Enhanced performance of printable mesoscopic perovskite solar cells

using ionic liquid additives

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Experimental Section

1. Material

All the chemicals were used directly without further purification. Unless otherwise specified all materials were purchased from Sigma-Aldrich. Lead iodide (PbI_2), 5-Ammonium valeric acid iodide (5-AVAI), γ -butyrolactone (GBL), anhydrous dimethylformamide (DMF) and anhydrous dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich.

2. Preparation of the perovskite precursor

MAPbI₃ perovskite precursor solution: 0.0954 g MAI powder and 0.2766 g PbI₂ powder were mixed in mixture solvent of 400 μ L DMF and 100 μ L DMSO. The solutions were transferred onto a magnetic stirring apparatus stirred overnight at room temperature (400 r/min).

 $(5-AVA)_XMA_{1-X}PbI_3$ perovskite precursor solution: 0.1227 g MAI powder, 0.2766 g PbI₂ and 0.0069 g 5-AVAI powder were mixed in 1000 µL GBL solvent. The solutions were transferred onto a magnetic stirring apparatus stirred overnight at room temperature (400 r/min).

MAPbI₃ \bigcirc 1-EC perovskite precursor solution: 0.0954 g MAI powder, 0.2766 g PbI₂ powder and different molar ratios of 1-EC powder were mixed in mixture solvent of 400 µL DMF and 100 µL DMSO (The molar ratio of 1-EC: PbI₂ is 2.5%, 5%, 7.5% and 10%). The solutions were transferred onto a magnetic stirring apparatus stirred overnight at room temperature (400 r/min).

 $(5-AVA)_XMA_{1-X}PbI_3 \ cost1-EC$ perovskite precursor solution: 0.1227 g MAI powder, 0.2766 g PbI_2, 0.0069 g 5-AVAI and 1-EC powder were mixed in 1000 µL GBL solvent (The molar ratio of 1-EC: PbI_2 is 10%). The solutions were transferred onto a magnetic stirring apparatus stirred overnight at room temperature (400 r/min).

3. Preparation of slurry

 TiO_2 slurry: 3.0 g TiO_2 raw material (Dyesol NR-30) was added into 12.0 g terpineol, then transferred onto a magnetic stirring apparatus stirred 12 h at room temperature (400 r/min).

 ZrO_2 slurry: 10 g ZrO_2 nanopowders (particle size: 20 nm) was added in a 30 mL terpineol solution, and 1 g ethyl cellulose were added into solution, followed by stirring vigorously using ball milling for 2 h.

Carbon slurry: 2g carbon black powders (particle size: 30 nm) was mixed with 6 g graphite powders in a solution of 30 mL terpineol, and then 1 g of 20 nm ZrO₂ nanopowders and 1 g ethyl cellulose were added into solution, followed by stirring vigorously using ball milling for 2 h.

4. Preparation of MPSCs

The FTO conducting glass was etched with a laser to form desired electrode patterns before being ultrasonically cleaned with a detergent solution, deionized water, and ethanol for 15 min, respectively. A compact layer of TiO₂ was deposited on the FTO-coated glass by spray pyrolysis deposition at 450 °C with diisopropoxide bis (acetylacetonate) solution and sintered for 30 min. After cooling down to room temperature naturally, a 500 nm mesoporous TiO₂ layer was deposited on top of the compact layer by screen printing use TiO₂ slurry and then sintered at 500 °C for 30 min. After then, a 3 μ m ZrO₂ spacer layer and a 15 μ m carbon layer were subsequently screen-printed on the top of the TiO₂ layer, and then the films were sintered at 400 °C. The equipment used for 500 °C and 400 °C sinter process is muffle furnace. And the pressure of screen printing is 0.75

kg. Then take the cells off from the hot plate and cooling down to room temperature. After that, a 2.5 μ L of perovskite precursor solution was dipped on the mesoporous carbon layer, followed by annealing at 100 °C for 20 min. The active area of each device is 0.8 cm².

