Supporting information

Dual-functional Additive for Stable Perovskite Thin Film

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Materials

The pre-patterned FTO glass-substrates (Pilkington, TEC8) were purchased from AMG-Tech. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine (PTAA), toluene(99.8), *N*, *N*-dimethylformamide (DMF, 99.8%), chlorobenzene (CB, 99.8%), phenyl-C_{61}-butyric acid methyl ester (PCBM, 99%), ethyl acetate (EA, 99.8%) and dimethyl sulfoxide (DMSO, 99.8%) were purchased from Sigma-Aldrich. Lead (II) bromide ($PbBr_2$) was bought from Lumtech. Cesium iodide (CsI, 99.0%) and Lead (II) iodide (PbI_2, 99.99%) were purchased from TCI. Tin (IV) oxide, 15% in H_2O colloidal dispersion, was purchased from Alfa Aesar. Formamidinium iodide (FAI, 99.99%) was purchased from Great Solar Cell.

Film and Device Fabrication

All perovskite films and precursors are prepared in ambient air conditions. The perovskite solar cells were prepared in an n-i-p configuration. First, the glasses were cleaned using ultrasonication with detergent, water, ethyl alcohol, and acetone for 15 min. Then, they were dried with blown nitrogen and dry at 80 °C. To increase their hydrophilicity, a further 15-min UV-Ozone treatment was applied. For films, the perovskite solution was directly spin-coated onto the glass substrate. The perovskite precursor solution composition is $Cs_{0.17}FA_{0.83}Pb(I_{0.77}Br_{0.23})_3$. The precursor solution was prepared by dissolving CsI, PbI_2, $PbBr_2$ and FAI in a DMF/DMSO mixture (vol/vol = 4/1). The solution was stirred and filtered (0.45 μm, PTFE) before spin-coating. As additives, BMIM-SCN or BMI-$Pb(SCN)_3$ was added to the perovskite precursor solution at a concentration of 0.03 μL/mL as additive. The perovskite solution was spin-coated at 500 rpm for 5 s, 1000 rpm for 10 s, and 5,000 rpm for 50 s in a three-step process. During the last coating step, 0.2 μL of EA was dropped on the spinning substrate 30 s before the end of the spin-coating, and then annealed at 100 °C for 1 h.

Perovskite solar cells (PSCs) were fabricated with a configuration of FTO / dense blocking TiO_2 layer (bl-TiO_2) / mesoporous TiO_2 (mp-TiO_2) / perovskite / PTAA / Au. Cleaned pre-patterned FTO glass substrates employed a bl-TiO_2 layer with spray coating of titanium diisopropoxide bis(acetylacetonate) dissolved in ethanol, and after the coating process, the substrates are annealed at 450 °C. mp-TiO_2 was formed by spin-coating TiO_2 paste nanoparticles dispersed in a mixed solvent (2-methoxy ethanol/terpineol = 3.5:1 w/w) at 2,500 rpm onto the FTO/bl-TiO_2 substrate and then heat-treated on a hot plate at 500 °C for 1 h. A PTAA solution for the hole transport material was prepared by dissolving 10 mg of PTAA in 1 ml of toluene with 3.75 μL of a Li-bis(trifluoromethanesulfonic)imide (Li-TFSI) solution (340 mg in 1 mL in acetonitrile), and 4-tert-butylpyridine (tBP) 3.75 μL in 1 mL of chlorobenzene. The solution was spin-coated at 3000 rpm for 30 s. Finally, an Au counter electrode (70 nm) was deposited by thermal evaporation in a vacuum at 10^{-5} torr.

Measurements and Characterization

Scanning Electron Microscopy

The scanning electron microscopy (SEM) was taken using Merlin Compact, Carl Zeiss (Germany) microscopes (beam accelerator voltages: 5 keV for surface morphology views of the perovskite films.)

J-V Measurement

The *J-V* measurement of the PSCs was performed by Ivium Stat MUM technologies under an Am 1.5 solar stimulator at an irradiation intensity of 100 mW cm^{-2}. To elucidate the PSCs performance and stability, 40 samples were evaluated.

SSPL and TRPL measurement

Spectroscopy used a time-correlated single-photon counting module (TCSPC FluoTime 300 by Picoquant, GmbH). The steady-state photoluminescence (SSPL) measured a 20 MHz frequency and 0.0125 μJ/cm^2/pulse energy density, and the time-resolved photoluminescence (TRPL) measured a 0.5 MHz frequency and 0.011 μJ/cm^2/pulse. The sample structure was Glass/perovskite.

PV-SCLC measurement

The *J–V* traces of pulsed voltage space charge limited current (PV-SCLC) were measured using a computer-controlled 2450 Series Keithley source meter at room temperature and room humidity under a dark state. The device configuration was Glass/Au /SnO_2/perovskite/PCBM /Au.

UV-Vis Analysis

The absorption of the perovskite films was measured by ultraviolet-visible absorption spectroscopy (UV–vis) spectrophotometer UV-red-PMT monochromator (MSH300PQ-0002, picoquant). The sample structure was Glass/perovskite.

TPC measurement

To estimate the transient photo-conductivity (TPC) analysis, we have used the following device architecture: glass/perovskite/Au. The Nd: YAG laser (SLII-10) excitation source was tuned to a wavelength of 532 nm and pumped at 10 Hz with 4 ns pulses.

PLQY measurement

The Photoluminescence Quantum Yield (PLQY) was measured using an integration sphere (Newport, 819C-IC-3.3). They were measured by QEPro (Ocean Insight, 350-950nm). For excitation, we employed a continuous 532nm laser (Lasercentury, GL405N3-200) source. We measured PLQY 7.62 uW/ cm^2·s energy density.

XPS Analysis

A K-alpha+Thermo Scientific (USA) was used to measure X-ray photoelectron spectroscopy (XPS) spectra of different samples for elemental analyses.

