Electronic supplementary information

Binary nonfullerene polymer solar cells with 430 nm thick active layer showing 15.39% efficiency and 73.38% fill factor

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Experimental section

Materials

PFN-Br was purchased from Solarmer Materials (Bejing) Inc. Polymer donor Si25 and acceptor Y14 were synthesized according to previous reports.[1,2] The processing solvents used in the device fabrication were purchased from Sigma Aldrich and used as received.

Device fabrication

All PSCs were fabricated with an inverted structure of ITO/ZnO/PFN-Br/active layer/MoO_3/Al. The patterned ITO-coated glass substrates with a sheet resistance of 15-20 ohm square^{-1} were cleaned by sequential sonication using detergent, acetone, deionized water, and ethanol, and dried in oven at 70 ℃ before used. A sol-gel processed ZnO layer of 30 nm was spun onto the substrate and annealed at 200 ℃ on a hot plate for 30 min. Then the substrate was transferred into a nitrogen-filled glove box. Afterward, around 5 nm PFN-Br layer (0.5 mg/mL in methanol, 2000 rpm) was spin-coated onto the ZnO layer. The Si25:Y14 (1:1.2 weight ratio) blend solutions with different concentrations were prepared with chlorobenzene or *o*-xylene as the solvent. Being heated and stirred at 100 ℃ for about 3 h, the blend solutions were spin-coated on the substrates at 450–800 rpm for 60 s to afford blend films with different thicknesses, and then dried at 110 ℃ for 10 min. Finally, 5 nm MoO_3 and then 100 nm aluminum (Al) were thermally deposited on top of the blend films through a shadow mask in a vacuum chamber at a pressure of 2×10^{-4} Pa. The active layer area of the device was defined to be 0.057 cm^2.

Instruments and characterization

UV-vis absorption spectra were recorded on an UV-3600 (Shimadzu Co.) spectrophotometer. The thickness values of the PEDOT:PSS and active layer were verified by a surface profilometer (Tencor, Alpha-500) while the thickness of the evaporated cathodes was monitored by a quartz crystal thickness/ratio monitor (Model: STM-100/MF, Sycon). The photovoltaic performance was measured under an AM 1.5G (air mass 1.5 global) spectrum from a solar simulator (Japan, SAN-EI, XES-40S1) (100 mW/cm^2). 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.

Grazing incidence X-ray diffraction (GIXD) experiments were carried out on a Xenocs Xeuss 2.0 system with an Excillum MetalJet-D2 X-ray source operated at 70.0 kV, 2.8570 mA, and a wavelength of 1.341 Å. The grazing-incidence angle was set at 0.20 °. Scattering pattern was collected with a Dectris Pilatus3R 1M area detector.

Hole-only and electron-only devices were fabricated to measure the hole and electron mobilities of active layers by using the space charge limited current (SCLC) method with hole-only devices of ITO/PEDOT:PSS/Active layer/MoO_3/Al and electron-only devices of ITO/ZnO/Active layer/Ca/Al. The mobilities (μ_h or μ_e) were determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

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

where J is the current, ε_0 is the permittivity of free space, ε_r is the material relative permittivity, d is the thickness of the active layer and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) from the applied voltage (V_{appl}), $V=V_{appl}-V_{bi}$. The mobility can be calculated from the slope of the $J^{1/2}$-V curves.

Supplementary Figures and Tables

Table S1. Photovoltaic parameters of the Si25:Y6 active layers processed with CB and CF[a)]

Solvent	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
CB	0.673	5.31	32.96	1.18
	(0.655 ±0.024)	(4.39 ±0.29)	(32.16 ±0.70)	(0.93 ±0.11)
CF	0.734	15.60	41.62	4.75
	(0.731 ±0.005)	(14.23 ±1.41)	(40.21 ±2.01)	(4.22 ±0.60)

[a)] Statistical data achieved from 10 independent devices.

