
Supporting Information

Ionic liquid additives for efficient and durable two-step perovskite photovoltaic devices

Fei Wang^{†1,2}, Yonggui Sun^{†2}, Taomiao Wang^{†2}, Guo Yang², Qiannan Li², Yongjun Li², Haoran Lin²,
Xuejuan Wan^{*1}, Gang Li^{*3} and Hanlin Hu^{*2}

1 Shenzhen Key Laboratory of Polymer Science and Technology, College of Materials Science and Engineering, Shenzhen University, Shenzhen, 518060, China

2 Hoffmann Institute of Advanced Materials, Postdoctoral Innovation Practice Base, Shenzhen Polytechnic, Nanshan District, Shenzhen, 518055, China

3 The Hong Kong Polytechnic University Shenzhen Research Institute, Guangdong, Shenzhen, 518057, China

Experimental Section

Materials: ITO glass substrates (sheet resistance of ca. $9\ \Omega\ \text{sq}^{-1}$) were purchased from OPVTECH Inc. PbI_2 (99.8%), 4-tert-butylpyridine (tBP, 96%) and bis (trifluoromethane) sulfonimide lithium salt (Li-TFSI, 99%), and ionic liquids (IL) 1-Hexyl-3-methylimidazolium Tetrafluoroborate (HMIMSO₄) were supplied from Sigma-Aldrich. Methylammonium chloride (MACl), methylammonium bromide (MABr), and Formamidinium Iodide (FAI) were purchased from Xi'an Polymer Light Technology Crop. Spiro-OMeTAD (purity. 99.5%) was purchased from Feiming Science and Technology Co., Ltd. IPA, DMF, and DMSO were purchased from TCI. Tin (IV) oxide was purchased from Alfa Aesar. All materials were used as received without any further treatment.

Device Fabrications: ITO glass substrates were sequentially rinsed by sonication in detergent, deionized (DI) water, and IPA for 30 min, respectively, and then dried under nitrogen gas. The ITO substrates were disposed by ultraviolet-ozone for 30 min, followed by the deposition of

Tin (IV) oxide solution on the substrate via spin-coating at 4000 rpm for 30 s, and subsequently annealed on a hotplate at 150 °C for 30 min. The perovskite composition is $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$. According to the literature, a modified two-step sequential process was employed to fabricate the perovskite layer in the glovebox. First, a 1.4 M PbI_2 precursor with 0 or 0.025, 0.05, and 0.1 mol% IL HMIMBF₄ was dissolved in a 950 ml DMF and 50 μL DMSO solution. The above solution was then spin-coated on the SnO_2/ITO substrate at 1500 rpm for 30 s, and dried at 70 °C for 1 min. Thereafter, a mixture solution of FAI:MABr:MACl (60 mg: 6 mg: 6 mg in 1 mL IPA) was dropped on the PbI_2 film at 1500 rpm for 30 s. The as-cast perovskite film was annealed at 150 °C for 15 min under 30-40% relative humidity. The Spiro-OMeTAD solution was made up of 72.3 mg Spiro-OMeTAD, 30 μL TBP, and 35 μL Li-TFSI solution (260 mg in 1 mL acetonitrile) in 1 mL chlorobenzene, and spin-coated on the above perovskite film for 30 s at 4000 rpm. Finally, a 100 nm Au electrode was deposited by thermal evaporation.

Characterization: GIWAXS measurements were performed at the Synchrotron and Printable Electronics lab at Shenzhen Polytechnic with SaxsFocus using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.5°. The J - V characteristics of the PSC devices were carried out using a IVS-KA6000 Enlitech sunlight simulator equipped with an AM 1.5 filter at 100 mW cm⁻² and Keithley SMU source after correcting the light intensity with a standard calibration cell. The corresponding EQE spectrum was acquired in air by a QE-R system from Enli Technology Co. Ltd. Static PL from 600 nm to 900 nm and TRPL measurements of perovskite film (2000 ns) were recorded by an Edinburgh FLSP1000 spectrophotometer equipped with an excitation source of 440 nm picosecond pulsed diode laser. Scanning electron microscopy (SEM) measurements of perovskite thin films were conducted to obtain the morphology on JSM-IT 800. The X-ray diffractometer spectra of the perovskite film with a scanning angle from 3 to 40° (2 θ) were measured by Bruker D8 Advance. UV-vis absorption spectra of the perovskite films were obtained by a UV-3600 Plus spectrophotometer.

