

A new dialkylthio-substituted naphtho[2,3-*c*]thiophene-4,9-dione based polymer donor for high-performance polymer solar cells

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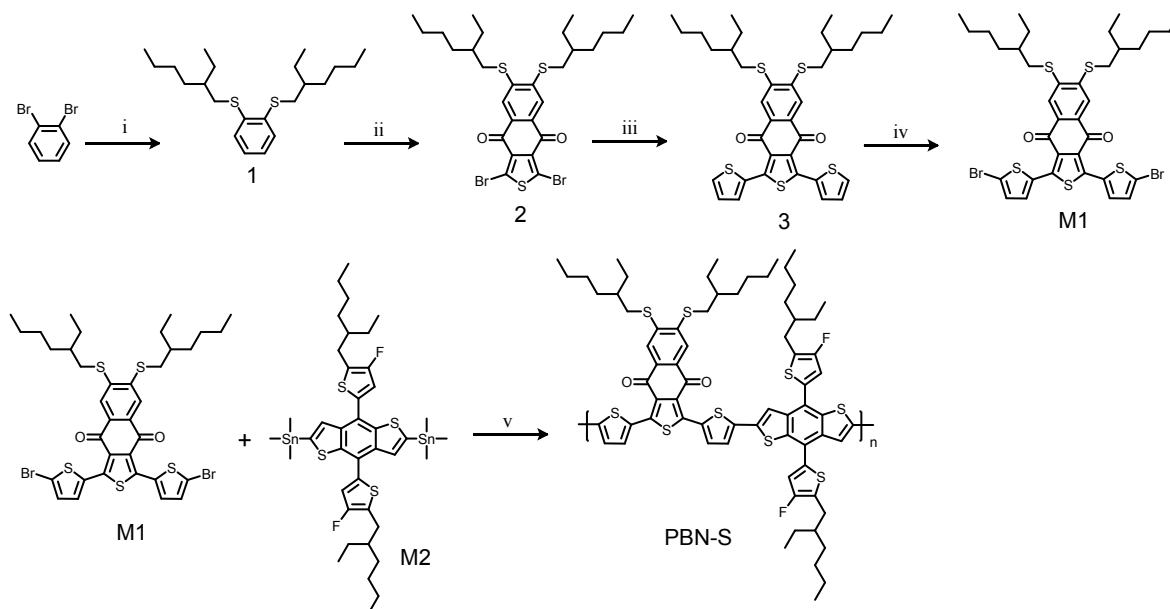
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1. Materials synthesis



Reagents and conditions: (i) 2-ethylhexanethiol, Cu₂O, ethanol, reflux; quinoline/pyridine, 160 °C, 4 h; (ii) oxalyl chloride, CH₂Cl₂/DMF, 2,5-dibromothiophene-3,4-dicarboxylic acid, 6 h; 1,2-dichloroethane, AlCl₃, ambient temperature, 3 h; (iii) 2-trimethyltinthiophene, Pd(PPh₃)₄, toluene, 110 °C, 24 h; (iv) CHCl₃, *N*-bromosuccinimide, ambient temperature, 12 h; (v) Pd(PPh₃)₄, toluene, 110 °C, 3.5 h

Scheme S1 Synthetic route of PBN-S.

1,2-Bis(2-ethylhexylthio)benzene (1)

2-ethylhexanethiol (20.0 g, 0.14 mol), freshly prepared cuprous oxide (10.1 g, 0.07 mol), and 150 mL 95% ethanol were added in a 250 mL two-necked flask, and then the mixture was heated to reflux until the brick red color of the cuprous oxide completely turned white. The cuprous 2-ethylhexylmercaptide was collected by filtration, washed several times with 95% ethanol, and dried under vacuum overnight. To a suspension of cuprous 2-ethylhexylmercaptide (19.2 g, 0.092 mol) in quinoline (150 mL) and pyridine (40 mL) were added *o*-dibromobenzene (10.0 g, 0.042 mol). The mixture was stirred and heated to 160 °C for 4 hours. Then the reactant was poured into a solution of ice (1000 g) and concentrated by hydrochloric acid. The mixture was filtered and the residue was washed several times with ether. The filtrate was extracted several times with ether and the combined organic layer was dried over anhydrous MgSO₄. After removal of the solvent, the crude product was purified via column chromatography (silica gel) using hexane as eluent to give compound 1 as yellow oil (11.2 g, yield 72%). ¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.37 (m, 2H), 7.12 (d, *J* = 3.5 Hz, 2H), 2.88 (d, 4H), 1.63 (dt, *J* = 12.1, 6.0 Hz, 2H), 1.56–1.18 (m, 16H), 0.90 (t, *J* = 7.0 Hz, 12H). ¹³C NMR (CDCl₃, 151 MHz), δ (ppm): 137.94, 128.52, 125.83, 38.90, 37.72, 32.26, 28.86, 25.80, 22.876, 14.10, 10.75.

*1,3-dibromo-6,7-bis((2-ethylhexyl)thio)naphtho[2,3-*c*]thiophene-4,9-dione (2)*

2,5-Dibromothiophene-3,4-dicarboxylic acid (3.0 g, 9.1 mmol) was dissolved in anhydrous CH₂Cl₂ (20 mL) with two drops *N,N*-dimethylformamide, and then oxalyl dichloride (3.1 mL, 36.4 mmol) slowly was added to the mixture. The mixture was stirred at room temperature for four hours. After removal of the solvent, the remnant and compound 1 (3.6 g, 9.8 mmol) were dissolved in anhydrous 1,2-dichloroethane (20 mL). Then anhydrous AlCl₃ (4.4 g, 32.8 mmol) was added to the mixture slowly under 0 °C and keep stirring at 0 °C for 0.5 hour and another 3 hours at room temperature. Then the reactant was poured into a solution of ice (100 g) and concentrated hydrochloric acid (20 mL) and stirred for about 1 hour. The mixture was extracted with CHCl₃ for several times and then the combined organic layer was dried over anhydrous MgSO₄. After removal of the solvent, the crude product was purified via column chromatography on a silica gel using hexane/CH₂Cl₂ (5:1) as eluent to give compound 2 as light yellow solid (2.3 g,

yield 42%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.01 (s, 2H), 3.10 (d, *J* = 6.2 Hz, 4H), 1.76 (m, *J* = 12.4, 6.2 Hz, 2H), 1.40–1.14 (m, 16H), 0.94–0.89 (t, 12H). ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 177.28, 145.88, 132.82, 130.36, 122.28, 120.69, 38.46, 37.01, 32.61, 31.57, 29.01, 25.84, 22.79, 14.09.

