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Electronic Supporting Information

Optimisation of processing solvent and molecular weight for the production of green-solvent-processed all-polymer solar cells with power conversion efficiency over 9%

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Experimental section

Materials

PTzBI samples were synthesised according to the methods reported in our previous work.[1] N2200 with different molecular weights was prepared according to the procedure reported in the literature.[2] All other chemicals were obtained commercially and were used as received unless otherwise stated.

Discussion about the expected cost of N2200 and PTzBI:

There are two described materials in the photoactive layer, N2200 and PTzBI. On the one hand, the N2200 has already been commercialized and can be ordered with reasonable price (for instance, from Polyera ActivInk™ N2200, or Solarmer Material Inc.). On the other hand, it is worth noting that the electron-rich unit of benzodithiophene moiety of PTzBI is exactly the same as the widely used copolymer poly[[2,6′-4,8-di(5-ethylhexylthienyl) benzo[1,2-*b*;3,3-*b*]dithiophene]-*alt*-[3-fluoro-2[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (namely PTB7-Th or PCE10). The synthetic procedure of the electron-withdrawing unit of PTzBI has comparable steps as that of the PTB7-Th counterpart. Despite several steps for the electron-withdrawing unit of PTB7-Th are very challenging,[3] it has been successfully scaled up and commercialized by many companies with affordable price. Consider that the electron-donating polymer PTzBI can be synthesized from multi-step reactions,[1] these involved reactions are essentially well-established and have been extensively used for synthesizing other imide-functionalized species or triazole-derivatives. Therefore, it is rational to surmise that the cost of PTzBI is reasonable and the price is supposed to be comparable to PTB7-Th.

Fabrication of all-PSCs

All-PSCs with conventional structure were fabricated with the configuration of ITO/PEDOT:PSS/active layer/PFNDI-Br/Al. The indium tin oxide (ITO) glass substrates were cleaned by sequential sonication using acetone, detergent, deionized water, and ethanol, and dried in oven at 70 ^{o}C before used. Followed by an oxygen plasma for 4 min, PEDOT:PSS (*CLEVIOS* P VP Al 4083, 1.0 mg mL^{-1} in water) was spun onto the substrates at 3000 rpm for 30 s, annealed at 150 ^{o}C on a hot plate for 15 min to give thin films with thickness about 40 nm. Then the substrates were transferred into a N_2 protected glove box. All-PSCs with inverted structure were fabricated with the configuration of ITO/ZnO/PFN-OX/active layer/MoO_3/Ag. ZnO (obtained from stirring the solution of 1.0 g

$Zn(CH_3COO)_2{\cdot}2H_2O$ in 10 mL ethylene glycol monomethyl ether and 275 μL ethylenediamine at 60 °C for 8 h) was spun onto the cleaned ITO at 3000 rpm for 30 s, which was annealed at 200 °C on a hot plate for 1h to give a thin film of about 35 nm. Then the substrates were transferred into a N_2 protected glove box and a cross-linkable cathode interfacial layer poly[(9,9-bis(3-(*N*,*N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-bis(3-ethyl(oxetane-3-ethyloxy)hexyl)fluorene)] (PFN-OX) was deposited on the ZnO layer from dilute methanol solution (0.5 mg mL^{-1}). The substrates were annealed at 150 °C for 20 min to obtain a thin (~ 5 nm) layer of PFN-OX.

For the *o*-DCB-processed samples, the concentration of PTzBI in 98 vol % o-DCB and 2 vol % chloronaphthalene (CN) was 13 mg mL^{-1}. After spin-coating the solution at 1400 rpm for 90 s, the robust film with thickness of about 95 nm was obtained. Here, the high concentration and relatively high rotating speed were chosen to accelerate the process of film drying. When chloroform (CF) was used as the processing solvent, a blend film with film thickness of about 85 nm was obtained from a dilute solution of PTzBI (5 mg mL^{-1} in 99 vol % CF and 1 vol % diiodooctane). The film is obtained by spin-coating at 1200 rpm for 40 s. The concentration of PTzBI in MeTHF was 4.5 mg mL^{-1}. This solution was heated at 80 °C overnight, which was then spin-coated at 1200 rpm for 40 s to give a blend film with thickness of about 105 nm. For the MeTHF solution of PTzBI:$N2200_{MW}$ and PTzBI:$N2200_{LW}$, the slightly improved PTzBI concentration of 5 mg mL^{-1} and 5.5 mg mL^{-1} by spin-casting at 1200 rpm for 40 s gave the film with thickness of about 90 nm and 88 nm, respectively. To obtain active layer of PTzBI:$N2200_{HW}$ with higher thicknesses of 120, 135, 160, and 230 nm, we kept a higher constant PTzBI concentration of 6 mg mL^{-1} and employed varied rotating speed of 2000, 1800, 1400, and 1000 rpm, respectively. For the fullerene based devices, the