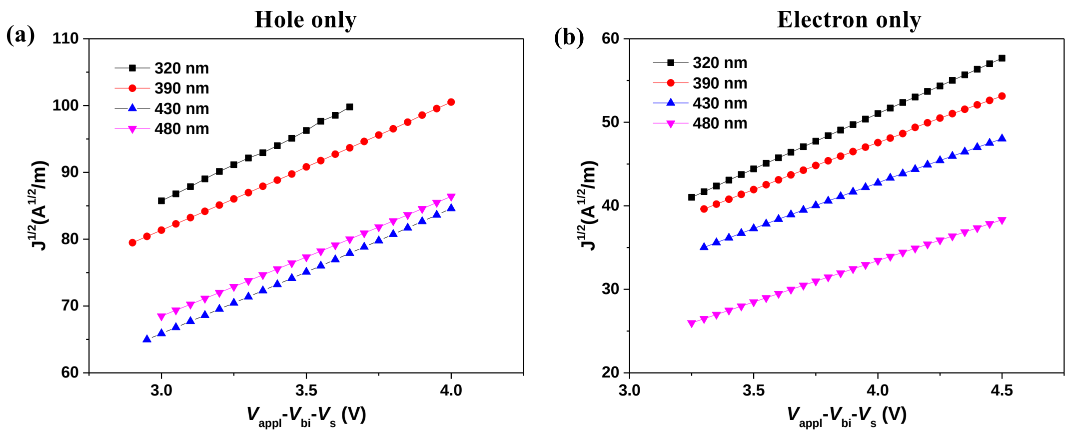

Fig. S1. SCLC $J^{0.5}$-V characteristics of the Si25:Y14 blend films of different thicknesses in (a) hole-only and (b) electron-only devices, with device configurations of ITO/PEDOT:PSS/blend film/MoO_3/Al and ITO/ZnO/blend film/PFN-Br/Al, respectively.

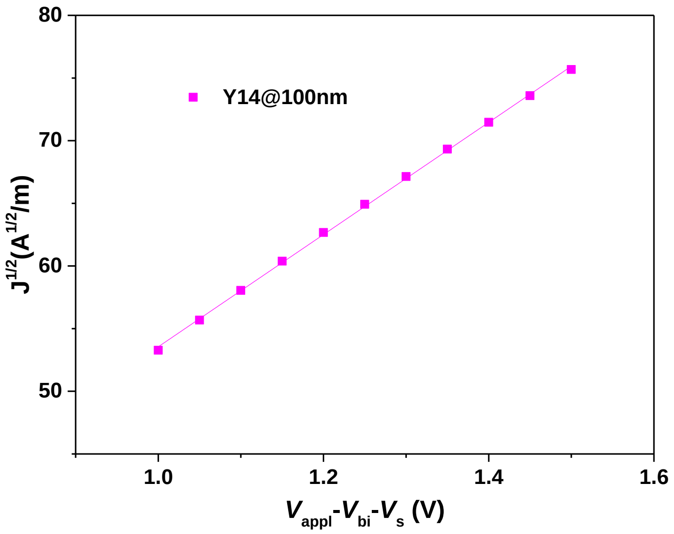

Fig. S2. SCLC $J^{0.5}$-V characteristics of the pristine Y14 film (100 nm) in electron-only device, with device configuration of ITO/ZnO/blend film/PFN-Br/Al. The calculated electron moblity for Y14 is 8.17×10^{-4} cm^2 V^{-1} s^{-1}.

Table S2. Photovoltaic parameters of the Si25:Y14 active layers with different DA ratio[a)]

D:A ratio	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
1:1	0.782	25.25	74.14	14.64
	(0.770 ±0.007)	(25.05 ±0.55)	(73.50 ±0.72)	(14.17 ±0.30)
1:1.2	0.772	26.47	72.28	14.77
	(0.767 ±0.006)	(26.93 ±0.62)	(69.86 ±1.75)	(14.42 ±0.25)
1:1.5	0.762	25.31	75.99	14.66
	(0.769 ±0.006)	(25.12 ±0.62)	(72.75 ±1.80)	(14.04 ±0.26)

[a)] Statistical data achieved from 18 independent devices.

Table S3. Photovoltaic parameters of the Si25:Y14 active layers with different CN content[a)]

CN content (%)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
0	0.782	26.82	73.38	15.39
	(0.781 ±0.004)	(26.59 ±0.14)	(72.41 ±0.56)	(15.03 ±0.17)
0.5	0.772	26.47	72.28	14.77
	(0.767 ±0.006)	(26.93 ±0.62)	(69.86 ±1.75)	(14.42 ±0.25)

[a)] Statistical data achieved from 18 independent devices.