6,7-bis((2-ethylhexyl)thio)-1,3-di(thiophen-2-yl)naphtho[2,3-c]thiophene-4,9-dione (3)

To a solution of compound 2 (1.0 g, 1.5 mmol) and 2-trimethyltinthiophene (1.2 g, 4.5 mmol) in toluene (30 mL) was added Pd(PPh₃)₄ (100 mg, 0.086 mmol). The mixture was stirred and heated to 110 °C for 24 hours under argon protection. After removal of the solvent toluene, the crude product was purified via column chromatography on a silica gel using hexane/CH₂Cl₂ (5:1) as eluent to give compound 3 as yellow solid (700 mg, yield 71%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.03 (s, 2H), 7.83 (d, *J* = 3.2 Hz, 2H), 7.56 (d, *J* = 4.8 Hz, 2H), 7.20–7.13 (m, 2H), 3.11 (d, *J* = 5.5 Hz, 4H), 1.75 (dt, *J* = 12.3, 6.1 Hz, 2H), 1.62–1.38 (m, 16H), 0.96–0.82 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 179.39, 145.72, 145.00, 143.78, 132.88, 131.07, 130.86, 129.78, 127.37, 122.50, 38.54, 37.01, 32.69, 31.60, 28.80, 25.89, 22.93, 14.07.

1,3-bis(5-bromothiophen-2-yl)-6,7-bis((2-ethylhexyl)thio)naphtho[2,3-c]thiophene-4,9-dione (M1)

Compound 3 (700 mg, 1.05 mmol) was dissolved in 20 mL CHCl₃ in a 50 mL two-necked flask. After being flushed by a gentle stream of argon for 5 min, *N*-bromosuccinimide (467 mg, 2.6 mmol) was added. The mixture was stirred at room temperature for 12 hours, and then was poured into 20 mL water. The mixture was extracted with chloroform (3 × 20 mL). After removal of the solvent, the crude product was purified via column chromatography on a silica gel using hexane/CH₂Cl₂ (5:1) as eluent to give compound 4 as yellow solid (692 mg, yield 80%). ¹H NMR (400 MHz, CDCl₃), δ (ppm): 8.02 (s, 2H), 7.53 (d, *J* = 3.9 Hz, 2H), 7.12 (d, *J* = 3.9 Hz, 2H), 3.12 (d, *J* = 5.8 Hz, 4H), 1.82–1.70 (m, 2H), 1.65–1.43 (m, 16H), 1.08–0.92 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ (ppm): 179.36, 145.43, 144.58, 143.67, 134.10, 130.91, 130.49, 129.45, 122.39, 118.61, 38.51, 37.02, 32.72, 31.50, 28.87, 25.92, 22.95, 14.09.

Synthesis of PBN-S: In a 25 mL flask, monomers M1 (0.247 mg, 0.03 mmol) and M2^[1] (0.271 mg, 0.03 mmol) were dissolved in 10 mL toluene, and the flask was flushed with argon for 10 min. Then 18 mg of Pd(PPh₃)₄ was added into the solution, and the mixture was flushed with argon for another 15 min. The solution was heated to reflux for 3.5 h under argon protection. After cooling to ambient temperature, the polymer was precipitated in 200 mL of methanol, filtered through a Soxhlet thimble. The precipitate was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. The polymer was precipitated from 100 mL of methanol. The precipitates were collected and dried under vacuum overnight to get polymer as solid.

PBN-S: $M_n = 16.2$ kDa, $M_w = 38.1$ kDa, PDI = 2.36.

2. Materials characterization

Cyclic voltammetry was performed on a Zahner IM6e electrochemical workstation with a three-electrode system in a solution of 0.1 M [Bu₄N]PF₆ acetonitrile solution at a scan rate of 100 mV s⁻¹. Glassy carbon disc coated with polymer film was used as the working electrode. A Pt wire was used the counter electrode and Ag/Ag⁺ was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as the external standard and its redox potential is 0.06 V versus Ag/Ag⁺. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potential of polymer using the following equations: HOMO = $-e(\varphi_{ox} + 4.74)$ (eV); LUMO = $-e(\varphi_{red} + 4.74)$ (eV), respectively.

3. Solar cells devices fabrication and characterization

The device was fabricated with a conventional architecture of glass/ITO/PDEOT:PSS/PBN-S:IT-4F/ZnO/Al. The ITO-coated glass was pre-cleaned and modified by a thin layer of PEDOT:PSS which was spin-cast from a PEDOT:PSS aqueous solution (Baytron P VP AI4083 from H. C. Stark) at 5000 rpm for 45 s, and then dried at 150 °C for 15 min in air. The thickness of the PEDOT:PSS layer is ~30 nm. Then the devices were transferred to a nitrogen-filled glove-box, where the active layer was

spin-coated from chlorobenzene solution containing PBN-S:IT-4F onto the PEDOT:PSS layer. For the optimized conditions, PBN-S and IT-4F (1:1, w/w) were dissolved in chlorobenzene with a concentration of 10 mg/mL (for PBN-S) and stirred under 80 °C for 12 h. After 1% (by volume) 1,8-diiodooctane (DIO) was added as additive, the solution was stirred at 80 °C for another 0.5 h. The blend film was spin-coated at 2800 rpm for 60 s, following by thermal annealing at 100 °C for 10 min. The ZnO buffer layer (thickness 20 nm) was deposited atop the active layer from the mixed methanol:chloroform:*n*-butyl alcohol (1:1:14) solution of ZnO nanoparticles at a concentration of 10 mg/mL with 4000 rpm for 30 s. The ZnO nanoparticles was prepared from nanoparticles suspension by the synthetic procedure described in literature.⁴ Finally, top 100 nm Al electrode was deposited in vacuum onto the ZnO layer at a pressure of 2.0×10^{-5} Pa. The active area defined by a shadow mask is 4 mm².