¹H nuclear magnetic resonance spectroscopy (NMR) spectra were recorded on a Bruker 400 MHz spectrometer. X-ray photoelectron spectroscopy (XPS) of the perovskite films was carried out using the Thermo Kalpha XPS. Fourier-transform infrared spectra of thin films were recorded from the wavenumber 4000 to 500 cm⁻¹ via Thermo Fisher Scientific Nicolet iS50. Atomic force microscope (AFM) characterizations were conducted on an OXFORD Instruments MFP-3D Origin.

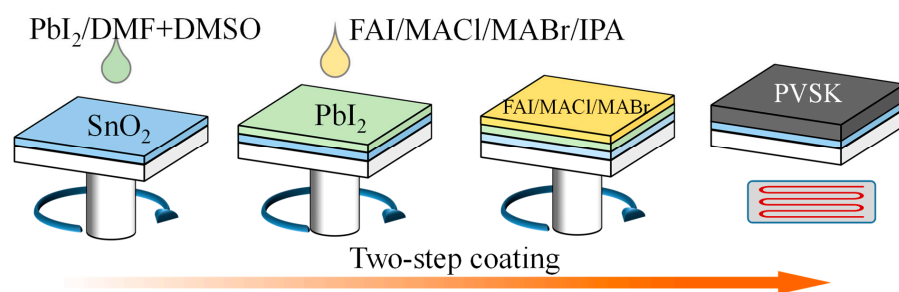


Figure S1. Schematic diagram of two-step preparation of perovskite films.

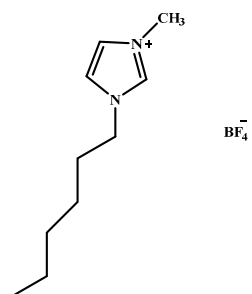


Figure S2. Chemical structure of the IL HMIMBF₄.

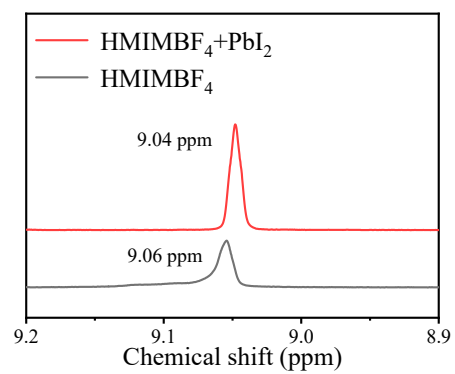


Figure S3. ^1H NMR spectra of HMIMBF_4 and $\text{HMIMBF}_4 + \text{PbI}_2$ samples.

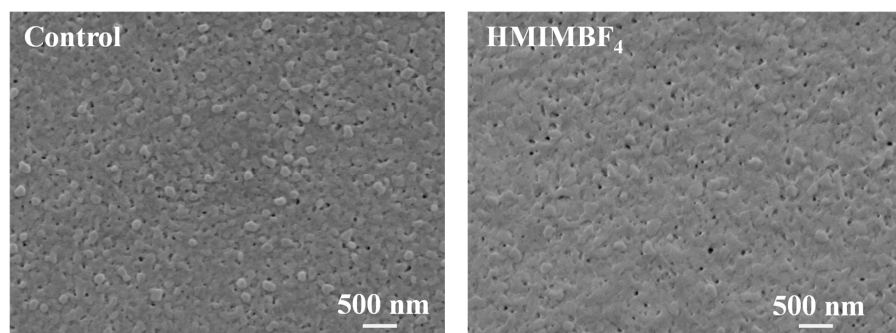


Figure S4. The top-view SEM images of control and HMIMBF₄-modified PbI₂ film.