XRD Analysis

The X-ray diffraction (XRD) measurements were carried out to check the surface crystallinity of perovskite film with and without additives using a MiniFlex II Rigaku (Japan) $\theta-2\theta$ goniometer with Cu Kα (λ = 1.54051 Å) radiation.

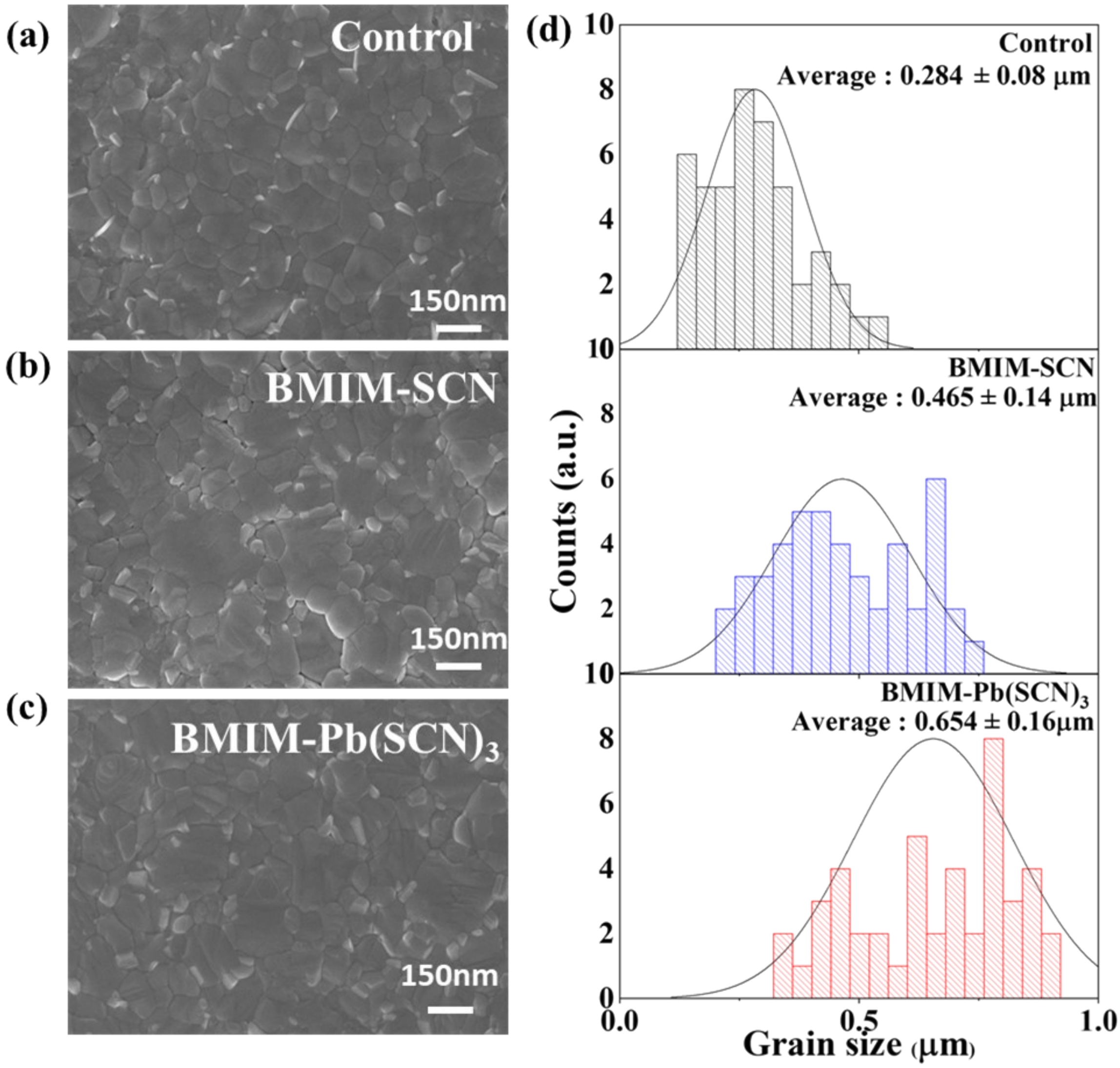

Fig. S1. SEM images of as prepared perovskite films (a) without additives, with (b) BMIM-SCN, and (c) BMIM-$Pb(SCN)_3$. (d) Histograms of calculated grain size corresponding to the films.

