Supporting information

Ternary organic electron transport layer for efficient and photostable perovskite solar cells under full spectrum illumination

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Experimental Section

Materials

Dimethylsulfoxide (DMSO, 99.9%), chlorobenzol (CB, 99.8%), Dimethyl Formamide (DMF, 99%) were purchased from Sigma-Aldrich. PCBM (99.5%) was purchased from 1-Material Inc. C_{60} was purchased from Luminescence Technology Corp. Lead iodide (PbI_2, 99%), Spiro-OMeTAD and CH_3NH_3I were purchased from Xi'an Polymer Light Technology Corporation. Diethyl ether was purchased from Sinopharm Chemical Reagent Co., Ltd. PFN was purchased from Derthon Optoelectronic Materials Science Technology Co LTD.

Device fabrication

The ITO (or FTO) was cleaned sequentially in deionized water, cleaning fluid, acetone, and ethanol under sonication for 5 min, respectively. Then the ITO was dried by nitrogen gas and treated with UV-Ozone machine for 20 min. PCBM, C_{60} and PFN were dissolved in chlorobenzol solution at 30, 8 and 12.5 mg/mL, respectively. All these solutions were stirred overnight at room temperature. For the PCBM ETLs, 12.5 mg/mL PCBM in chlorobenzol solution was prepared. For the PCBM:C_{60} ETLs, we mixed the PCBM (30 mg/mL), C_{60} chlorobenzol solution (8 mg/mL) and chlorobenzol (CB) with different ratio: PCBM:C_{60}:CB=396μL/78μL/526μL, 354μL/234μL/412μL, 315μL/391μL/294μL and 271μL/547μL/182μL. For the PCBM:PFN and PCBM:C_{60}:PFN ETLs, we added 10 μL of PFN solution in 1 ml PCBM or PCBM:C_{60} (3:1 by weight) chlorobenzol solution. The ETLs on ITO were attained by spin-coating the chlorobenzol solution with concentrations of 12.5 mg mL^{-1} at a rate of 1000 rpm for 60 s. The 120 nm ITO/PCBM:C_{60}:PFN sample for EDS measurements was attained by spin-coating the chlorobenzol solution of PCBM:C_{60}:PFN (75:25:2 by weight) with 25 mg mL^{-1} at a rate of 1000 rpm. These ITO/ETLs were followed by thermal annealing at 100 °C for 10 min. For planar TiO_2 ETLs, an acidic solution of titanium isopropoxide in ethanol (the concentrations of titanium isopropoxide/2M HCl/ethanol=254μL/34μL/2mL) was spin-coated on the FTO at 2000 rpm for 40 s, and then annealed in air at 500 °C for 30 min.

The 461 mg of PbI_2, 159 mg of CH_3NH_3I, and 78 mg of DMSO (molar ratio 1:1:1) were mixed in 600 mg of DMF solution. The prepared solution was dropped on different ETL substrates and then rapidly spin-coated at 1000 rpm for 10 seconds and 5000 rpm for another 20 seconds. 0.6 ml of diethyl ether was drop–casted quickly 15 seconds before the 5000 rpm spin–coating ended. The perovskite films were heated at 70 °C for 1 min and 100 °C for 10 min on a hotplate respectively. After several minutes, a hole-transport material was spin-coated on the top of perovskite film at the rotation speed of 3000 rpm for 30 s in the glove box. The hole-transport solution was prepared by dissolving 72.3 mg spiro-MeOTAD, 17.5 µL of a stock solution of 520 mg mL^{-1} lithium bis(trifluoromethylsulphonyl)imide in acetonitrile and 28.8 µL 4-tert-butylpyridine in 1 mL chlorobenzene. At last, 100 nm thick Au electrode was deposited under high vacuum ($<1.0\times10^{-3}$ Pa). For all devices, the active area is 10 mm^2 defined by the cross section of the electrodes. All the devices were unpaged and measured in air with ~ 45% humidity.

Preparation of the sample for Kelvin probe measurement

The ITO/PFN was prepared by spin-coating a chlorobenzol solution of PFN with 1 mg mL^{-1} on the top of ITO at the rotation speed of 3000 rpm for 40 s. The ITO/PCBM, ITO/PCBM:PFN, ITO/PCBM:C_{60} (3:1 by weight), ITO/PCBM:C_{60}:PFN samples were prepared by the same method as before.