PTzBI:PC$_{71}$BM (1:1, wt:wt) blends were dissolved in *o*-DCB with the PTzBI concentration of 11 mg mL^{-1} and stirred at 50 ^{o}C overnight. This solution was spin-coated on the substrates at 1000 rpm for 60 s to attain a blend film of around 85 nm. All the above active layers were thermally annealed at 130 ^{o}C for 10 min.

For all-PSCs with conventional structure, before spin-coating of 5 nm PFNDI-Br as cathode interface, the *o*-DCB and CF-processed samples were put in low vacuum at a pressure of 0.1 mbar for at least 3 h to remove the residual solvent additives. For all-PSCs with inverted structure, molybdenum oxide (MoO_3, 10 nm) was thermally deposited on the substrates. Finally, 80 nm aluminum (Al) was thermally deposited on top of the interface through a shadow mask in a vacuum chamber at a pressure of 4×10^{-7} torr. The active layer area of the device was defined to be 0.0516 cm^2, which was further confined as 0.04 cm^2 by a non-refractive mask to improve the accuracy of measurements.

Instruments and Characterization

The photovoltaic performance was measured under an AM 1.5G solar simulator (Taiwan, Enlitech SS-F5). The current density-voltage (*J-V*) characteristics were recorded with a Keithley 2400 source meter. The light intensity of the light source was calibrated before the testing by using a standard silicon solar cell with a KG5 filter, as calibrated by a National Renewable Energy Laboratory (NREL) certified silicon photodiode, giving a value of 100 mW cm^{-2} in the test. The external quantum efficiency (EQE) spectra were performed on a commercial EQE measurement system (Taiwan, Enlitech, QE-R3011). The light intensity at each wavelength was calibrated by a standard single-crystal Si photovoltaic cell. The transient photocurrent of devices was measured by applying 580 nm laser pulses with a pulse width of

120 fs and a low pulse energy to the short circuited devices in dark. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti:sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (SpectraPhysics Spitfire Ace). The photocurrent produced a transient voltage signal on a 50 Ω resistor, which was recorded by an oscilloscope (Tektronix TDS 3052C). Tapping-mode AFM images were obtained by using a Bruker Multimode 8 Microscope. Transmission electron microscopy (TEM) images were obtained by using a JEM 2100F Microscope. Optical microscopy (OM) images were obtained by using an Mshot MF30 fluorescence microscopy and a Canon EOS 70D camera.

During the measurements of SCLC, J_{ph}–V_{eff}, AFM, and TEM, the active layers were prepared with exactly the same concentration and rotating speed as those of corresponding samples prepared for J–V measurement. Specifically, the concentration/rotating speed/thickness for *o*-DCB-processed PTzBI:N2200$_{HW}$, CF-processed PTzBI:N2200$_{HW}$, MeTHF-processed PTzBI:N2200$_{HW}$, MeTHF-processed PTzBI:N2200$_{MW}$, MeTHF - processed PTzBI:N2200$_{LW}$ was 13 mg mL^{-1}/1400 rpm/96 nm, 5 mg mL^{-1}/1200 rpm/84 nm, 4.5 mg mL^{-1}/1200 rpm/103 nm, 5 mg mL^{-1}/1200 rpm/90 nm, 5.5 mg mL^{-1}/1200 rpm/88 nm, respectively. Also, all the active layers were annealed at 130 ^{o}C for 10 min for these measurements. For TEM measurements, the preparation of samples was carried out through the wetting transfer method. After the deposition of the active layers, the substrates of ITO/PEDOT:PSS (40 nm)/active layer were immersed into deionized water. Then, the active layers up-floated within 30 min due to the water-soluble property of PEDOT:PSS. A copper grid was used to hold up the up-floated active layers by a sharp tweezers. The substrates of cooper grid/active layer were standing in air to evaporate the water. Before testing, the substrates were transferred into vacuum at a pressure of 0.1 mbar for at least 6 h.