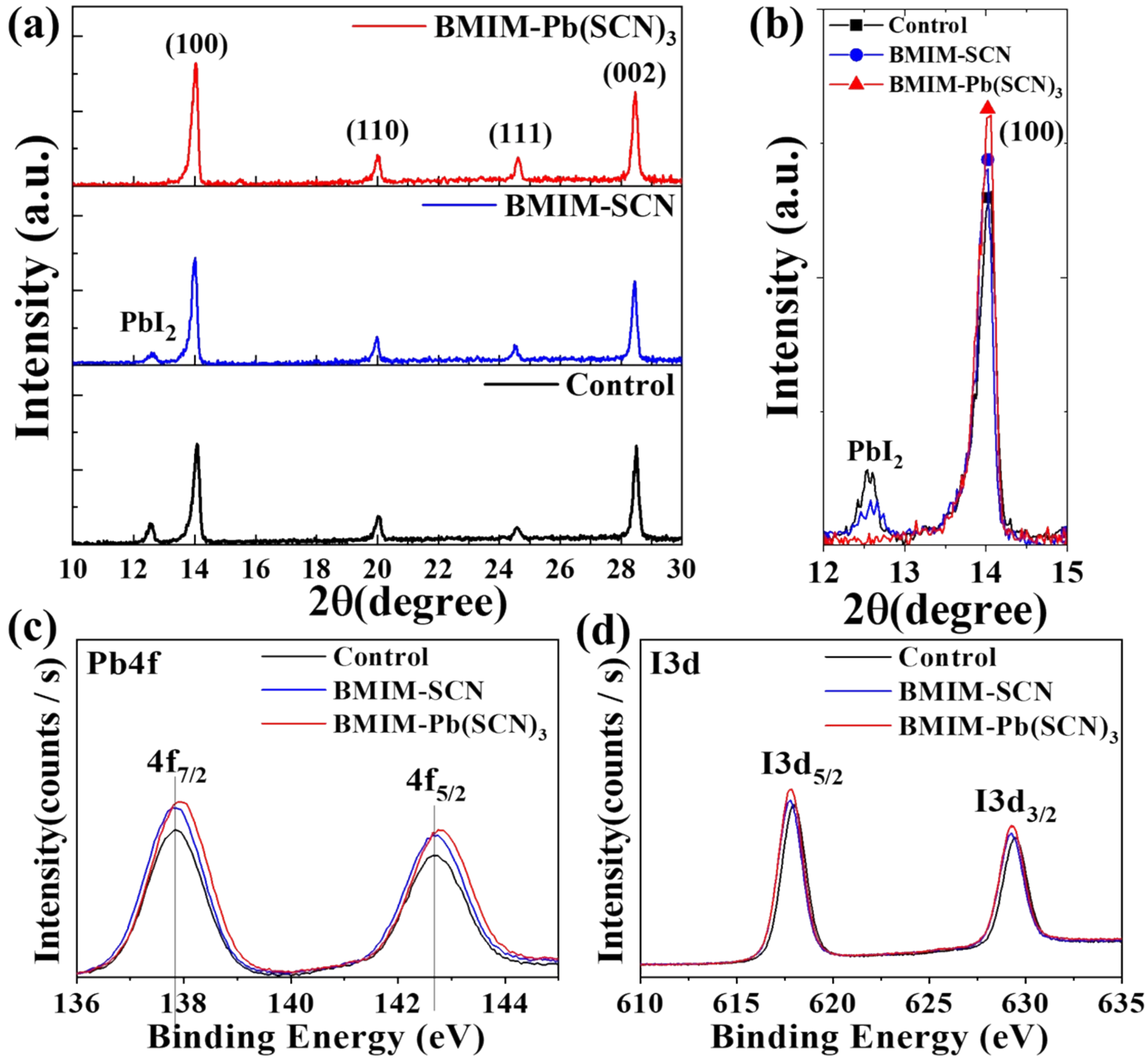

Fig. S2. (a) XRD results of as prepared perovskite films without and with additives (b) expansion view around (100) and PbI_2 peak. (c) XPS spectra of the as-prepared perovskite film for Pb 4f, and (d) I 3d

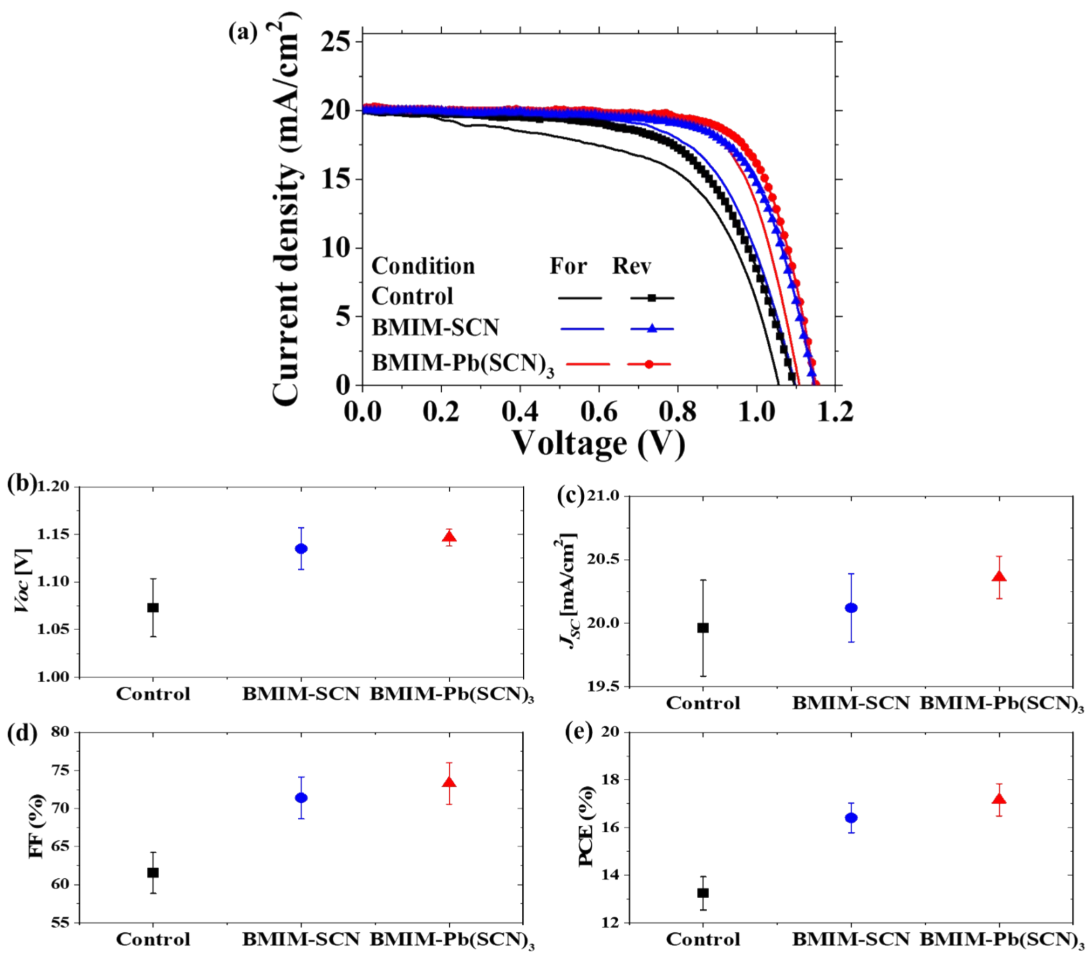

Fig. S3. Summary of power conversion efficiency (PCE) of perovskite solar cells (PSCs) without and with additives. (a) Current density–voltage (J–V) trace for reverse (line with diagram) and forward (solid line) bias sweep. Distribution plot of characteristics of PSCs without and with additives, (b) open-circuit voltage (V_{oc}), (c) short-circuit current density (J_{sc}), (d) fill factor(FF), and (e) PCE.