Current–voltage measurements

The current density versus voltage (*J–V*) characteristics of solar cells were measured by a Keithley 2400 source meter with a solar simulator (94022A, Newport) under AM 1.5 G conditions at an illumination intensity of 100 mW cm^{-2}, calibrated by a standard Si solar cell (PVM937, Newport). The *J*−*V* measurements were carried out in ambient air. These devices were measured in reverse scan (1.4 V → −0.2 V) and forward scan (−0.2 V → 1.4 V), and the scan rate was 80 mV/s.

Scanning electron microscopy

The SEM data were scanned by an S−4800 (Hitachi) field-emission scanning electron microscope (FESEM).

Photoluminescence spectroscopy

The time-resolved photoluminescence (TRPL) spectroscopy was measured with the PL spectrometer (Edinburgh Instruments, FLS 920). The samples were excited by a pulsed laser, with a wavelength and frequency of 635 nm and 1 MHz. A band pass filter at 655 nm was used to filter out the excitation light in the transient PL measurements.

X-ray diffraction (XRD)

XRD patterns were characterized by X-ray diffraction powder diffraction (Bruker D8 Advance) with Cu Kα radiation (λ=1.5406 A), 40 mA and 40 mV.

External quantum efficiency (EQE) measurement

The external quantum efficiency (EQE) of solar cells was measured by an EQE measurement system (Model QEX10, PV Measurements, Inc.) across a wavelength range of 300−850 nm.

Stability test

For the stability measurements, all the perovskite devices were unpaged stored in a nitrogen-filled glove box. All of the devices were aged under constant full-spectrum simulated AM1.5, ~70 mA cm^{-2} irradiance including UV radiation, using a xenon lamp (CEL-HXF300, Beijing China Education Au-light Co., Ltd). It is noted that we do not apply any additional ultraviolet filter during the ageing process.

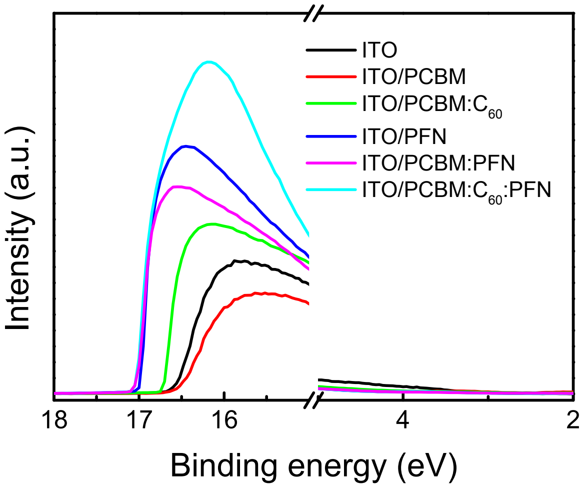


Figure S1 UPS of the ITO, ITO/PCBM, ITO/PCBM:C$_{60}$, ITO/PFN, ITO/PCBM:PFN, ITO/PCBM:C$_{60}$:PFN.

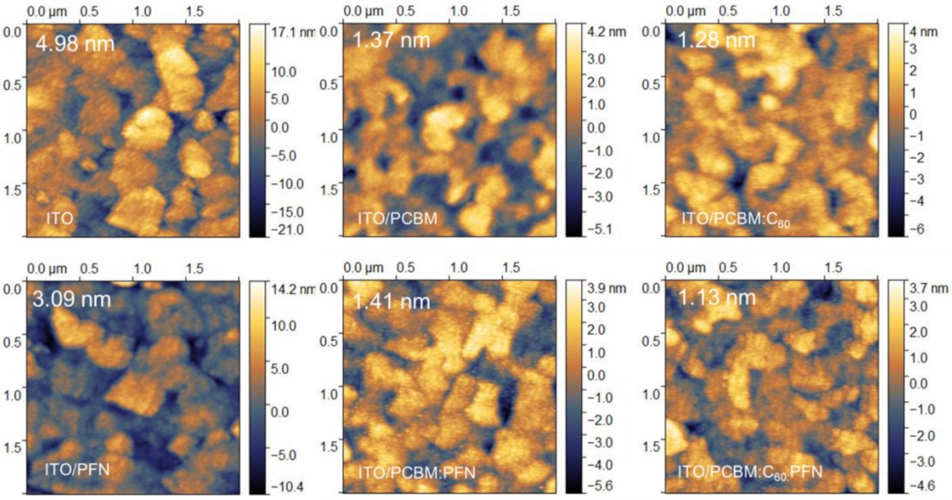


Figure S2 AFM of the ITO, ITO/PCBM, ITO/PCBM:C_{60}, ITO/PFN, ITO/PCBM:PFN, and ITO/PCBM:C_{60}:PFN.