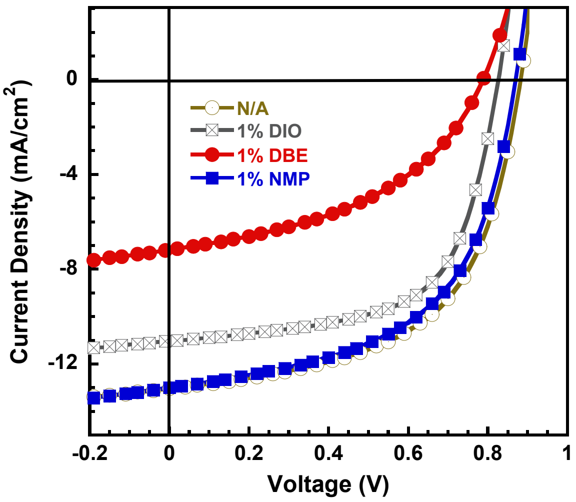

Fig. S1 *J–V* curves for all-PSCs with the active layers processed by MeTHF and various solvent additives without thermal annealing.

Table S1. Photovoltaic parameters of MeTHF-processed all-PSCs with the active layers processed by various solvent additives.

donor:acceptor	D/A ratio (wt:wt)	Solvent additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTzBI:N2200$_{HW}$	1:0.5	N/A	0.88	13.04	57.09	6.55
		1% DIO	0.83	11.05	61.82	5.67
		1% DPE	0.79	7.19	44.42	2.52
		1% NMP	0.87	13.01	55.27	6.25

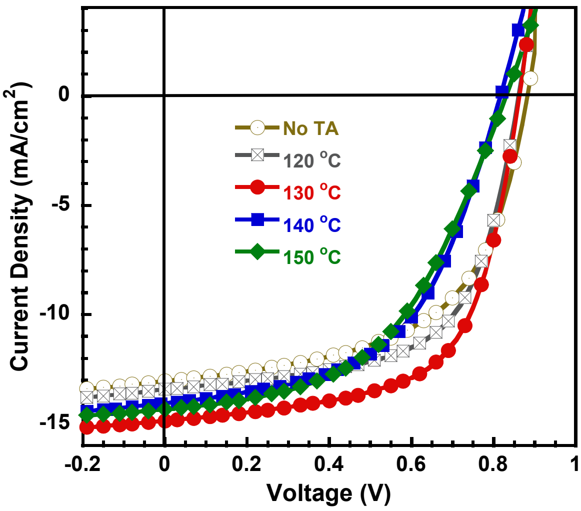

Fig. S2 *J*–*V* curves for all-PSCs with the active layers processed by MeTHF w/o or w/ thermal annealing (TA) for 10 min at different temperatures.

Table S2. Photovoltaic parameters of MeTHF-processed all-PSCs w/o or w/ thermal annealing (TA) for 10 min at different temperatures.

donor:acceptor	D/A ratio (wt:wt)	Solvent additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTzBI:N2200$_{HW}$	1:0.5	/	0.88	13.04	57.09	6.55
		120 °C	0.86	13.11	63.35	7.14
		130 °C	0.86	14.87	63.02	8.06
		140 °C	0.82	14.06	53.27	6.14
		150 °C	0.83	14.33	49.94	5.94