Blade-coating method: the PEDOT:PSS modified ITO glass substrates were placed on the platform of the film applicator coater (ZEHNTNEN, ZAA 2300) under the temperature of 60 °C. Approximately 20 µl of the PBN-S:IT-4F mixed solution was dropped on the substrate area in air, the gap between the scraper (ZEHNTNER, ZUA 2000) and substrate is 80 µm, the speed of coating is 35 mm/s.

Spreading method: drop the solution on the substrate, and then use a piece of glass to smoothly spread the solution on the substrate (as shown in Fig. S13).

The current density-voltage (*J-V*) measurement of the PSCs were measured under a illumination of AM 1.5G (100 mW cm⁻²) using a SS-F5-3A solar simulator (AAA grade, 50 × 50 mm² photobeam size) of Enli Technology CO., Ltd.. The EQE was measured by using a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The light intensity at each wavelength was calibrated by a standard single-crystal Si solar cell.

Mobility Measurement: The hole and electron mobilities were calculated by using the space-charge-limited current (SCLC) method.^[2,3]

$$J \cong (9/8)\epsilon\epsilon_0\mu_0V^2 \exp(0.89\sqrt{V/E_0L})/L^3$$

where ε is the dielectric constant of the polymers, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, and L is the thickness of the film.

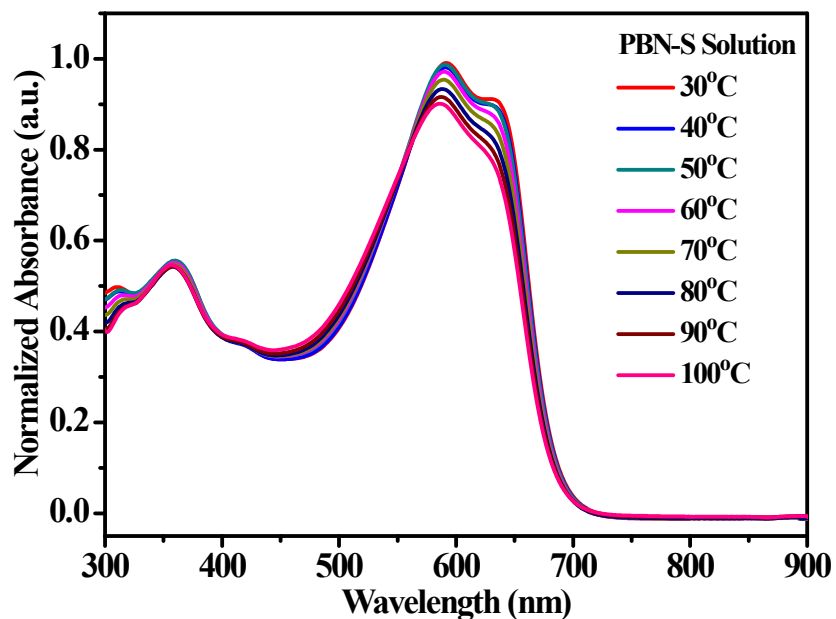


Fig. S1 UV-vis absorption of PBN-S in chlorobenzene solution at temperature as indicated.

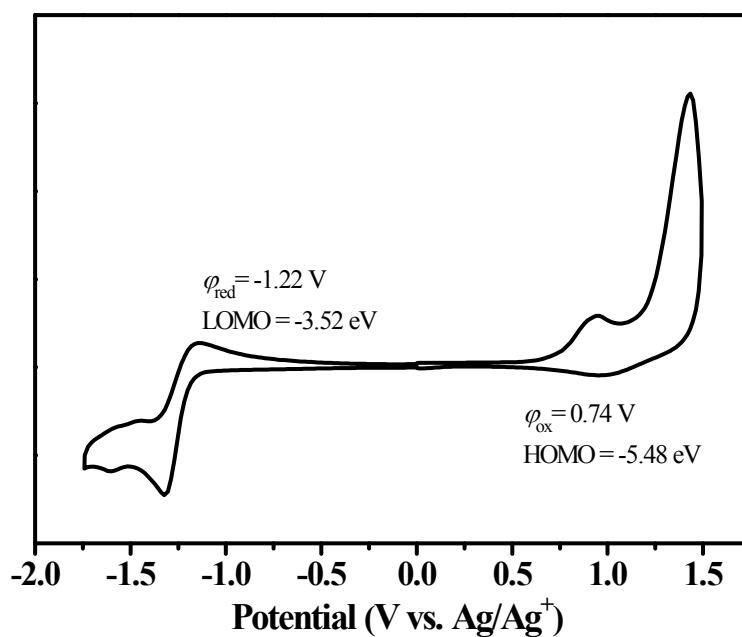


Fig. S2 Cyclic voltammetry of PBN-S film on a glass carbon electrode measured in 0.1 mol L⁻¹ Bu₄NPF₆ acetonitrile solution at a scan rate of 100 mV s⁻¹.