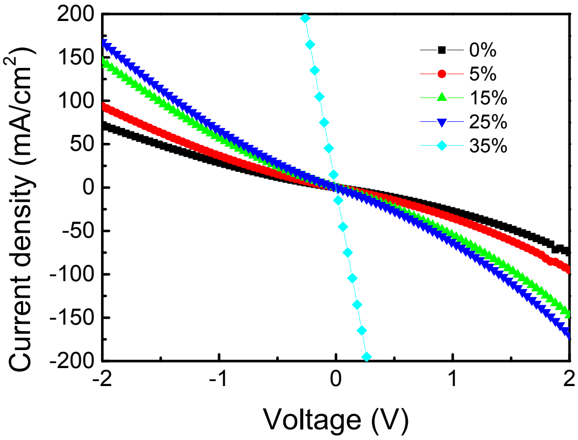


Figure S3 *J*-*V* characteristics of the device ITO/PCBM:C_{60}/Ag.

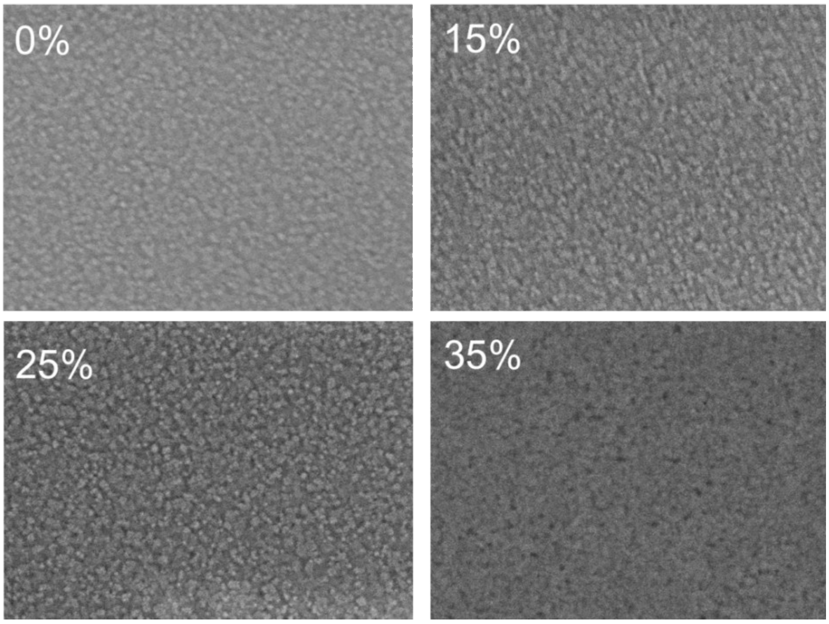


Figure S4 SEM images of PCBM film with adding different content C_{60}.

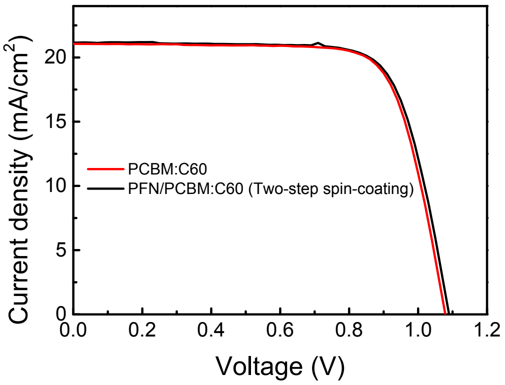


Figure S5 Typical J-V curves of the PSCs based on different ETLs.

Table S1 τ_1 and τ_2 from PL decay spectra with different substrates.