5. Characterizations

The morphology of samples was observed by a field-emission scanning electron microscope (SEM) (FEI Nova NanoSEM450). The mesoscopic film thickness was measured by using a profilometer (Dektak XT, Brucker). The XRD spectra were measured with an X'pert PRO X-ray Diffractometer using Cu K α radiation under operating conditions of 40 kV and 40 mA from 5° to 70°. Device performance was characterized by a Keithley 2400 source/meter and a Newport solar simulator (model 91192) which offered the simulated AM 1.5G illumination of 100 mW cm-2, calibration was done using a NIST-certified monocrystalline Si solar cell (Newport 532 ISO1599). The J-V curves have measured by reverses scan (1.2 V to -0.2 V) with a scan rate of 100 mV s-1. A mask with a circular aperture (0.101 cm2) was applied for J-V measurements. Incident photo-to-current conversion efficiency was performed using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source. Time-resolved photoluminescence (TRPL) decay transients were measured at 770 nm using excitation with a 478 nm light pulse from a HORIBA Scientific DeltaPro fluorimeter. The UV-vis was measured by using a SolidSpec-3700 Ultraviolet-visible near-infrared spectrophotometer. The steady-state photoluminescence (PL) spectra were taken on a Horiba JobinYvon LabRAM HR800s with a 532 nm wavelength excitation source. The in situ grazing incidence X-ray diffraction (GIXRD) were performed at the BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) with an X-ray energy of 10 keV. We use a custom-built experimental chamber to cast the precursor perovskite solution on to the scaffold structure within a controlled sample environment. 2D XRD patterns were acquired by a MarCCD X-ray detector at a distance of 268.35 mm from the sample, with an exposure time of 5 s. A grazing incidence angle of 1.2° was adopted. The X-ray scattering data were processed and analyzed with the software FIT2D.

Supporting tables

Additive	Structure	Efficiency/Stability	Mechanism	Reference
1-ethylpyridinium chloride	ITO/PEDOT:PSS/CH3 NH3PbI3/PCBM/Al	11.8%/None	- Passivate surface defects	1
1-(4-ethenylbenzyl)-3- (3,3,4,4,5,5,6,6,7,7,8,8, 8- tridecafluorooctylimida -zolium iodide)	FTO/c-TiO2/mp-TiO2/ CH3NH3PbI3/Spiro- OMeTAD/Au	19.51%/MPPT(700h,A r,60°C)、high thermal stabilization、high moisture stabilization	- Inhibit out-diffusion of MA+	2
1-ethylamine hydrobromide-3- methylimidazolium hexafluorophosphate	FTO/c-TiO ₂ /mp-TiO ₂ / CH ₃ NH ₃ PbI ₃ /C	13.01%/ 94% of its initial PCE(dark、 20%RH、unsealing)	 Passivate defects Improve the filling of perovskite on mesoporous TiO₂ Increased carrier transmission rate Moisture barrier 	3
1-butyl-3- methylimidazolium tetrafluoroborate	FTO/NiO/(FA _{0.83} MA _{0.1} ₇) _{0.95} Cs _{0.05} Pb(I _{0.9} Br _{0.1}) ₃ / PCBM/BCP/Cr/Cr ₂ O ₃ / Au	19.8%/5% degradation for 1,885 h (encapsulated, continuous sunlight, ambient air, 70 - 75 °C)	- Suppressed ion migration	4
1-Allyl-3- methylimidazolium iodide	FTO/c-TiO ₂ /mp-TiO ₂ / CH ₃ NH ₃ PbI ₃ /Spiro- OMeTAD/Au	19.21%/55% of the initial PCE for 460h (continuous light, Ar, MMPT)	- Improved crystal growth	5
1-butyl-3- methylimidazolium tetrafluoroborate	FTO/TiO ₂ /CH ₃ NH ₃ PbI ₃ /PTAA/Au	19.42%/None	 Enhanced electron mobility Decreased trap-state density Well-matched work function 	6
1-butyl-2, 3- dimethylimidazolium chloride	FTO/c-TiO ₂ /mp-TiO ₂ /CsPbBr ₃ /[BMMIm]Cl /C	9.92%/ 98.5% of the initial PCE for 30 days (20%RH, 20°C or 0%RH, 80°C, continuous light, unencapsulated)	 Passivate surface defects Improved energy level matching 	7
1-ethyl-3- methylimidazolium hexafluorophosphate	FTO/c- TiO ₂ /[EMIM]PF ₆ /CH ₃ NH ₃ PbI ₃ /Spiro- OMeTAD/Au	18.42%/None	- Efficient electron transport	8
1-butyl-3- methylimidazolium iodide	FTO/c-TiO ₂ /mp-TiO ₂ / CH ₃ NH ₃ PbI ₃ / Spiro- OMeTAD/Au	15.6%/None	 High-quality crystallization Slow down the rate of interfacial chemical reaction 	9

Table S1. The mechanism of different ionic liquid additives on perovskite solar cells.

1 able 52.1 with 01 the (002), (021) and (022) peak of intermediate with 01 0318 2D10150.	Table S2. FWHM of the (002),	(021) and (022) peak of interm	rediate MA ₂ Pb ₃ I ₈ · 2DMSO.
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Sample	(002)	(021)	(022)
DMF/DMSO-MAPbI ₃	0.10813	0.12551	0.13808
DMF/DMSO-MAPbI3031-EC	0.09846	0.12028	0.13776

Table S3. Detailed Parameters of TRPL Results and Calculated Electron Transfer Rates.