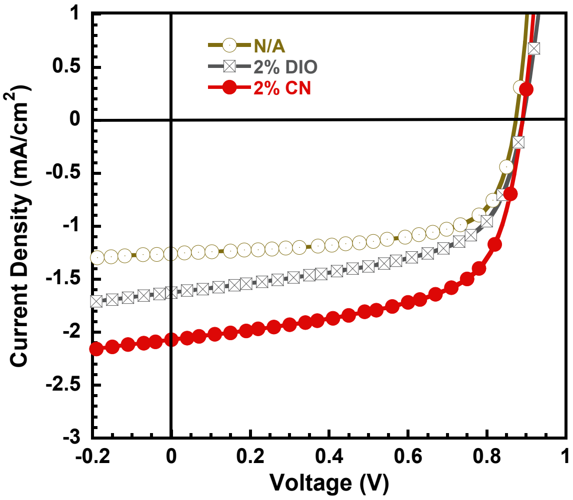

Fig. S3 *J*–*V* curves for all-PSCs with the active layers processed by *o*-DCB and various solvent additives with thermal annealing at 130 °C for 10 min.

Table S3. Photovoltaic parameters of *o*-DCB-processed all-PSCs with the active layers processed by various solvent additives with thermal annealing at 130 °C for 10 min.

donor:acceptor	D/A ratio (wt:wt)	Solvent additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTzBI:N2200$_{HW}$	1:0.5	N/A	0.87	1.26	65.71	0.72
		2% DIO	0.89	1.63	57.97	0.84
		2% CN	0.87	2.18	63.73	1.21

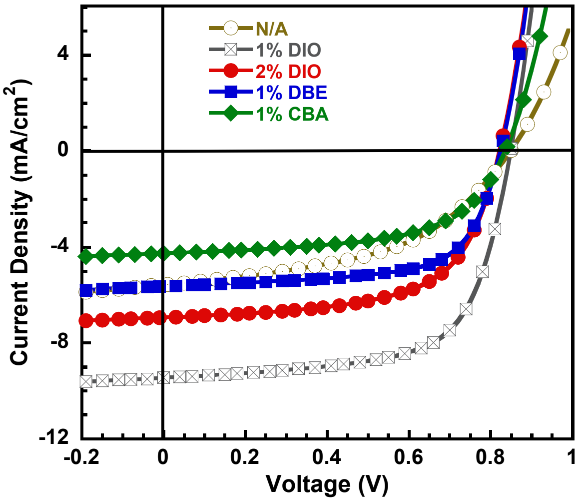

Fig. S4 *J–V* curves for all-PSCs with the active layers processed by CF and various solvent additives with thermal annealing at 130 °C for 10 min.

Table S4. Photovoltaic parameters of CF-processed all-PSCs with the active layers processed by various solvent additives with thermal annealing at 130 °C for 10 min.

donor:acceptor	D/A ratio (wt:wt)	Solvent additive	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTzBI:N2200$_{HW}$	1:0.5	N/A	0.85	5.58	47.99	2.28
		1% DIO	0.85	9.45	65.68	5.27
		2% DIO	0.82	6.94	62.12	3.53
		1% DBE [a]	0.82	5.63	66.57	3.07
		1% CBA [b]	0.84	4.27	58.27	2.09

[a] DBE refers to dibenzylether; [b] CBA refers to *o*-chlorobenzaldehyde.

Table S5. Polymer solubility test at different temperatures with certain concentrations in MeTHF.

Polymer	Total Conc. (mg mL^{-1})	Solubility [b] (100 °C)	Solubility [b] (50 °C)	Solubility [b] (R.T. ≈ 20 °C)
PTzBI	20	+++	+++	++
N2200 [a]	10	+++	++ [c]	+ [c]
PTzBI:N2200 [a] (1:0.5)	15	+++	++ [c]	++ [c]

[a] High molecular weight (M_n = 75.1 kg mol^{-1}); [b] +++ represents good solubility, ++ represents soluble but with high viscosity, + represents forming nearly gel state;[4] [c] stirred at 100 °C for 30 min and then cooled down to 50 °C or R.T.