Substrate	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ	$k_{ct}=1/\tau-1/\tau_0$ (ns^{-1})
glass	-	164.4	-	100	164.4 (τ_0)	0
PCBM	10.2	36.4	55.3	44.7	21.9	0.0395
PCBM:C$_{60}$	5.9	19.7	49.9	50.1	12.8	0.0719
PCBM:PFN	6.7	21.8	35.5	64.5	16.4	0.0547
PCBM:C$_{60}$:PFN	5.2	20.2	58.5	41.5	11.4	0.0814

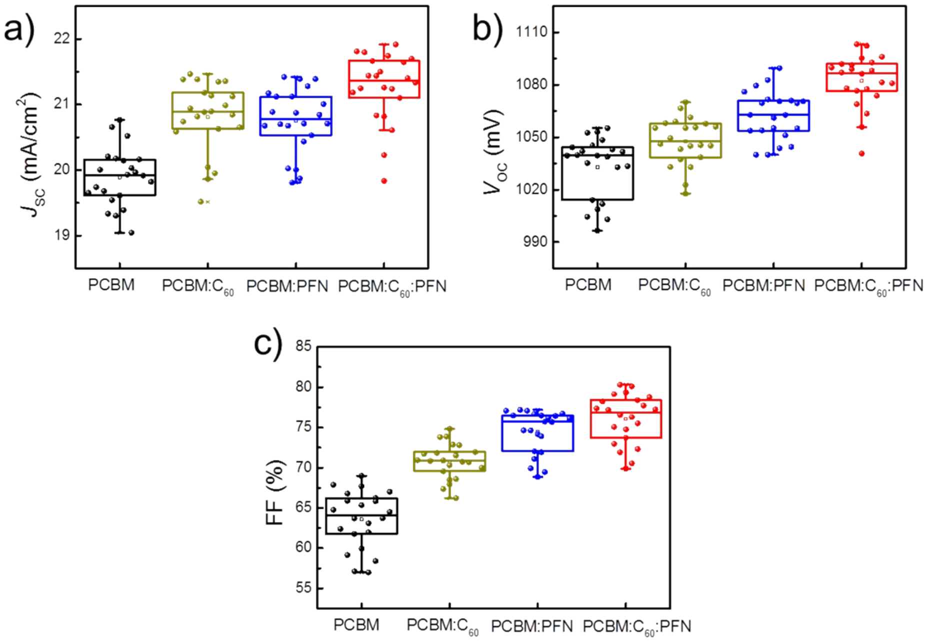


Figure S6 Device statistics of (a) J_{SC}, (b) V_{OC}, and (c) FF of perovskite solar cell employing different ETLs.

Table S2 Photovoltaic parameters of the champion PSCs with different ETLs under different scanning direction.

ETLs	Scan directions	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
PCBM	Reverse	1.05	20.55	67.4	14.57
	Forward	1.05	20.46	66.8	14.38
PCBM:C_{60}	Reverse	1.07	21.30	73.3	16.70
	Forward	1.07	21.34	72.5	16.54
PCBM:PFN	Reverse	1.09	21.26	77.7	18.04
	Forward	1.09	21.20	76.6	17.73
PCBM:C_{60}:PFN	Reverse	1.10	21.78	80.3	19.31
	Forward	1.10	21.71	79.6	19.13

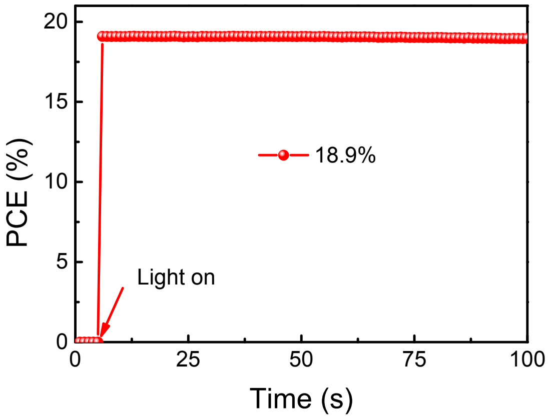


Figure S7 Stable-state PCE output of the device based on PCBM:C_{60}:PFN measured at the maximum power point (V_{mp}=0.953 V).