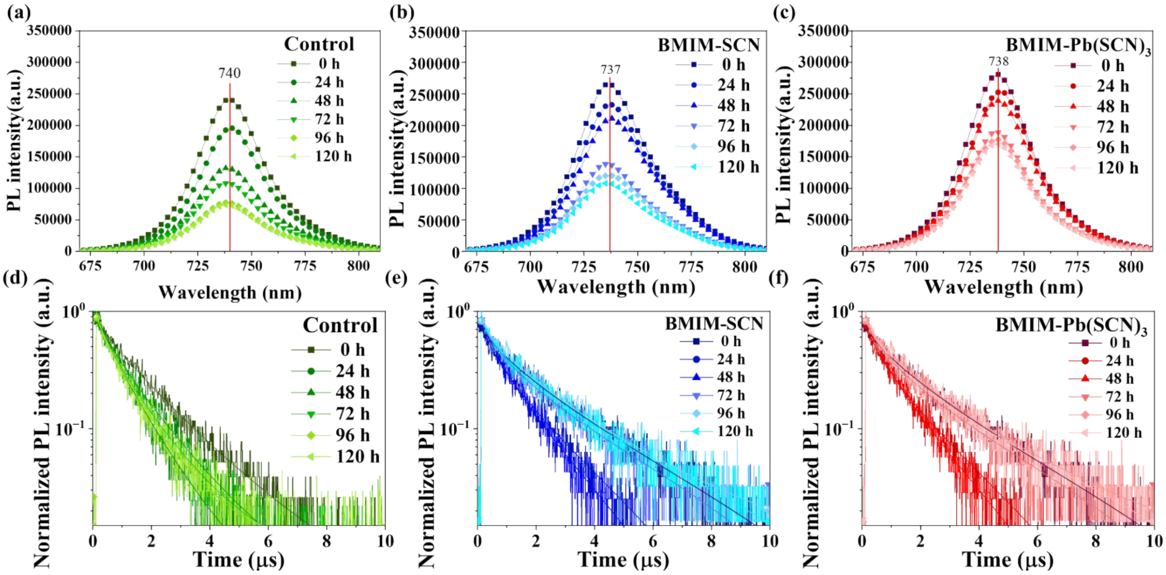

Fig. S4. Steady-state photoluminescence (SSPL) results of perovskite film over the time; (a) without additive, (b) with BMIM-SCN, (c) BMIM-PB(SCN)$_3$. Corresponding time-resolved photoluminescence (TRPL) results for the analogous samples; (d) without additive, (e) with BMIM-SCN, (f) BMIM-PB(SCN)$_3$, respectively.

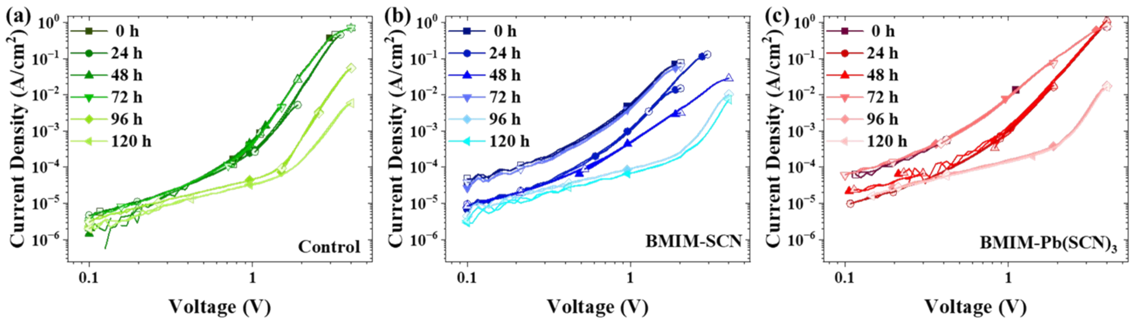

Fig. S5. The result of PV-SCLC from as prepared to 120 h. The result of (a) control sample, (b) BMIM-SCN, (c) BMIM-Pb(SCN)$_3$.

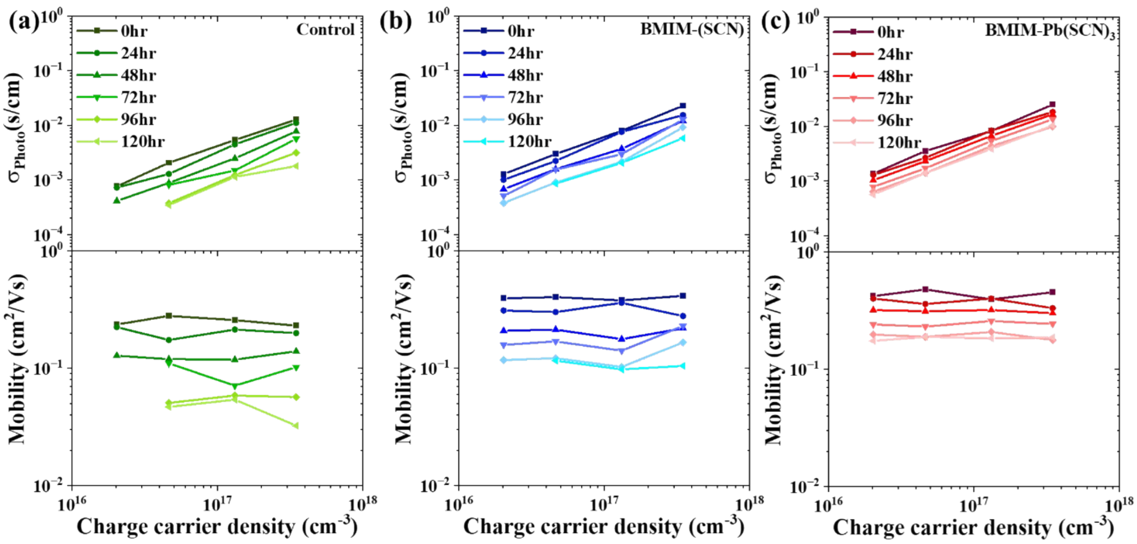

Fig. S6. The result of calculated photo-conductivity and mobility measured by the TPC method from as prepared to the 120 h, (a) the result of control sample, (b) BMIM-SCN, (c) BMIM-Pb(SCN)$_3$.