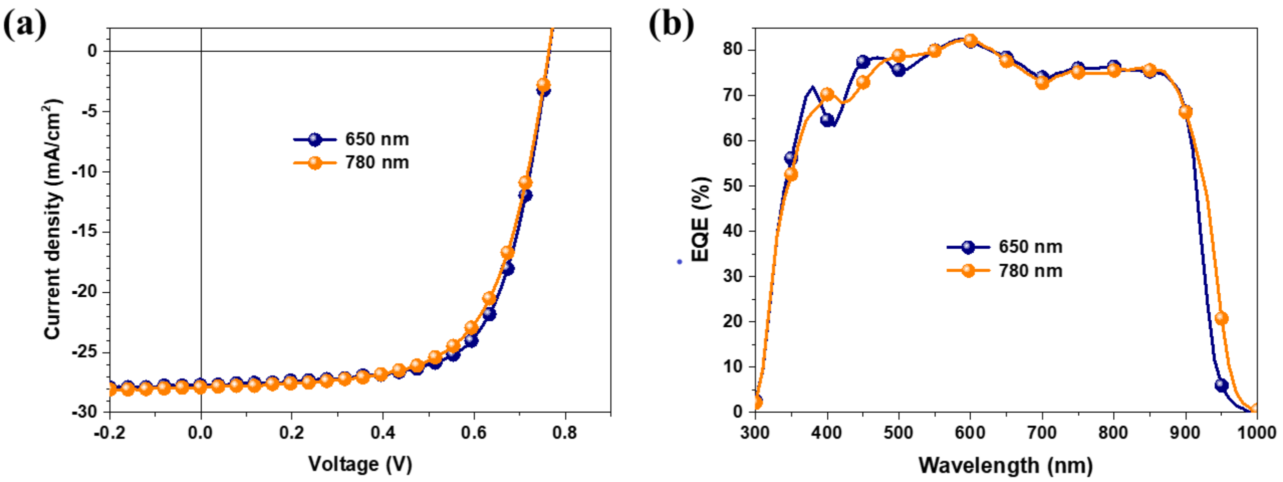

Fig. S3. (a) the *J-V* curves and (b) EQE spectra based on Si25:Y14 blend films of 650 and 780 nm thicknesses.

Table S4. Photovoltaic parameters of Si25:Y14 blend films with thicknesses of 650 and 780 nm.[a)]

Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	Integrated J_{sc} (mA/cm^2)	FF (%)	PCE (%)
650	0.762	27.69	26.21	67.57	14.26
	(0.764 ±0.008)	(27.26 ±0.27)		(65.60 ±1.39)	(13.67 ±0.30)
780	0.762	27.89	26.66	64.19	13.64
	(0.759 ±0.007)	(27.83 ±0.31)		(60.60 ±2.54)	(12.81 ±0.61)

[a)] Statistical data achieved from 18 independent devices.