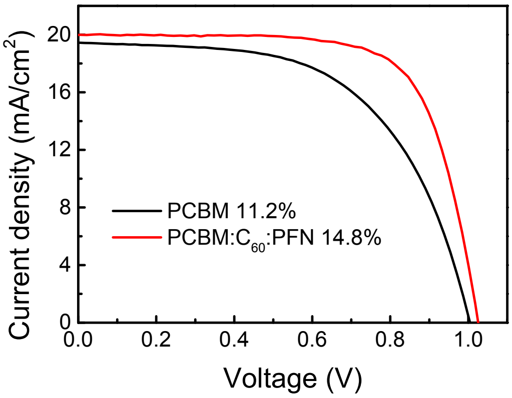


Figure S8 *J*–*V* curves of the flexible PSCs with different ETLs.

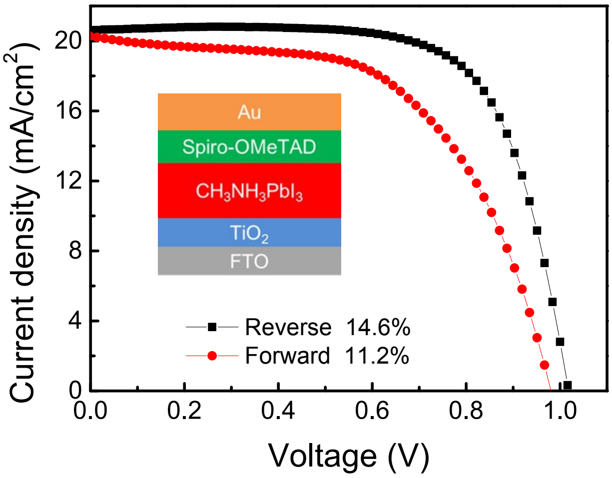


Figure S9 Performance for the PSCs with TiO_2 ETLs.

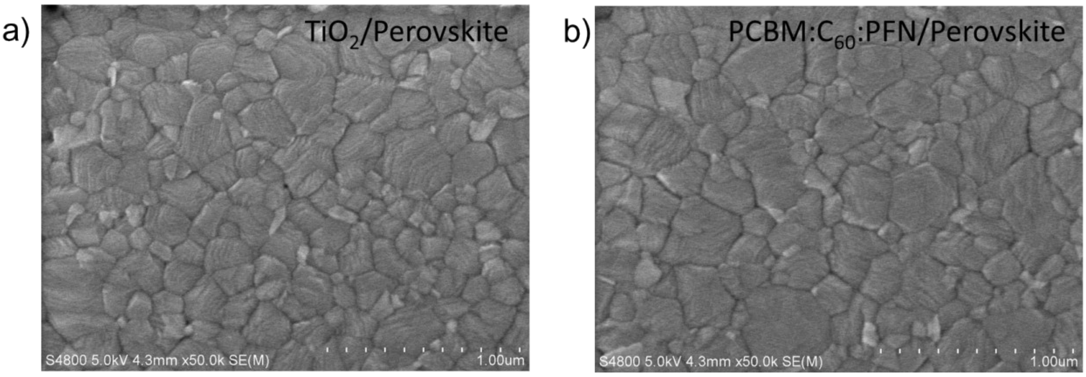


Figure S10 SEM images of the perovskite film on a) TiO_2 and b) PCBM:C_{60}:PFN.

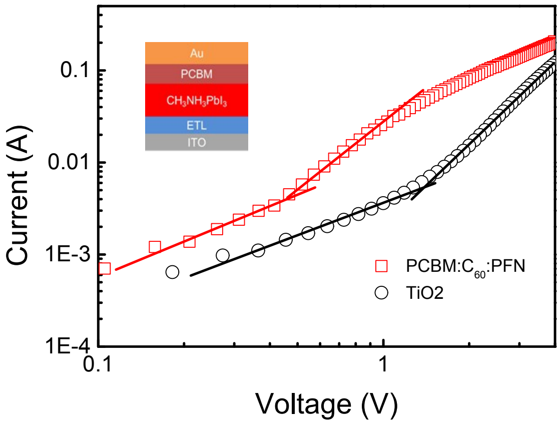


Figure S11. Dark *I*-*V* measurement of the electron-only devices.

