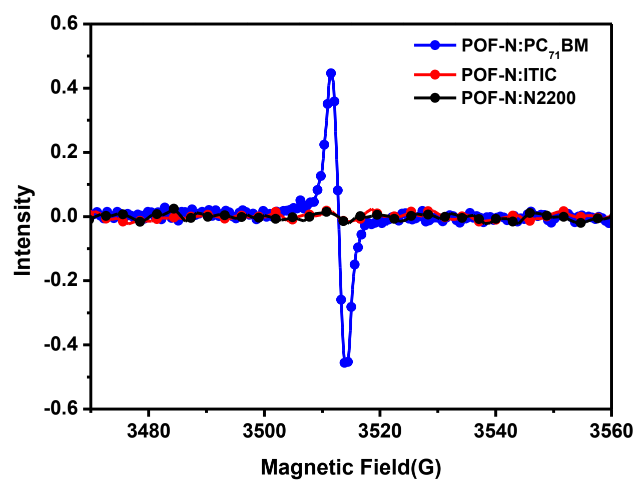

Figure S6. ESR spectra of POF-N:$PC_{71}BM$, POF-N:ITIC and POF-N:N2200 in solid state.