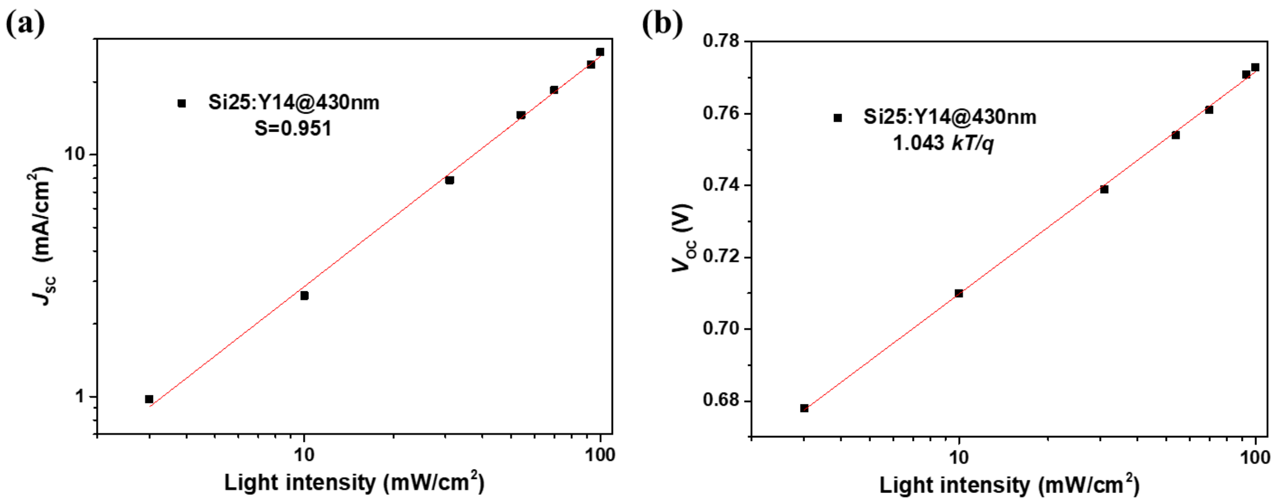

Fig. S4. Dependence of (a) J_{sc} and (b) V_{oc} on the light intensity for PSCs based on Si25:Y14 blend films processed by CB.

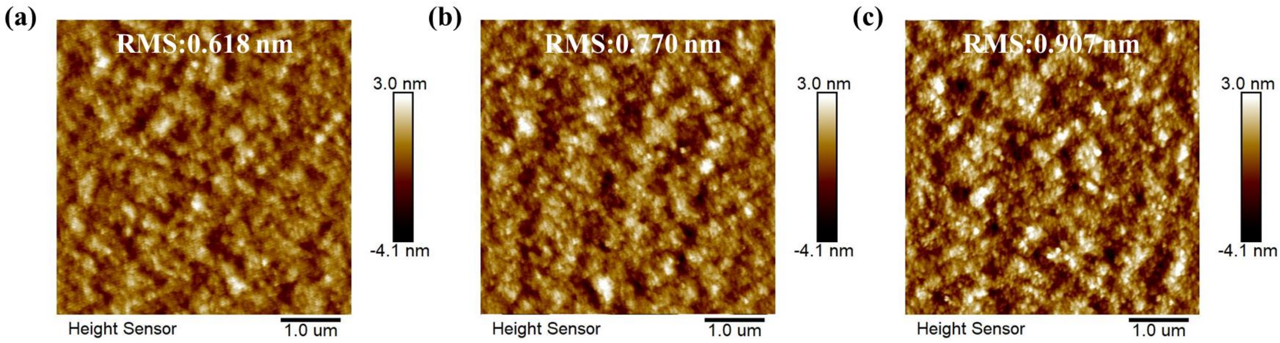

Fig. S5. The AFM height images (5×5 μm) of Si25:Y14 active layers with thickness of (a) 210, (b) 430, and (c) 600 nm, respectively.

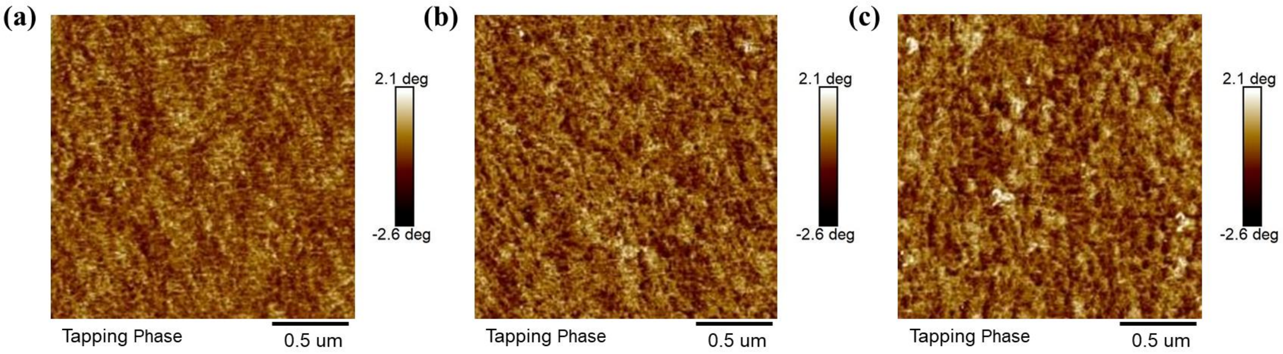

Fig. S6. The AFM phase images (2×2 μm) of Si25:Y14 active layers with thickness of (a) 210, (b) 430, and (c) 600 nm, respectively.