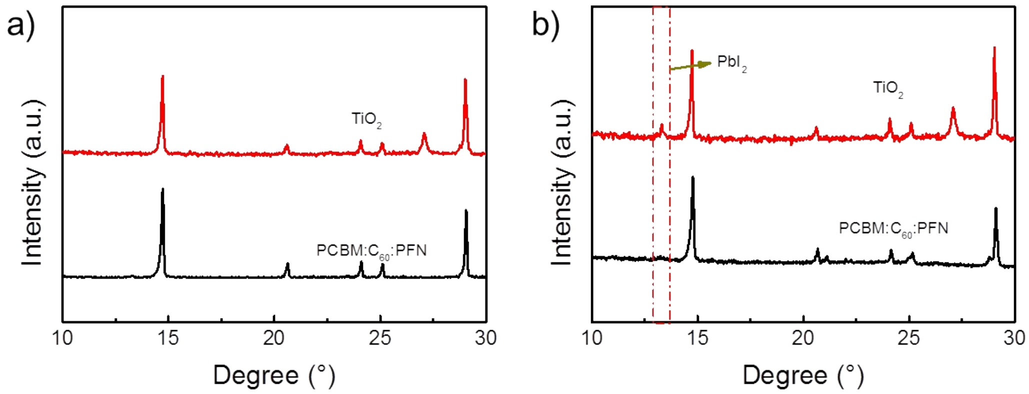


Figure S12 XRD patterns of the PSCs with different ETLs (a) before and (b) after 1200 h full spectrum illumination.

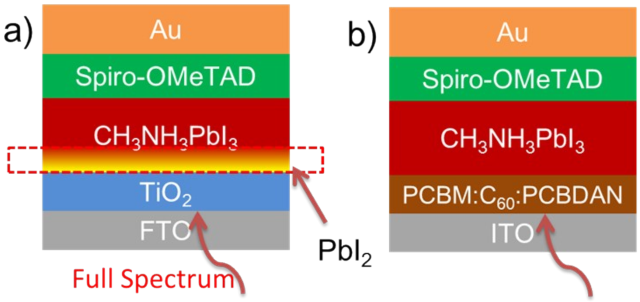


Figure S13 Schematic illustration of the perovskite solar cells with different ETLs after full spectrum illumination.

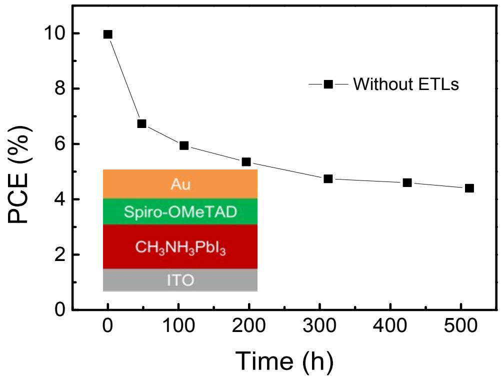
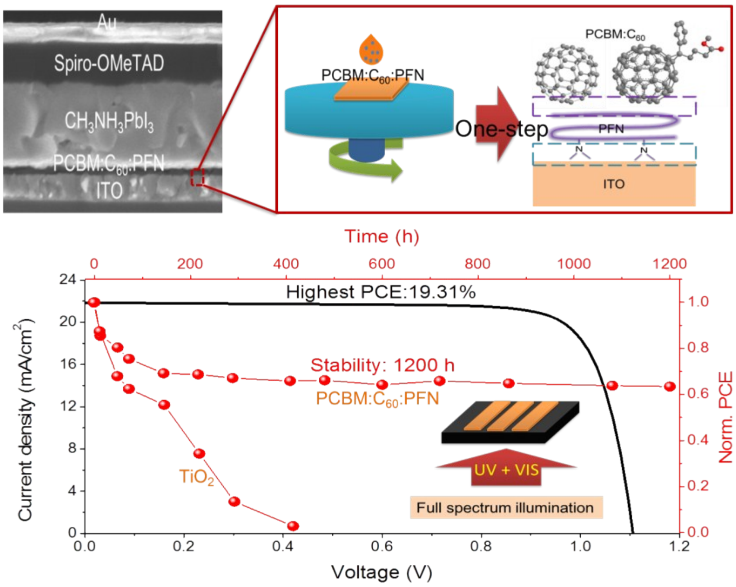


Figure S14 Device performance of the unpaged devices without ETLs exposed in N_2 glove box under full spectrum illumination (AM1.5, 70 mW cm^{-2}).



The PSCs used low-temperature processed PCBM:C_{60}:PFN as ETL achieved a 19.31% efficiency and showed high photo-stability under full spectral illumination.