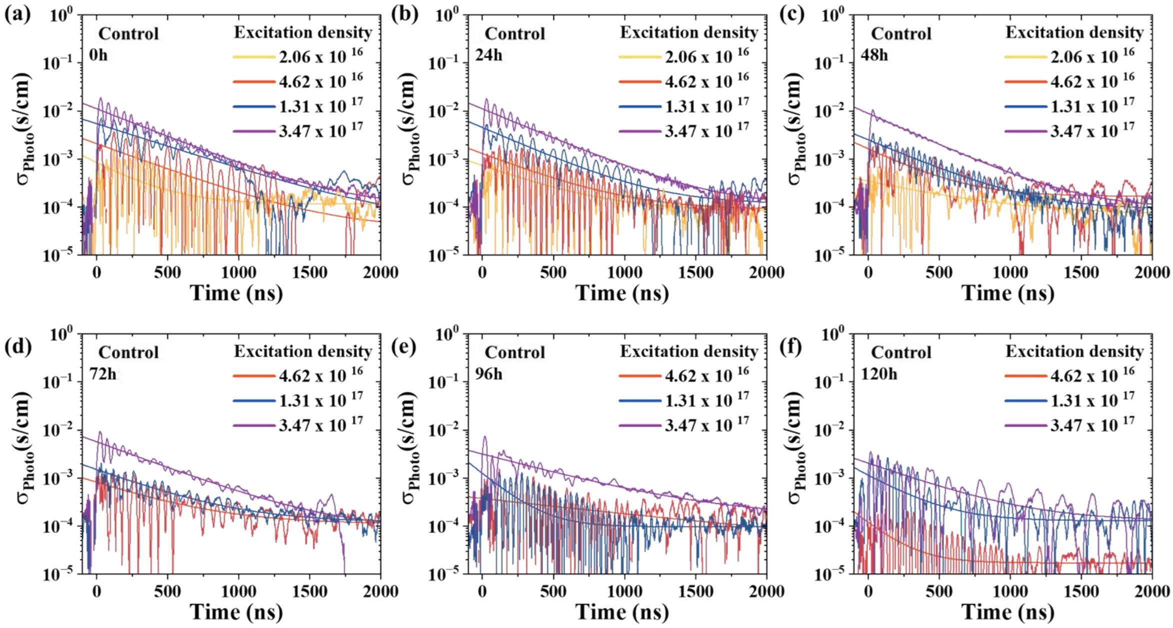

Fig. S7. The TPC result of control sample varying photon flux with (a) as prepared, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h, (f) 120 h storage time in ambient air condition.

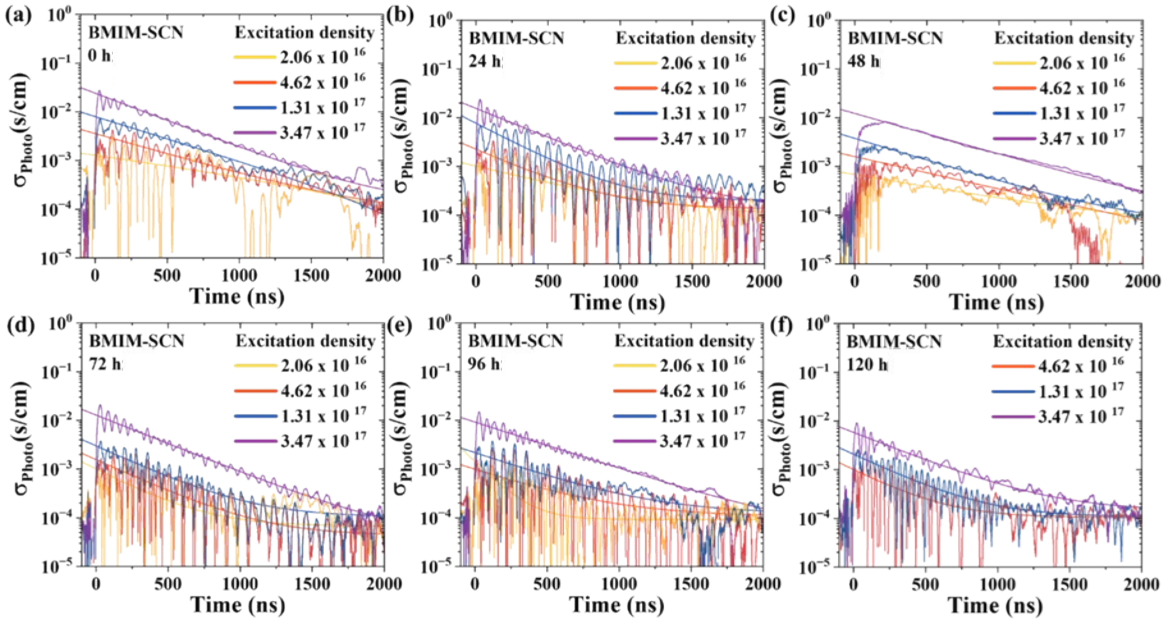

Fig. S8. The TPC result of BMIM-SCN sample varying photon flux with (a) as prepared, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h, (f) 120 h storage time in ambient air condition.