Table S5. The *q* vector, *d*-spacing, FWHM, and coherence length (CL) for the observed (100) and (010) peaks.

Film	In plane (100)/Out of plane (100)				Out of plane (010)/In plane (010)			
	q_{xy} (Å^{-1})	*d*-spacing (Å)	FWHM (Å^{-1})	CL (Å)	q_z (Å^{-1})	π-π distance (Å)	FWHM (Å^{-1})	CL (Å)
Si25	-/0.27	-/23.27	-/0.04	-/146.08	-/1.74	-/3.61	-/0.12	-/48.69
Y14	0.40/-	15.71/-	0.08/-	73.04/-	1.76/-	3.57/-	0.29/-	20.15/-
Blend	0.25/0.27	25.13/23.27	0.04/0.05	146.08/116.87	1.77/-	3.55/-	0.17/-	34.37/-
	0.42/-	14.96/-	0.06/-	104.72/-				

Table S6. Photovoltaic parameters of Si25:Y14 blend films with thicknesses of 400 and 530 nm processed by *o*-xylene.

Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
400	0.772	26.69	70.03	14.43
530	0.762	27.47	68.07	14.25

Table S7. Summary of some highly efficient PSCs based on non-halogen solvent processed active layers.

Active layer	Solvent[a)]	PCE(%)/thickness	Reference
PBQ-4F:ITIC	THF / IPA	11.34 / (100 nm)	3
PTB7-Th:$PC_{71}BM$:PTN	EBz	11.44 / (120 nm)	4
BDTSTNTTR:$PC_{71}BM$	CS_2	11.53 / (100 nm)	5
PBDB-T:IT-M	XY / PN	11.6 / (100 nm)	6
PB3T:IT-M	Anisole	11.9 / (100 nm)	7
PBDB-BzT:IT-M	THF	12.10 / (100 nm)	8
PBDT-F-C4T:IT-4F	TMB / DIO	12.5 / (100 nm)	9
PBDTS-TDZ:ITIC	XY	12.80 / (100 nm)	10
PM6:IT-4F	XY	12.9 / (100 nm)	11
PBTA-TF:IT-M	XY / PN	13.1 / (100 nm)	12
T1:IT-4F	THF / NMP	14.2 / (100 nm)	13
PM6:Y6	TMB	15.6 / (100 nm)	14
T1:BTP-4F-12	THF	16.1 / (100 nm)	15
PM6:DTY6	XY	16.1 / (100 nm)	16
PM6:BTP-BO-4Cl	Toluene	17.33 / (100 nm)	17
PffBT4T-C_9C_{13}: $PC_{71}BM$	TMB / PN	11.7 / (375 nm)	18
PTzBI-Si:N2200	CPME / DBE	11.0 / (130 nm) 9.9 / (200 nm) 9.5 / (300 nm) 9.3 / (350 nm)	19
PTzBI:PBTA-BO:N2200	MeTHF / DBE	10.12 / (120 nm) 9.26 / (241 nm) 9.01 / (304 nm)	20
PBTA-Si:PTzBI-Si:N2200	MeTHF / DBE	9.80 / (130 nm) 10.09 / (250 nm) 10.54 / (380 nm)	21

		10.05 / (530 nm)	
Si25:Y14	XY	14.43 / (400 nm) 14.25 / (530 nm)	**This Work**

[a)] Abbreviations for the solvents. THF = tetrahydrofuran, IPA = isopropanol, EBz = ethylbenzene, CS_2 = carbon disulfide, XY = *o*-xylene, PN = 1-phenylnaphthalene, TMB = 1,2,4-triethylbenzene, DIO = 1,8-diiodooctane, NMP = N-methyl pyrrolidone, CPME = cyclopentyl methyl ether, DBE = Benzyl ether, MeTHF = 2-methyltetrahydrofuran.

Table S8. Photovoltaic parameters of thick-film PSCs based on FBT-Th_4(1,4):Y14 blend films processed by chlorobenzene (CB) and *o*-xylene.

Solvent	Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
CB	310	0.802	25.54	64.85	13.28
	420	0.800	26.93	65.07	14.05
	500	0.799	26.41	64.84	13.73
o-xylene	400	0.799	26.47	65.07	13.81

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