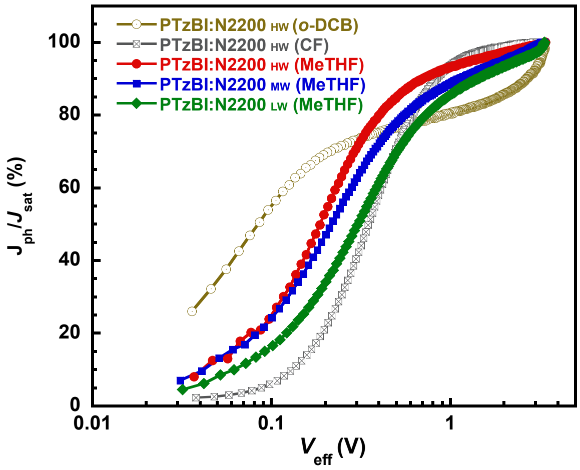

Fig. S5 J_{ph}/ J_{sat}–V_{eff} curves for all-PSCs based on PTzBI:N2200 (1:0.5, wt:wt).

Table S6. Relevant parameters obtained from J_{ph}–V_{eff} curves.

donor:acceptor	Solvent	V_0 (V)	J_{sat} (mA cm^{-2})	G_{max} (m^{-3} s^{-1})	$P(E,T)^a$ (%)	L (nm)
PTzBI:N2200$_{\mathrm{HW}}$	*o*-DCB	0.896	2.52	1.64×10^{27}	79.78	96
	CF	0.898	8.65	6.44×10^{27}	91.26	84
	MeTHF	0.907	15.3	9.28×10^{27}	92.77	103
PTzBI:N2200$_{\mathrm{MW}}$	MeTHF	0.871	13.2	9.17×10^{27}	87.64	90
PTzBI:N2200$_{\mathrm{LW}}$	MeTHF	0.872	11.3	8.03×10^{27}	83.71	88

[a] Under the short-circuit condition ($V_{\mathrm{eff}} = V_0$).

Table S7. Relevant parameters obtained from J_{SC}□P_{light} curves and transient photocurrent measurements (TPC).

donor:acceptor	Solvent	S (J_{SC}-P_{light})	τ (μs)	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
PTzBI:N2200$_{\mathrm{HW}}$	*o*-DCB	0.940	0.27	4.17×10^{-6}	1.67×10^{-5}	24.9
	CF	0.945	0.26	7.75×10^{-6}	4.96×10^{-6}	1.56
	MeTHF	0.965	0.18	1.11×10^{-3}	5.72×10^{-5}	19.4
PTzBI:N2200$_{\mathrm{MW}}$	MeTHF	0.935	0.22	2.99×10^{-4}	1.37×10^{-5}	21.8
PTzBI:N2200$_{\mathrm{LW}}$	MeTHF	0.927	0.24	3.65×10^{-4}	4.42×10^{-6}	82.6