Sample	A_1	τ_1 (ns)	A ₂	τ_2 (ns)	$\tau_{\rm ave}({\rm ns})$
Pristine MAPbI ₃	0.59	5.2	0.41	13.4	8.56
2.5%1-EC	0.53	8.3	0.47	20.4	13.99
5%1-EC	0.39	9.4	0.61	21.9	17.02
7.5%1-EC	0.20	7.4	0.80	21.2	18.44
10%1-EC	0.07	5.8	0.93	31.2	29.42

Table S4. Detailed Parameters of TRPL Results and Calculated Electron Transfer Rates.

Sample	A ₁	τ_1 (ns)	A_2	τ_2 (ns)	τ _{ave} (ns)
DMF/DMSO-MAPbI ₃	0.67	2.5	0.33	21.5	24
DMF/DMSO-MAPbI3031-EC	0.74	2.4	0.26	13	15.4

Table S5. Detailed Parameters of EIS Results of MAPbI₃ perovskite.

Sample	R _s	R ₁	R ₂
DMF/DMSO-MAPbI ₃	19 Ω	249 Ω	175 kΩ
DMF/DMSO-MAPbI3031-EC	18.4 Ω	50.2 Ω	90.7 kΩ

Table S6. Performance of the studied solar cells under AM 1.5G illumination.

Sample	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF	PCE (%)
DMF/DMSO-MAPbI ₃	906	18.87	0.573	9.79
DMF/DMSO-MAPbI3031-EC	966	20.69	0.758	15.14

Table S7. The parameters of different devices in DMF and DMSO solvent.

DMF/DMSO-MAPbI ₃	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF	PCE (%)
1	906	18.87	0.573	9.79
2	905	17.05	0.628	9.69
3	894	17.95	0.586	9.4
4	898	18.46	0.566	9.38
5	913	18.66	0.536	9.14
6	900	18.08	0.557	9.07
7	890	19.79	0.513	9.03
8	866	16.11	0.642	8.96
9	835	15.89	0.647	8.59
10	925	17.03	0.54	8.53
11	855	14.85	0.67	8.51

12	875	16.76	0.576	8.45
13	885	17.29	0.552	8.44
14	911	16.7	0.554	8.43
15	863	17.16	0.564	8.36
16	844	15.37	0.64	8.25
17	888	18.13	0.486	7.82
18	851	14.93	0.61	7.72
19	823	14.46	0.61	7.26
20	849	16.55	0.51	7.23
Average	878.8	17.0045	0.578	8.6025

Average	878.8	17.0045	0.578	8.6025
DMF/DMSO-MAPbI3C31-EC	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF	PCE (%)
1	966	20.69	0.758	15.14
2	950	20.64	0.76	14.92
3	953	19.96	0.783	14.89
4	940	20.22	0.78	14.82
5	957	20.05	0.765	14.68
6	958	21.94	0.7	14.67
7	946	20.3	0.759	14.57
8	948	21.31	0.72	14.46
9	955	19.88	0.752	14.29
10	956	20.34	0.732	14.22
11	934	20.04	0.758	14.19
12	953	22.74	0.65	14.14
13	942	21.35	0.692	13.92
14	943	19.05	0.773	13.89
15	953	20.37	0.685	13.28
16	966	19.32	0.706	13.17
17	962	20.31	0.671	13.11
18	919	23.44	0.6	12.87
19	949	18.04	0.75	12.81
20	950	20.47	0.66	12.79
Average	950	20.523	0.7227	14.0415

GBL-(5-AVA) _X MA _{1-X} PbI ₃	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF	PCE (%)
1	887	23.52	0.686	14.31
2	881	23.71	0.682	14.24
3	879	23.73	0.68	14.18
4	882	23.61	0.68	14.17
5	872	23.61	0.686	14.12
6	885	23.6	0.676	14.11
7	885	23.6	0.676	14.11
8	881	23.63	0.675	14.06
9	879	23.73	0.673	14.04
10	891	23.48	0.67	14.03
11	882	23.65	0.672	14.01
12	878	23.42	0.681	14
13	894	23.45	0.667	13.99
14	891	23.4	0.668	13.92
15	887	23.45	0.668	13.9
16	889	23.46	0.665	13.87
17	875	23.84	0.664	13.86
18	868	23.83	0.67	13.85
19	895	23.4	0.659	13.8
20	888	23.51	0.656	13.69
Average	883.45	23.5815	0.6727	14.013
GBL-(5-AVA) _X MA _{1-X} PbI ₃ cs1-EC	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF	PCE (%)
1	932	23.57	0.696	15.29
2	930	23.58	0.693	15.19
3	925	23.46	0.699	15.18
4	918	23.36	0.708	15.17
5	926	23.51	0.695	15.12
6	916	22.74	0.725	15.11
7	927	23.51	0.693	15.09
8	923	23.73	0.688	15.06
9	923	23.52	0.693	15.04
10	927	23.54	0.688	15.02
11	921	23.62	0.688	14.95
12	926	23.55	0.685	14.94

Table S8. The parameters of different devices in GBL solvent.