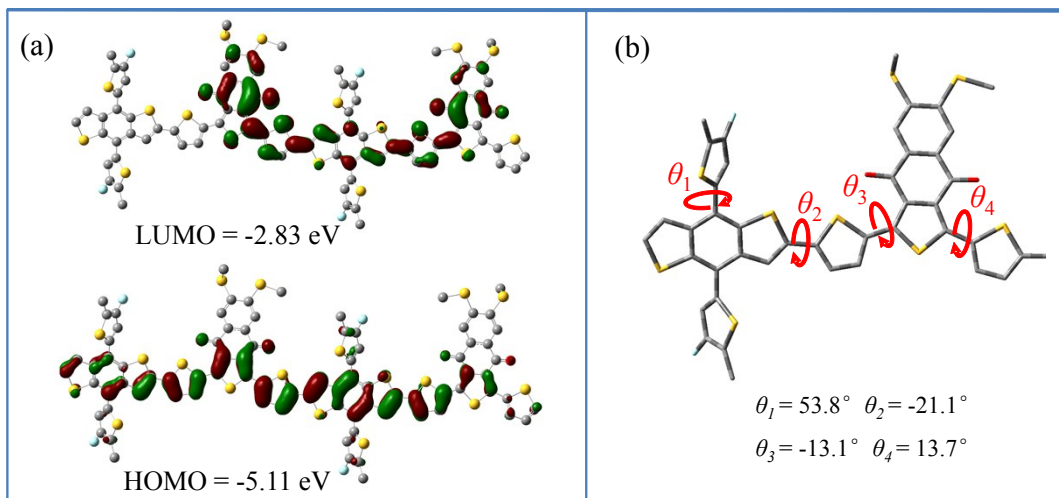


Fig. S3 (a) Frontier molecular orbital surfaces and (b) optimized molecular conformations of PBN-S by DFT calculations at the B3LYP/6-31G(d, p) level.

Table S1 Photovoltaic performance of the PSCs with different D/A ratio under the illumination of AM 1.5 G at 100 mW cm⁻².

D/A ratio	V_{oc} [V]	J_{sc} [mA cm ⁻²]	FF [%]	PCE [%] ^a
1:0.5	0.929	17.77	50.6	8.36 [8.13]
1:1	0.908	19.01	58.9	10.16 [10.05]
1:1.2	0.905	20.05	53.0	9.62 [9.48]
1:1.5	0.896	18.06	45.2	7.31 [7.15]

^a The average values in brackets were obtained from 6 devices.

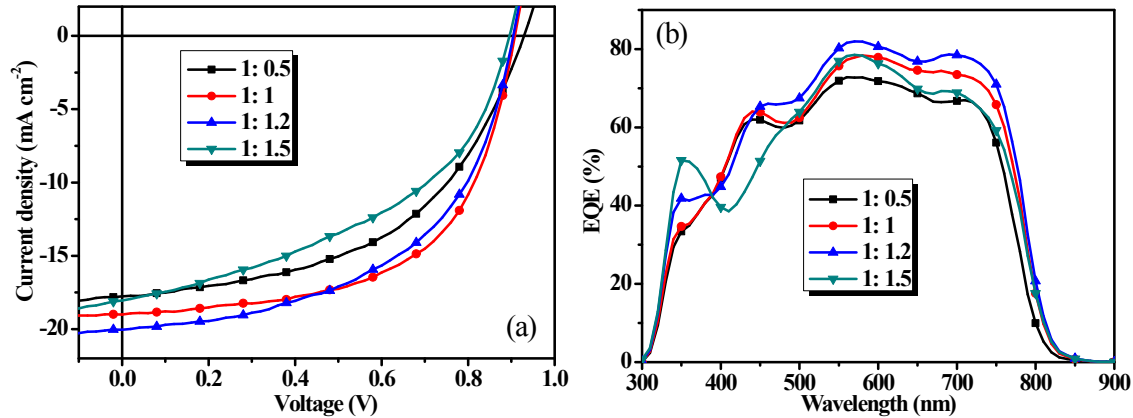


Fig. S4. (a) J - V curves and (b) EQE spectra of the PSCs with different D/A ratio.

Table S2 Photovoltaic performance of the PSCs based on PBN-S:IT-4F (1:1, w/w) with different post-treatment under the illumination of AM 1.5 G at 100 mW cm^{-2} .

Post-treatment	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%] ^{a)}
TA at 60 °C	0.910	19.41	57.4	10.13 [10.02]
TA at 80 °C	0.908	19.71	56.9	10.19 [10.11]
TA at 100 °C	0.910	19.91	56.4	10.23 [10.17]
TA at 120 °C	0.908	19.34	54.8	9.62 [9.56]
0.5% DIO + TA at 80 °C	0.880	21.11	64.1	11.91 [11.72]
1% DIO + TA at 80 °C	0.881	21.26	65.7	12.30 [12.23]
1% DIO + TA at 100 °C	0.891	21.03	69.9	13.10 [13.01]
1% DIO + TA at 120 °C	0.874	21.61	63.6	11.82 [11.73]
1.5% DIO + TA at 80 °C	0.879	21.30	65.2	12.20 [12.11]

^a The average values in brackets were obtained from 6 devices.