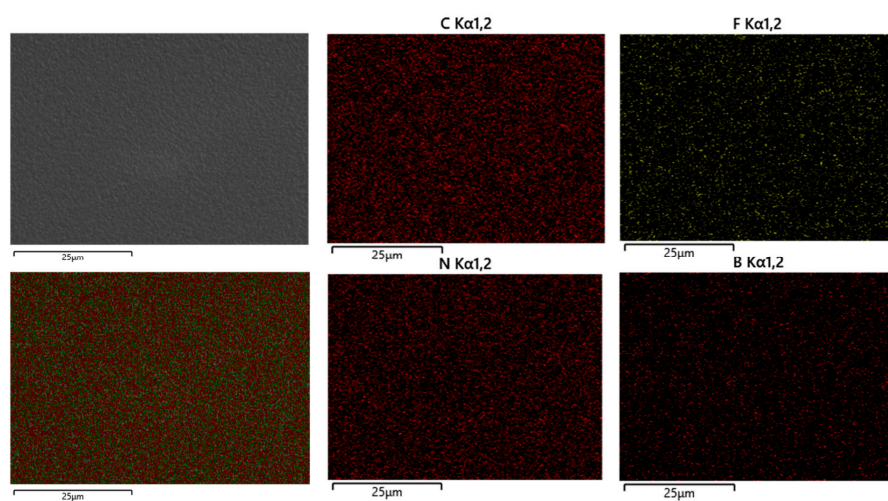


Figure S5. EDS images of HMIMBF₄-modified perovskite film.

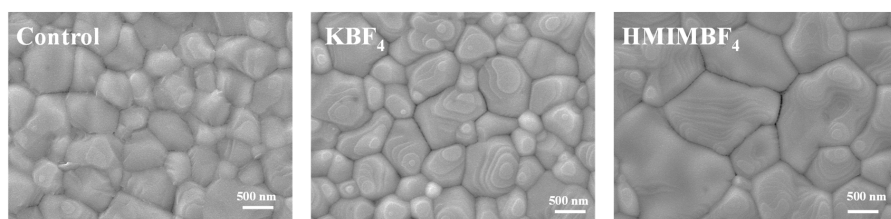


Figure S6. SEM images of control, KBF₄, and HMIMBF₄-modified perovskite films.

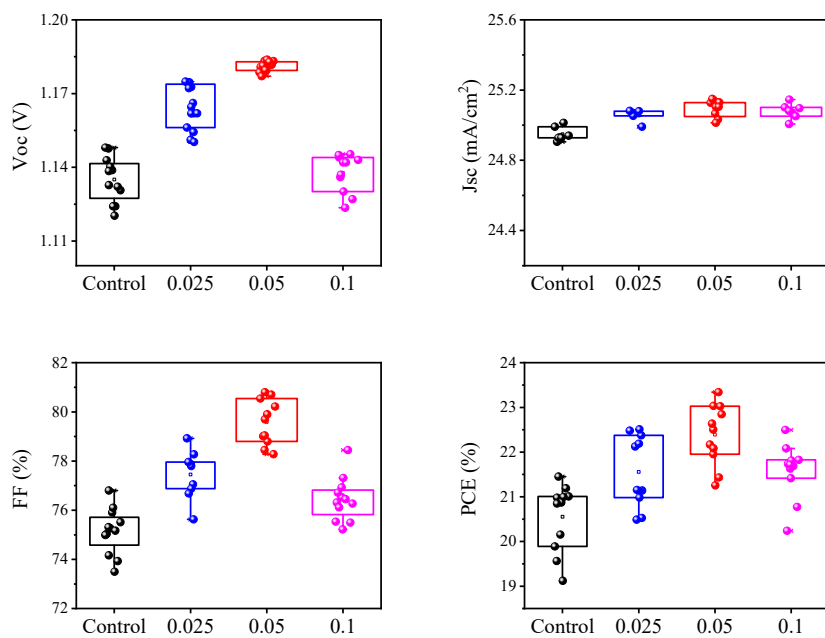


Figure S7. The statistics of photovoltaic performance parameters of HMIMBF₄-treated PSCs: PCE, V_{oc} , FF, and J_{sc} .