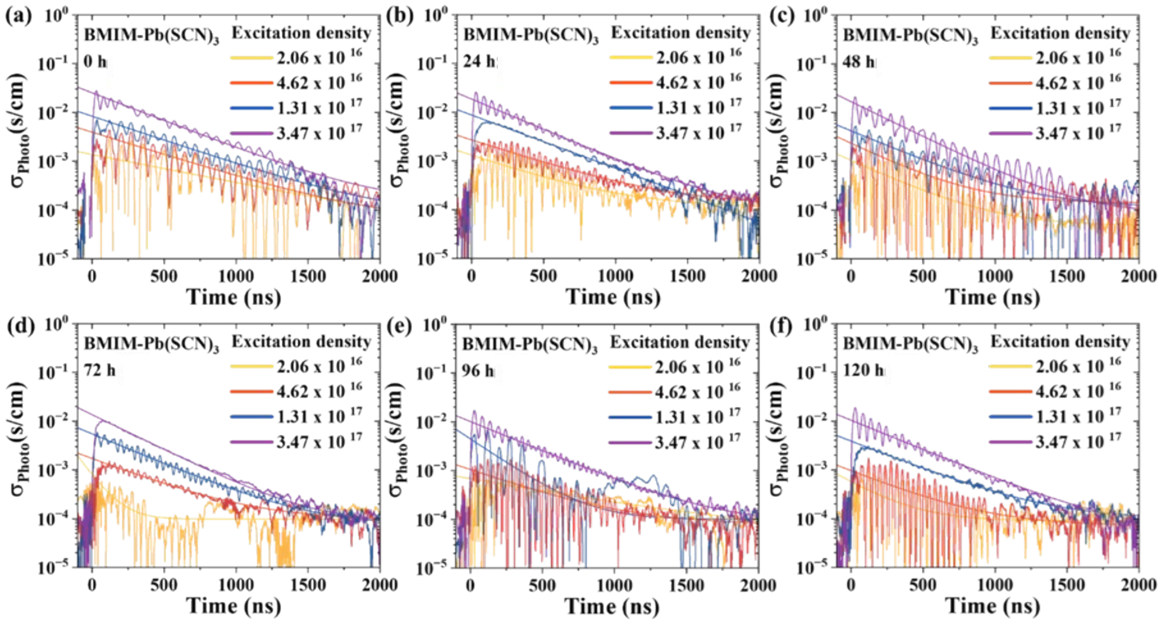

Fig. S9. The TPC result of BMIM-Pb(SCN)$_3$ sample varying photon flux with (a) as prepared, (b) 24 h, (c) 48 h, (d) 72 h, (e) 96 h, (f) 120 h storage time in ambient air condition.

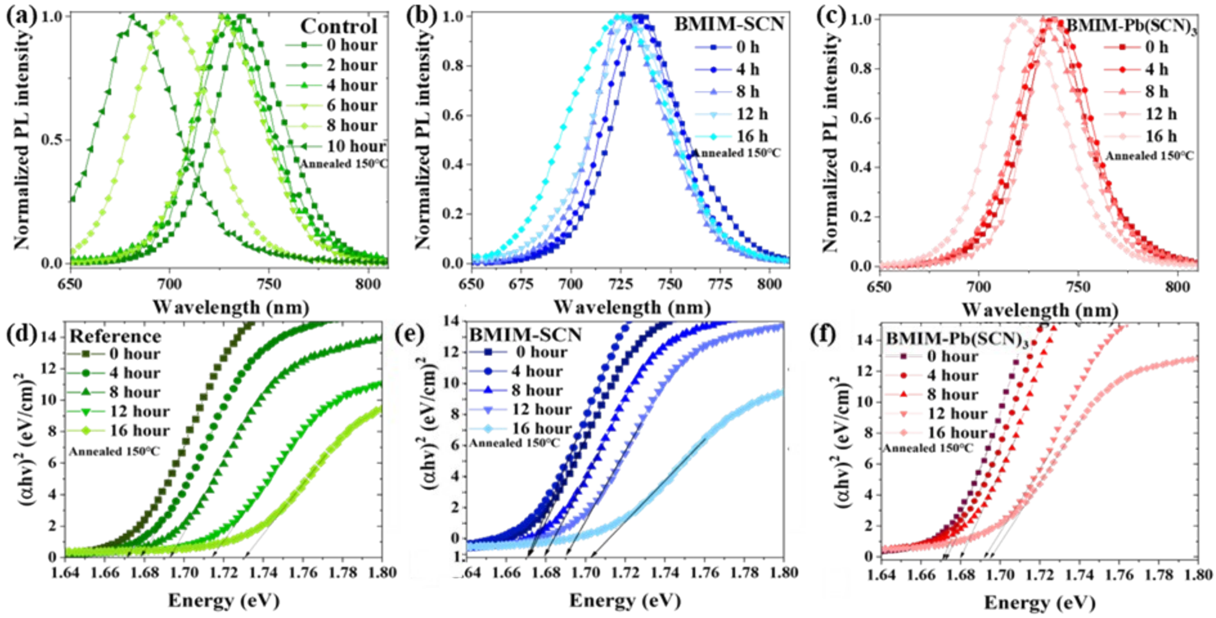

Fig. S10. Optical properties of perovskite films after thermal treatment (annealing at 150 °C for 16 h in ambient air). (a–c) Normalized PL spectra and (d–f) optical bandgaps of perovskite films; (a, d) without additive, (b, e) with BMIM-SCN, and (c, f) with BMIM-$Pb(SCN)_3$ additives.