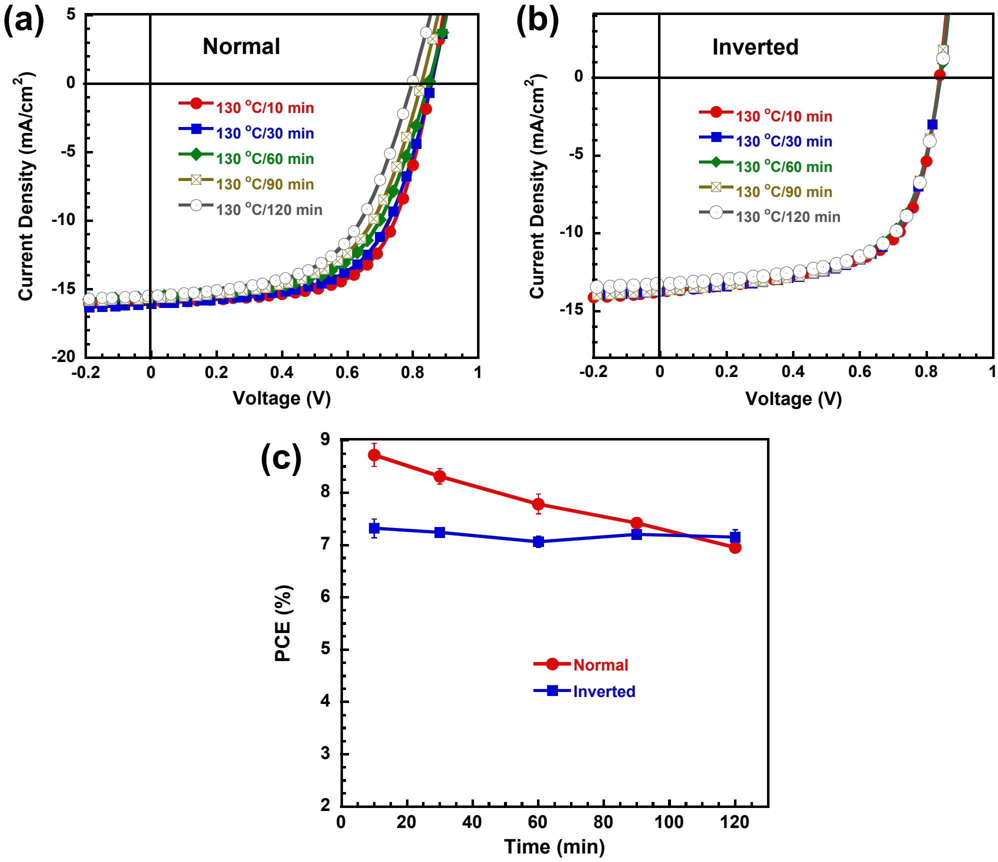

Fig. S6 *J*-*V* curves for normal (a) and inverted (b) devices based on PTzBI:N2200$_{HW}$ (1:0.5, wt:wt) processed with MeTHF after thermal treatment at 130 °C for 10 min, 30 min, 60 min, 90 min, and 120 min; (c) PCE variation under different annealing time.

Table S8. Photovoltaic performance of all-PSCs under thermal annealing at 130 ^{o}C for 10 min, 30 min, 60 min, 90 min, and 120 min, with the structure of ITO/PEDOT:PSS/active layer (120 nm)/PFNDI-Br/Al and ITO/ZnO/PFN-OX/active layer/MoO_3/Ag. , under AM 1.5G, 100 mW cm^{-2} illumination.

Donor:acceptor [a]	Structure	Thermal annealing	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE [avg] [b] (%)
PTzBI:N2200$_{HW}$	Normal	10 min	0.86	15.97	63.47	8.72 (8.57±0.22)
		30 min	0.86	16.08	60.08	8.31 (8.16±0.15)
		60 min	0.85	15.56	58.84	7.78 (7.63±0.19)
		90 min	0.83	15.69	57.03	7.42 (7.35±0.07)
		120 min	0.80	15.45	56.17	6.95 (6.83±0.10)
	Inverted	10 min	0.84	13.78	63.33	7.32 (7.14±0.18)
		30 min	0.84	13.75	62.74	7.24 (7.16±0.08)
		60 min	0.84	13.32	63.07	7.06 (6.97±0.11)
		90 min	0.84	13.73	62.42	7.20 (7.13±0.07)
		120 min	0.84	13.27	64.11	7.15 (7.01±0.14)

[a] The donor:acceptor ratio of PTzBI:N2200$_{HW}$ is 1:0.5; [b] the PCE values are obtained from 8 separate devices.

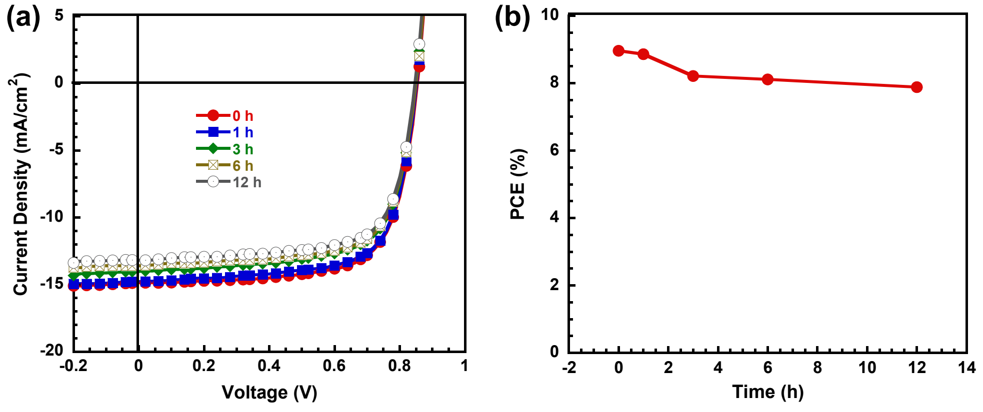

Fig. S7 *J-V* curves (a) and PCE variation (b) for normal devices based on PTzBI:N2200$_{HW}$ (1:0.5, wt:wt) processed with MeTHF under continuous AM 1.5G illumination within 12 h in nitrogen atmosphere.