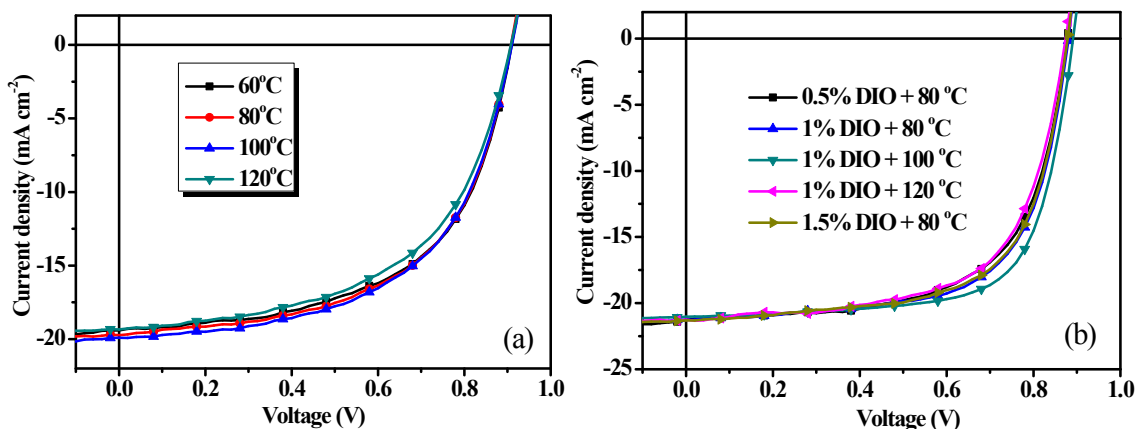


Fig. S5 J - V curves of the PSCs based on PBN-S:IT-4F (1:1, w/w) with (a) thermal annealing and (b) dual treatment of thermal annealing and DIO under the illumination of AM 1.5 G at 100 mW cm^{-2} .

Table S3 The color coordinates, CRI, and correlated color temperature (CCT) of the transmitted light of the semitransparent devices with different thick Ag cathode.

Ag [nm]	CIE [x, y]	CRI	CCT [K]
10	(0.220, 0.251)	95	4616
15	(0.213, 0.240)	92	8657
20	(0.205, 0.231)	92	9501

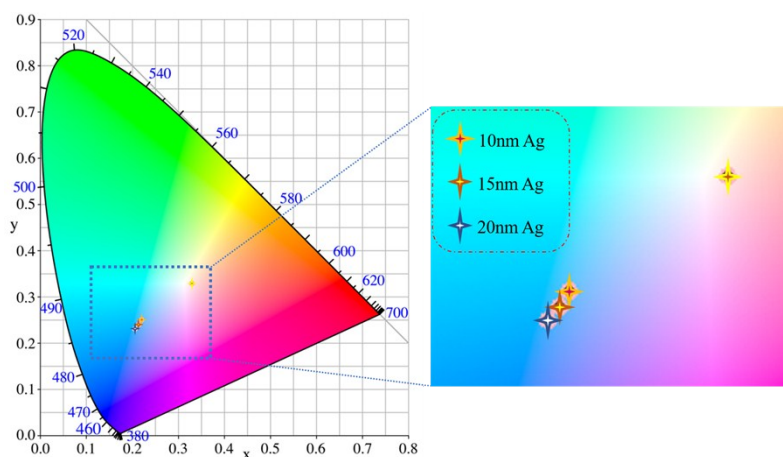


Fig. S6 CIE coordinates of the transmission spectra of devices with different Ag thicknesses using AM1.5G solar simulated input spectrum.

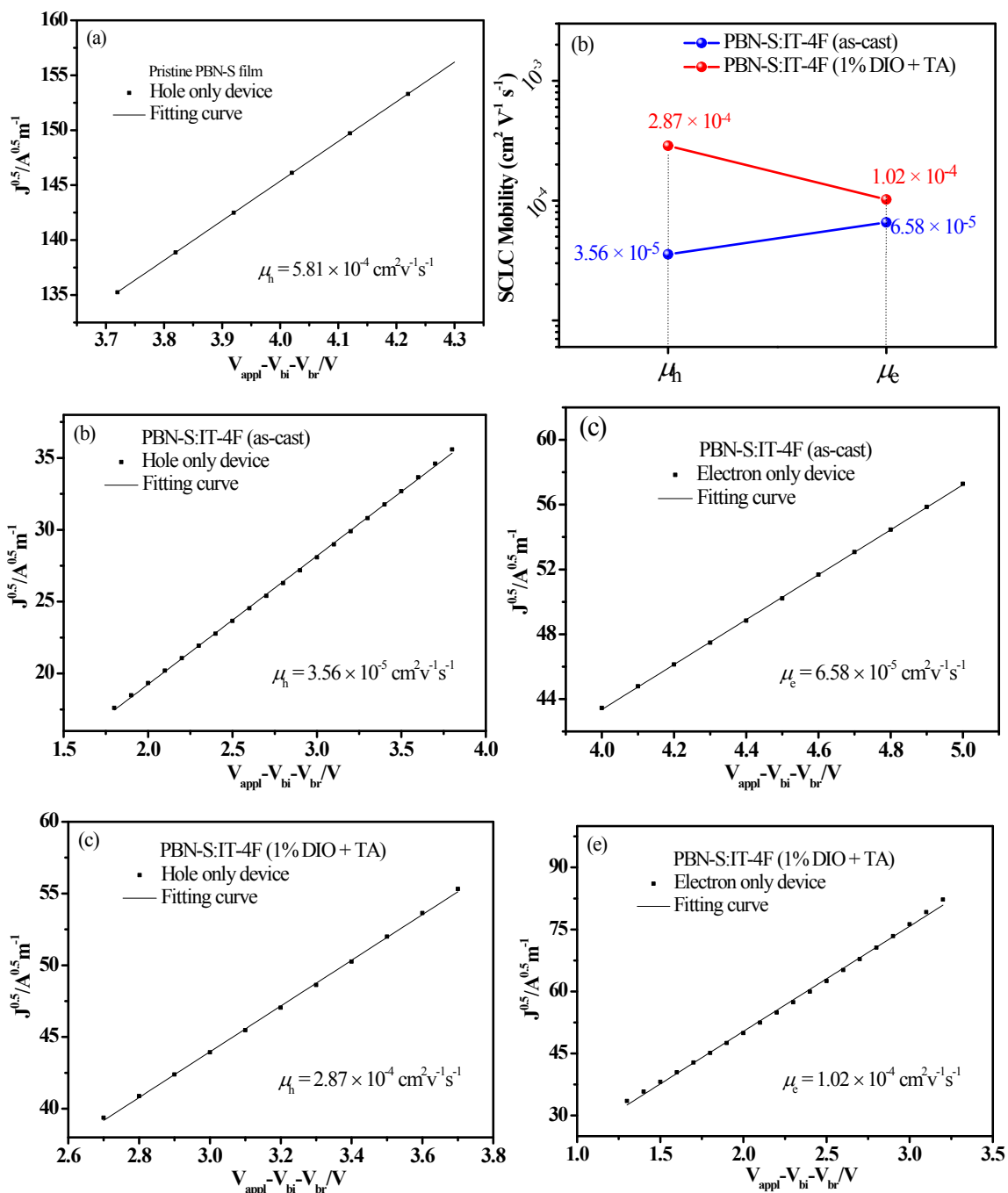


Fig. S7 $J^{0.5}$ vs $(V_{\text{app}} - V_{\text{bi}} - V_{\text{br}})$ plots hole-only and electron only devices of pristine PBN-S and PBN-S:IT-4F (1:1, w/w) blend film, respectively.