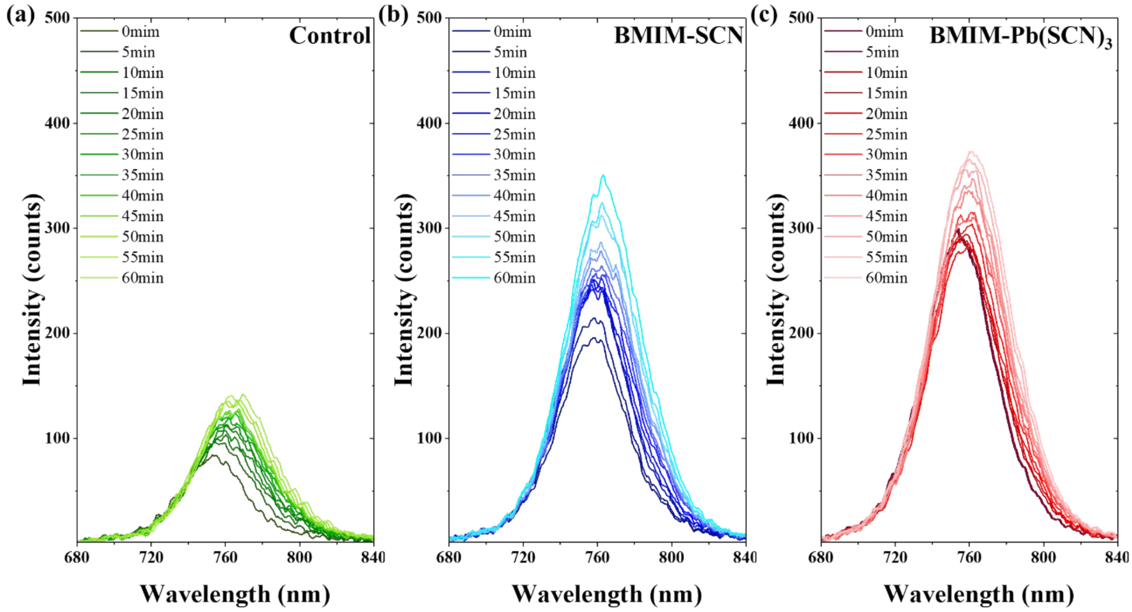

Fig. S11. Optical properties change under the light illumination over the time (interval 5min for 1 h). (a) without additive, (b) with BMIM-SCN, and (c) with BMIM-Pb(SCN)$_3$ additives.

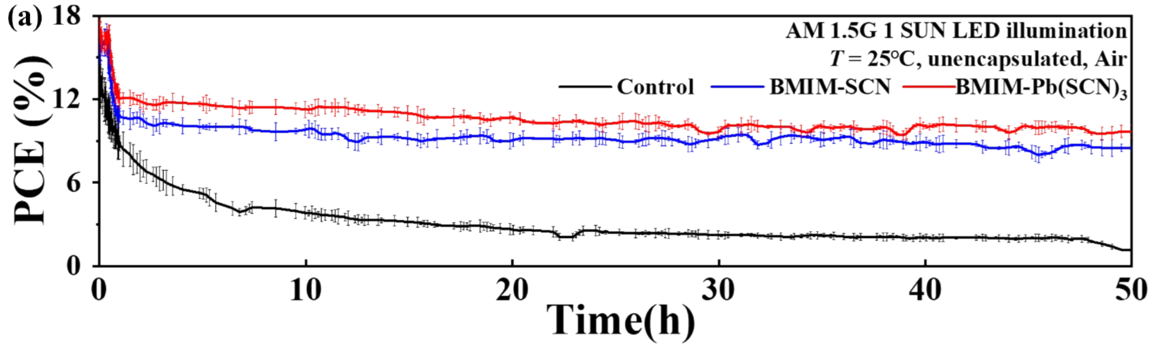

Fig S12. PCE of PSCs without and with additives obtained from MPP measurement of unencapsulated PSCs under RT, 20 samples were evaluated

	Forward			Reverse		
Condition	**Control**	**BMIM-SCN**	**BMIM-Pb(SCN)$_3$**	**Control**	**BMIM-SCN**	**BMIM-Pb(SCN)$_3$**
V_{oc} **[V]**	**1.01 ±0.08**	**1.06 ±0.07**	**1.13 ±0.06**	**1.11 ±0.07**	**1.15 ±0.06**	**1.16 ±0.05**
J_{sc} **[mA/cm²]**	**20.00 ±0.38**	**20.38 ±0.27**	**20.42 ±0.18**	**20.01 ±0.42**	**20.18 ±0.35**	**20.21 ±0.25**
FF [%]	**58.7 ±4.74**	**65.3 ±3.76**	**69.8 ±2.71**	**63.2 ±4.32**	**75 ±2.76**	**75.3 ±2.63**
PCE [%]	**11.86 ±0.70**	**14.1 ±0.62**	**16.11 ±0.57**	**14.04 ±0.72**	**17.4 ±0.63**	**17.65 ±0.64**

Table S1. The summarized average PSCs efficiency in Fig. S2.

Table S2. The summarized charge carrier lifetime average by the stretched fitting mode of the perovskite film with various additives from as-prepared to 120 h

	τ (ns)			β		
Time (h)	Control	BMIM-SCN	BMIM-Pb(SCN)$_3$	Control	BMIM-SCN	BMIM-Pb(SCN)$_3$
0	306.35 ±26.11	321.33 ±13.52	376.98 ±16.95	0.75 ±0.05	0.88 ±0.05	0.66 ±0.04
24	233.92 ±14.83	279.97 ±16.46	351.62 ±17.31	0.72 ±0.06	0.84 ±0.07	0.68 ±0.02
48	186.90 ±23.92	248.39 ±19.17	292.40 ±18.23	0.86 ±0.03	0.84 ±0.03	0.59 ±0.05
72	216.22 ±13.49	314.63 ±17.21	341.26 ±12.79	0.72 ±0.03	0.84 ±0.02	0.68 ±0.03
96	179.42 ±17.49	203.77 ±11.98	262.44 ±18.85	0.74 ±0.04	0.83 ±0.04	0.61 ±0.04
120	127.13 ±15.22	159.98 ±16.68	231.62 ±24.47	0.69 ±0.02	0.66 ±0.04	0.59 ±0.04

Table S3. The summarized electric properties from PV-SCLC measurement of the perovskite film with various additives from as-prepared to 120 h.