Table S9. Photovoltaic performance of PTzBI:N2200$_{\mathrm{HW}}$ (1:0.5, wt:wt) based all-PSCs with normal structure under continuous AM 1.5G illumination within 12 h in nitrogen atmosphere.

Donor:acceptor [a] (wt:wt)	Illumination	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
PTzBI:N2200$_{\mathrm{HW}}$ (1:0.5)	0 h	0.854	14.86	70.61	8.96
	1 h	0.852	14.76	70.47	8.86
	3 h	0.849	14.02	68.98	8.21
	6 h	0.850	13.60	70.17	8.11
	12 h	0.847	13.18	70.59	7.88

[a] The blend films were processed by MeTHF and treated with 130 °C for 10 min.

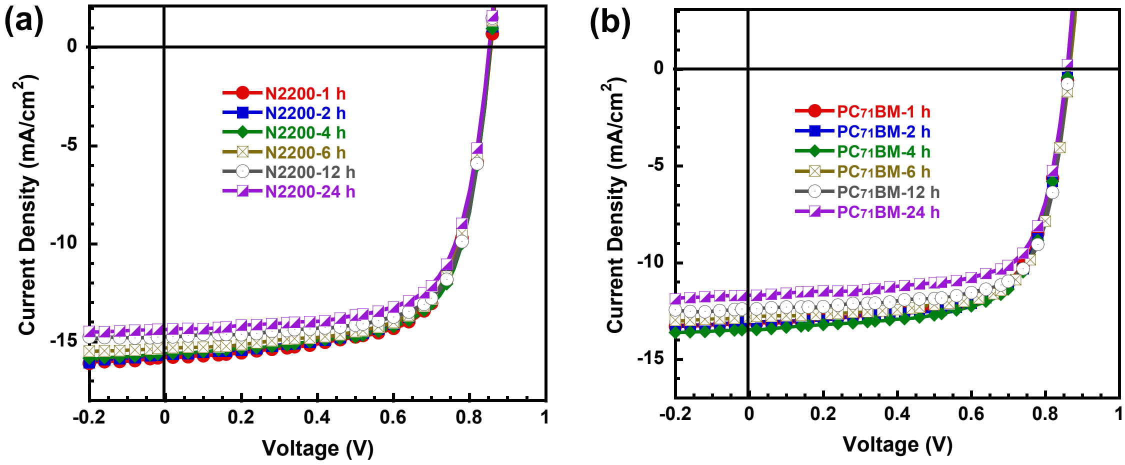

Fig. S8 *J-V* curves for normal devices based on PTzBI:N2200$_{\mathrm{HW}}$ (1:0.5, wt:wt) processed with MeTHF and PTzBI:PC$_{71}$BM (1:1, wt:wt) processed by *o*-DCB under thermal annealing at operating temperature (80 °C) within 24 h.