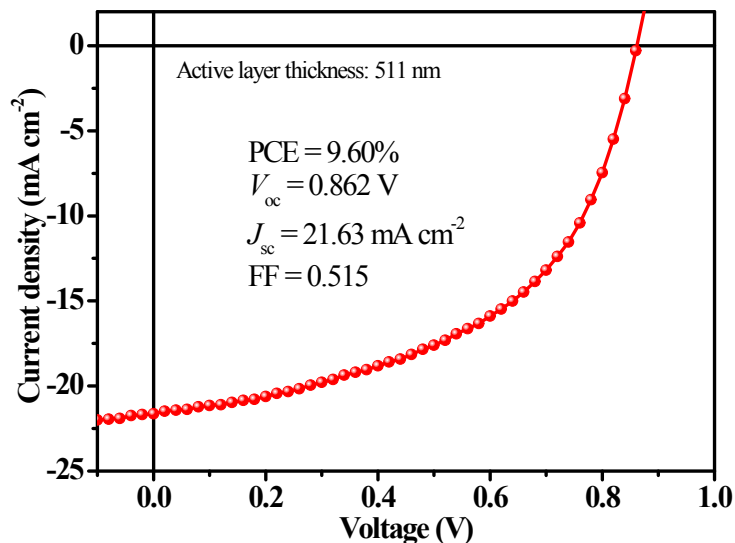


Fig. S8 J - V curves of the PBN-S:IT-4F (1:1, w/w) based device with active layer thickness of 511 nm under the illumination of AM 1.5 G at 100 mW cm⁻².

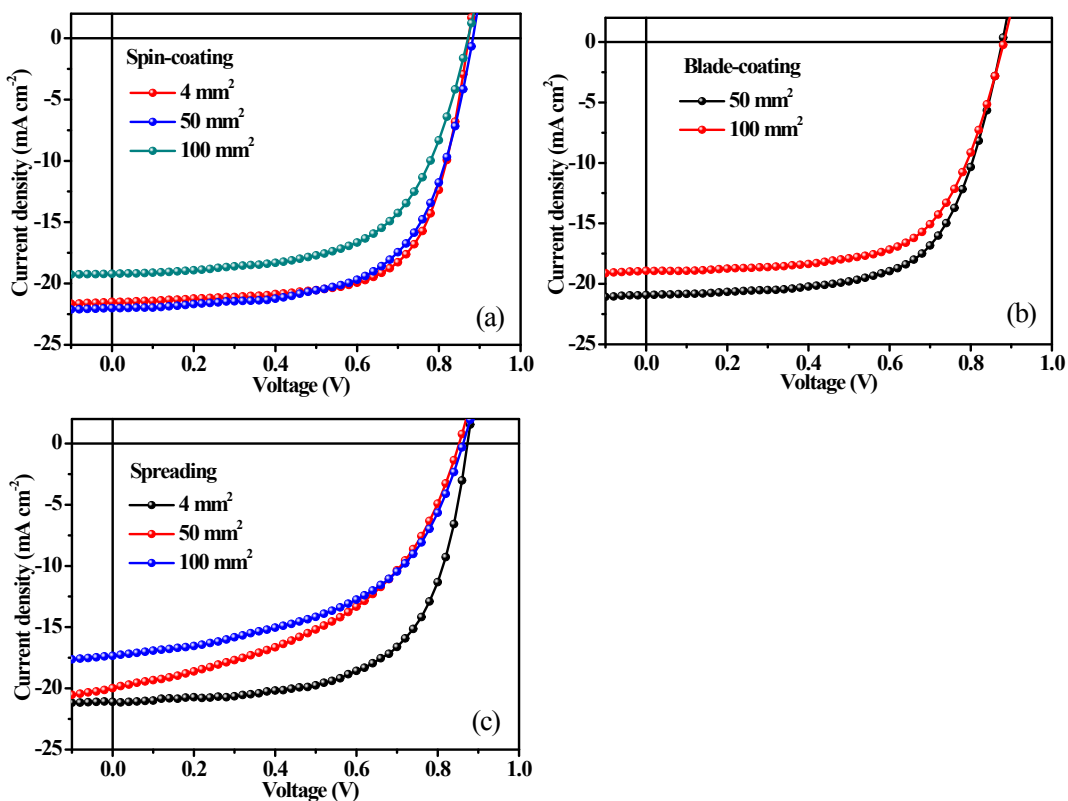


Fig. S9 J - V curves of the PSCs based on PBN-S:IT-4F (1:1, w/w) with different active area processed by (a) spin-coating, (b) blade-coating, and (c) spreading method.