13	927	22.66	0.71	14.91
14	919	23.6	0.685	14.87
15	924	23.69	0.678	14.86
16	919	23.64	0.684	14.85
17	919	23.61	0.682	14.8
18	922	23.03	0.686	14.58
19	926	23.39	0.66	14.3
20	945	22.55	0.665	14.17
Average	924.75	23.393	0.69005	14.925

Table S9. Performance of the studied solar cells under AM 1.5G illumination.

Sample	V _{OC} (mV)	J _{SC} (mA cm ⁻²)	FF	PCE (%)
GBL-(5-AVA) _X MA _{1-X} PbI ₃	887	23.52	0.686	14.31
GBL-(5-AVA) _X MA _{1-X} PbI ₃ cg1-EC	932	23.57	0.696	15.29

Detailed Parameters of IPCE Results of (5-AVA)_XMA_{1-X}PbI₃ perovskite

Sample		Integrated current density (mA cm ⁻²)			
GBL-(5-AVA) _X MA _{1-X} PbI	3	16.58			
GBL-(5-AVA) _X MA _{1-X} PbI ₃ C3	1-EC	18.2	3		
Detailed Parameters of	of EIS Results of	f (5-AVA) _X MA _{1-X} PbI ₃ p	erovskite		
Sample	R _s	\mathbf{R}_{1}	R ₂		
GBL-(5-AVA) _x MA _{1-x} PbI ₃	22 Ω	12.2 kΩ	183 kΩ		

 $3.62 \; k\Omega$

 $387 \ k\Omega$

20.5 Ω

GBL-(5-AVA)xMA1-xPbI3C81-EC

Supporting figures



Figure S1. Two-dimensional GIXRD pattern of perovskite film collected at an X-ray incident angle of 1.2° in the first stage.



Figure S2. Evolution of the scattering features with respect to the scattering vector q and time for the MAPbI₃ perovskite in the DMSO and DMF solvent.



Figure S3. The azimuthally integrated intensity plots of the GIXRD patterns for the MAPbI₃ perovskite and MAPbI₃ perovskite mixed with 1-EC additive.



Figure S4. FWHM of the (110) perovskite diffraction peak in (a) and the derived crystalline size in (b) as functions of time, respectively.



Figure S5. The azimuthally integrated intensity plots of the GIXRD patterns at different time for the

(a) MAPbI₃ perovskite and (b) MAPbI₃ perovskite mixed with 1-EC additive.



Figure S6. Two-dimensional GIXRD pattern of perovskite film collected at an X-ray incident angle of 1.2° in the end of the experiment.



Figure S7. FTIR spectra of pure 1-EC, perovskite film without and with 1-EC additive.



Figure S8. Intensity and FWHM of the perovskite (110) diffraction peak from the MPSCs as functions of their 1-EC concentration.



Figure S9. (a) Comparison of the TRPL spectra of MAPbI₃ with and without 1-EC films deposited on TiO_2/FTO substrates (the wavelength for monitoring the TRPL is 770 nm). (b) Nyquist plots of devices based on MAPbI₃ with and without 1-EC films at a bias of 0V in the dark.

Each Nyquist diagram consists of two semicircles, the starting point of the real part corresponds to the series resistance (Rs). The first small arc is due to the charge transfer resistance (Rct). It is involved in hole transport at carbon and charge transfer/exchange at the carbon/perovskite interface. The second largest arc is the resistance to recombination (Rrec). This reflects the recombination reaction between m-TiO₂ and perovskites.



Figure S10. (a) J–V curves of hole-conductor-free printable MPSCs based on $(5-AVA)_XMA_{1-X}PbI_3$ w/o 1-EC, and the corresponding photovoltaic parameters are plotted in the inset. (b) IPCE spectra and integrated current of $(5-AVA)_XMA_{1-X}PbI_3$ w/o 1-EC based devices. (c) Current density and steady-state power output (SPO), measured for 100 s at a fixed voltage near the maximum power point (MPP) identified in the J–V curves. (d) Nyquist plots of devices based on $(5-AVA)_XMA_{1-X}PbI_3$ with and without 1-EC films at a bias of 0V in the dark.

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