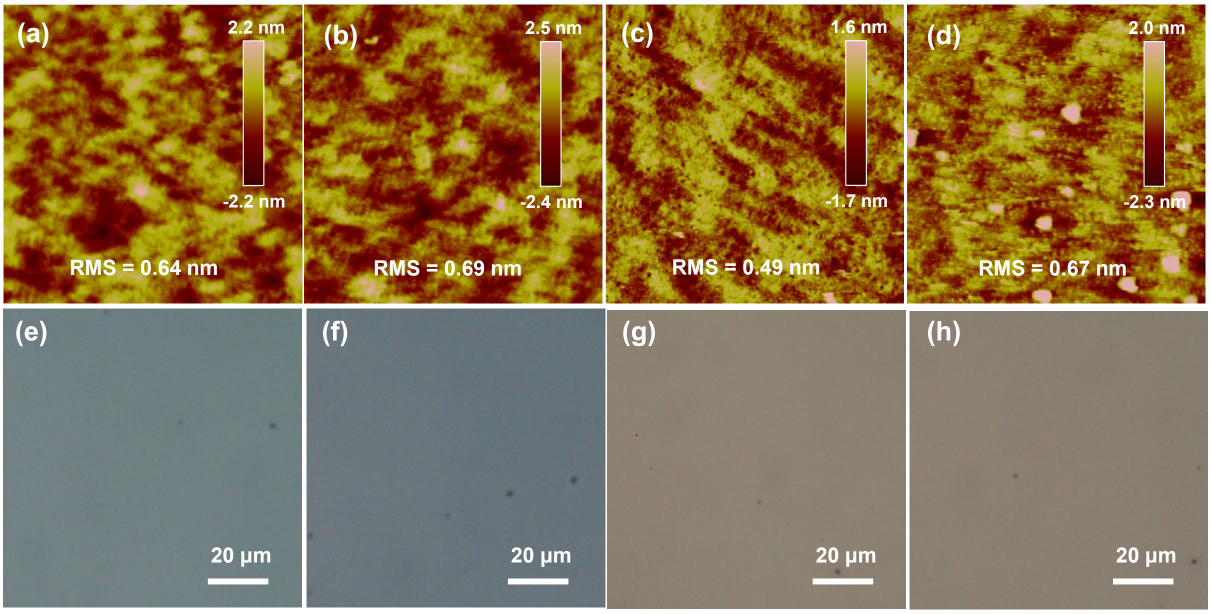

Fig. S9 AFM height images (3×3 μm^2) and optical microscopy (OM) images for PTzBI:N2200$_{HW}$ (1:0.5, wt:wt) based all-PSCs under thermal annealing at 80 ^{o}C for 2 h (a, e) and 24 h (b, f), and PTzBI:PC$_{71}$BM (1:1, wt:wt) based PSCs under 80 ^{o}C heating for 2 h (c, g) and 24 h (d, h), respectively.

Table S10. Photovoltaic performance of all-PSCs with normal structure under thermal annealing at operating temperature (80 °C) within 24 h.

Donor :Acceptor [a]	Thermal annealing	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE [b] (%)	PCE_{best} (%)
PTzBI :N2200$_{HW}$	80 °C/1 h	0.857±0.003	15.36±0.58	67.74±1.12	8.91±0.21	9.12
	80 °C/2 h	0.855±0.003	15.06±0.50	66.68±1.69	8.59±0.34	8.97
	80 °C/4 h	0.855±0.002	15.31±0.64	67.99±1.29	8.92±0.28	9.14
	80 °C/6 h	0.854±0.002	14.99±0.62	68.92±1.15	8.82±0.21	9.03
	80 °C/12 h	0.852±0.001	14.22±0.71	71.28±0.30	8.63±0.40	8.94
	80 °C/24 h	0.849±0.002	14.03±0.40	70.37±0.93	8.38±0.14	8.52
PTzBI :PC$_{71}$BM	80 °C/1 h	0.861±0.005	12.89±0.25	68.27±0.44	7.57±0.15	7.71
	80 °C/2 h	0.861±0.004	12.88±0.17	67.99±1.23	7.54±0.21	7.78
	80 °C/4 h	0.863±0.003	13.24±0.19	68.41±0.42	7.82±0.09	7.96
	80 °C/6 h	0.867±0.002	12.79±0.07	69.97±0.71	7.76±0.07	7.83
	80 °C/12 h	0.865±0.002	11.97±0.38	71.25±0.61	7.38±0.26	7.64
	80 °C/24 h	0.860±0.002	11.47±0.31	71.39±0.76	7.04±0.10	7.11

[a] The donor:acceptor ratio of PTzBI:N2200$_{HW}$ and PTzBI:PC$_{71}$BM are 1:0.5 and 1:1, respectively, and all the blend films were treated with 130 °C for 10 min initially; [b] the PCE values are obtained from 8 separate devices.

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