	Conductivity (S/cm)			Mobility ($cm^2/V{\cdot}S$)			Trap density (cm^{-3})		
Time (h)	Control	BMIM-SCN	BMIM-$Pb(SCN)_3$	Control	BMIM-SCN	BMIM-$Pb(SCN)_3$	Control	BMIM-SCN	BMIM-$Pb(SCN)_3$
0	4.88x10^{-9} ±2.52x10^{-10}	2.90x10^{-8} ±2.66x10^{-9}	4.68x10^{-8} ±6.91x10^{-9}	1.92x10^{-4} ±3.05x10^{-5}	9.09x10^{-4} ±3.26x10^{-5}	1.25x10^{-3} ±5.00x10^{-5}	7.42x10^{15} ±5.12x10^{14}	6.57x10^{15} ±2.86x10^{14}	5.47x10^{15} ±1.98x10^{14}
24	2.44x10^{-9} ±2.66x10^{-10}	8.02x10^{-9} ±6.91x10^{-10}	1.70x10^{9} ±3.37x10^{-10}	1.65x10^{-4} ±9.91x10^{-5}	4.68x10^{-4} ±6.49x10^{-5}	6.37x10^{-4} ±5.30x10^{-5}	8.39x10^{15} ±5.26x10^{14}	7.94x10^{15} ±6.27x10^{14}	6.73.x10^{15} ±5.09x10^{14}
48	1.34x10^{-10} ±6.31x10^{-11}	4.74x10^{-9} ±1.07x10^{-10}	9.87x10^{-9} ±1.23x10^{-10}	1.13x10^{-4} ±3.47x10^{-5}	3.67x10^{-4} ±1.91x10^{-5}	5.93x10^{-4} ±6.81x10^{-5}	9.82x10^{15} ±5.46x10^{14}	8.45x10^{15} ±5.10x10^{14}	6.82x10^{15} ±2.81x10^{14}
72	1.46x10^{-9} ±4.51x10^{-10}	1.59x10^{-8} ±3.27x10^{-9}	2.68x10^{-8} ±5.53x10^{-9}	1.34x10^{-4} ±3.00x10^{-5}	4.66x10^{-4} ±2.58x10^{-4}	8.23x10^{-4} ±5.08x10^{-4}	1.58x10^{16} ±1.05x10^{14}	8.40x10^{15} ±5.16x10^{14}	6.92x10^{15} ±2.81x10^{14}
96	7.46x10^{-10} ±2.52x10^{-10}	3.61x10^{-9} ±7.91x10^{-10}	7.19x10^{-9} ±4.54x10^{-10}	2.47x10^{-5} ±1.57x10^{-5}	4.95x10^{-5} ±5.35x10^{-5}	8.58x10^{-5} ±7.70x10^{-6}	2.33x10^{16} ±1.48x10^{14}	1.65x10^{16} ±1.65x10^{14}	1.02x10^{16} ±1.07x10^{14}
120	2.69x10^{-10} ±1.59x10^{-10}	2.74x10^{-9} ±5.27x10^{-10}	6.38x10^{-9} ±2.10x10^{-10}	1.20x10^{-5} ±2.14x10^{-5}	6.43x10^{-5} ±2.07x10^{-5}	9.80x10^{-5} ±6.44x10^{-6}	2.47x10^{16} ±1.71x10^{14}	1.96x10^{16} ±8.51x10^{14}	1.25x10^{16} ±1.09x10^{14}

Table S4. The summarized electric properties from TPC measurement of the perovskite film with various additives from as-prepared to 120 h. The conductivity was calculated when the free charge carrier density is 3.47x10^{17}

	Conductivity (σ/cm)			Mobility ($cm^2/V\cdot S$)		
Time (h)	**Control**	**BMIM-SCN**	**BMIM-Pb(SCN)$_3$**	**Control**	**BMIM-SCN**	**BMIM-Pb(SCN)$_3$**
0	1.28×10^{-2} $\pm 9.00\times10^{-4}$	2.30×10^{-2} $\pm 2.53\times10^{-3}$	2.52×10^{-2} $\pm 1.46\times10^{-3}$	2.50×10^{-1} $\pm 2.23\times10^{-2}$	3.97×10^{-1} $\pm 1.51\times10^{-2}$	4.36×10^{-1} $\pm 3.72\times10^{-2}$
24	1.11×10^{-2} $\pm1.10\times10^{-3}$	1.55×10^{-2} $\pm1.63\times10^{-3}$	1.85×10^{-2} $\pm1.29\times10^{-3}$	2.02×10^{-1} $\pm2.17\times10^{-2}$	3.12×10^{-1} $\pm3.49\times10^{-2}$	3.73×10^{-1} $\pm3.33\times10^{-2}$
48	7.76×10^{-3} $\pm8.05\times10^{-4}$	1.21×10^{-2} $\pm1.22\times10^{-3}$	1.67×10^{-2} $\pm1.84\times10^{-3}$	1.26×10^{-2} $\pm9.72\times10^{-4}$	2.43×10^{-2} $\pm1.88\times10^{-2}$	3.14×10^{-1} $\pm9.01\times10^{-3}$
72	5.68×10^{-3} $\pm6.00\times10^{-4}$	1.28×10^{-2} $\pm1.60\times10^{-3}$	1.35×10^{-2} $\pm9.05\times10^{-4}$	9.44×10^{-2} $\pm2.06\times10^{-3}$	1.74×10^{-2} $\pm3.82\times10^{-2}$	2.43×10^{-1} $\pm1.10\times10^{-2}$
96	3.16×10^{-3} $\pm3.51\times10^{-4}$	9.23×10^{-3} $\pm9.12\times10^{-4}$	1.01×10^{-2} $\pm9.90\times10^{-4}$	5.54×10^{-2} $\pm4.11\times10^{-3}$	1.27×10^{-1} $\pm2.73\times10^{-2}$	1.92×10^{-1} $\pm1.28\times10^{-2}$
120	1.81×10^{-3} $\pm2.12\times10^{-4}$	5.83×10^{-3} $\pm6.40\times10^{-4}$	9.09×10^{-3} $\pm9.85\times10^{-4}$	4.44×10^{-2} $\pm1.10\times10^{-3}$	1.06×10^{-1} $\pm9.24\times10^{-3}$	1.83×10^{-1} $\pm1.21\times10^{-2}$