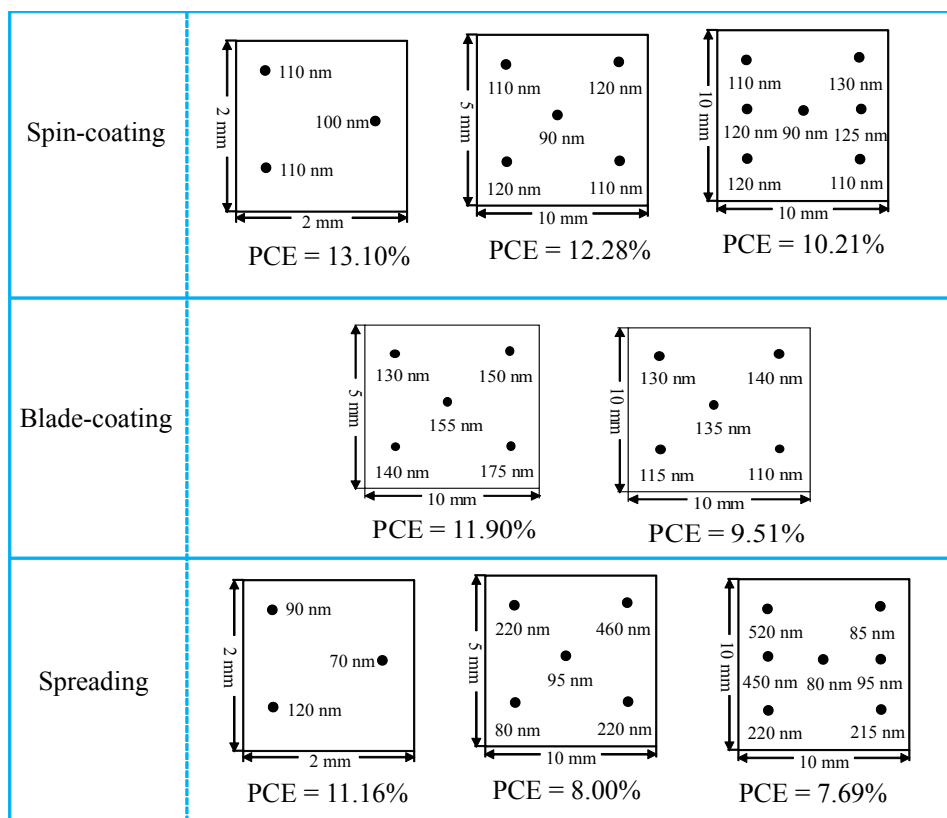


Fig. S10 Diagrammatic sketches of the active layer thickness for the devices with different active area processed by spin-coating or spreading. The black spots indicate the approximate location we measured the thickness of the devices.

Inverted PBN-S based devices with solution-processable buffer layers

According to the requirement of roll-to-roll printed modules, it is important to demonstrate that solution-processable hole-transporting material (HTM) can be deposited on top of the active layer without losing too much efficiency.⁵⁻⁷ To evaluate the large-area capability of PBN-S from the point of view of device architecture, we fabricate the inverted devices with the buffer layers deposited from solution. Firstly, we fabricated inverted PBN-S based devices with configuration of glass/ITO/ZnO/PBN-S:IT-4F/MoO₃/Al. The inverted device exhibited a lower PCE of 11.02% than the conventional one, with $V_{oc} = 0.883$ V, $J_{sc} = 17.55$ mA cm⁻², and FF = 0.711 (Table S4 and Fig. S11a). Then we replaced MoO₃ with PEDOT:PSS as HTM on top PBN-S:IT-4F to fabricate inverted devices. However, we found that the PEDOT:PSS can't be deposited

atop PBN-S:IT-4F blend no matter what kind of PEDOT:PSS was used. By treating the active layer with oxygen plasma for 5 s, PEDOT:PSS layer was successfully coated atop PBN-S:IT-4F by spin-coating with 3000 rpm for 60 s. The key parameters of the inverted devices with different HTM are listed in Table S4 and the corresponding J - V curves are shown in Fig. S11. In comparison with the inverted device using MoO_3 as HTM, significantly lower V_{oc} and FF values were only obtained from the devices with PEDOT:PSS as HTM, delivering to the significantly lower PCEs ($\text{PCE} \leq 3\%$). Such huge difference between these two kinds of devices is mainly due to the technical reasons. We have no experience to felicitously coat PEDOT:PSS atop the active layer in this case. Moreover, the treatment of oxygen plasma may change the morphology of active layer in this case, resulting in the lower photovoltaic performance.

Table S4 Key parameters of the PSC devices with the inverted architecture of glass/ITO/ZnO/PBN-S:IT-4F/HTM/Al.

HTM	HTM thickness	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
MoO_3	-	0.883	17.55	71.1	11.02
AI4083 ¹	23 nm	0.370	17.19	47.1	3.00
AI4083 ²	21 nm	0.222	15.15	37.6	1.27
PH1000	27 nm	0.237	15.37	40.6	1.48
N-PEDOT ¹	20 nm	0.246	15.55	40.7	1.56
N-PEDOT ²	22 nm	0.086	5.82	29.6	0.15

AI4083¹: diluting AI4083 in H_2O , AI4083: H_2O = 1:1, v/v;

AI4083²: diluting AI4083 in isopropyl alcohol (IPA), AI4083:IPA = 1:3, v/v;

PH1000: diluting PH1000 in IPA, PH100:IPA = 1:3, v/v;

N-PEDOT¹: diluting neutral-PEDOT:PSS (N-PEDOT), N-PEDOT:IPA = 1:3, v/v;

N-PEDOT²: diluting N-PEDOT in Capstone FS-31 solution (10 mg/3 mL), N-PEDOT:FS-31 solution = 1:3, v/v.

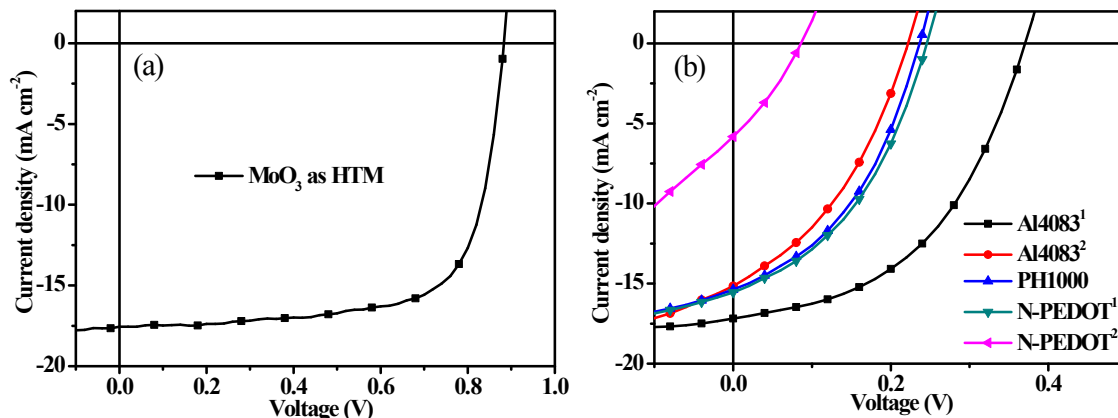


Fig. S11 J - V curves of the PBN-S:IT-4F (1:1, w/w) based inverted PSCs with (a) MnO_3 and (b) different PEDOT:PSS as HTM.

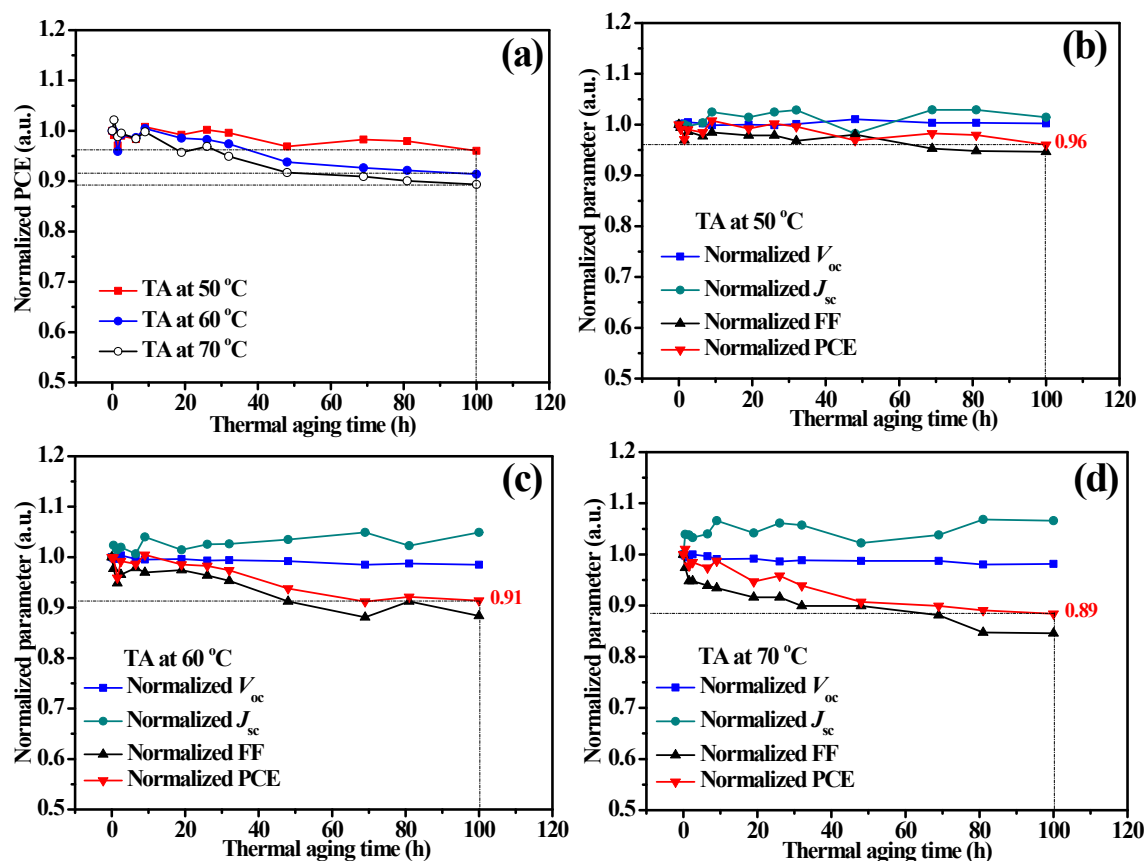
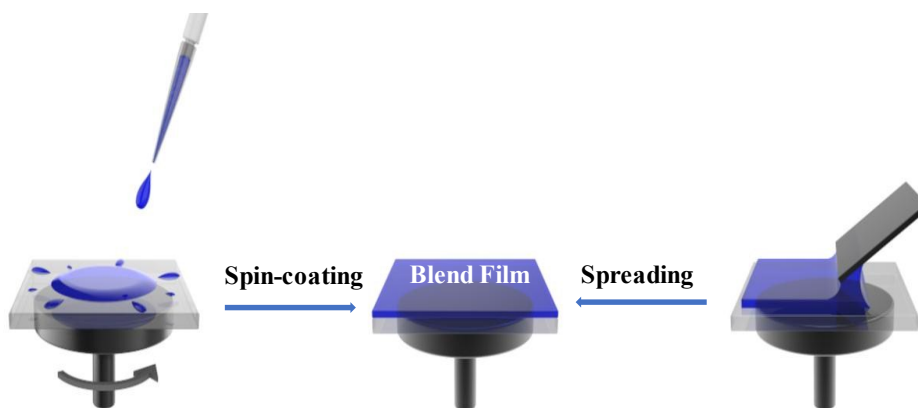


Fig. S12 Normalized photovoltaic parameters of unencapsulated devices with conventional architecture of glass/ITO/PDEOT:PSS/PBN-S:IT-4F/ZnO/Al with different thermal aging time of 50 °C, 60 °C, and 70 °C in a nitrogen-filled glove-box.



Fig, S13 Diagrammatic drawing of spin-coating and spreading method.

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