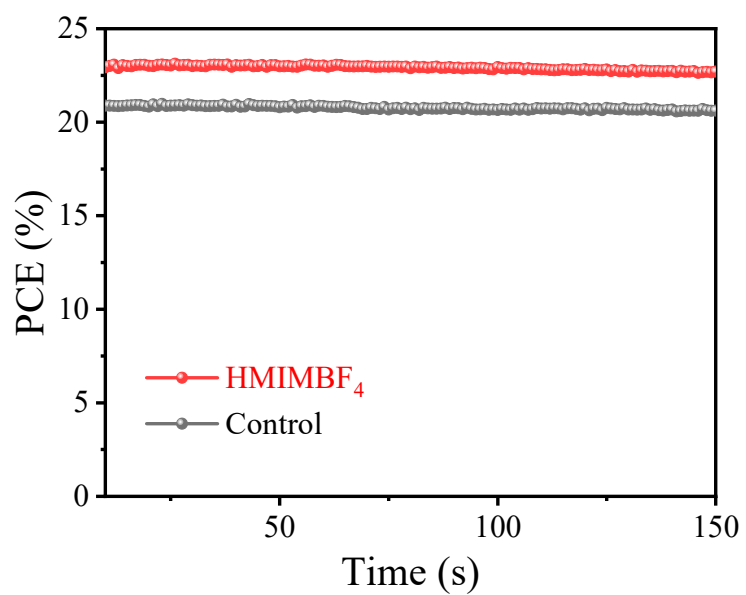


Figure S8. Steady-state PCE of control and HMIMBF₄-treated PSCs by maximum power point tracking.

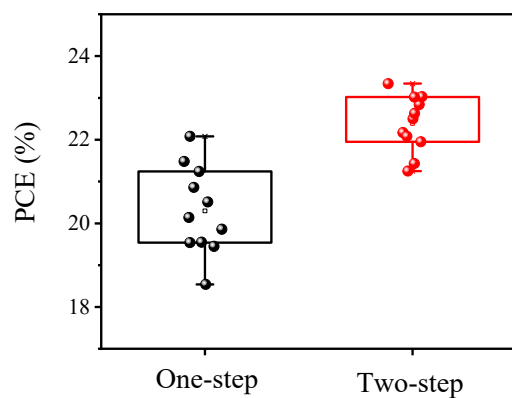


Figure S9. The statistics of PCE of HMIMBF₄-treated PSCs via one-step and two-step methods, respectively.

Commented [-1]: Please check that intended meaning has been retained.

Commented [非2R1]: OK

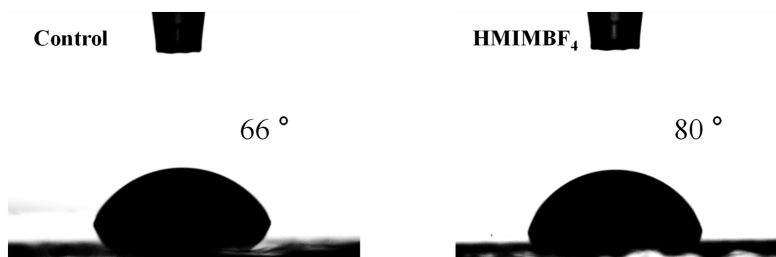


Figure S10. The water contact angle of the control and HMIMBF₄-perovskite film.

Table S1. Photovoltaic parameters of PSCs under AM 1.5G illumination at 100 mW cm⁻²

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Control	24.76	1.139	75.90	21.45
HMIMBF ₄	24.94	1.179	79.37	23.34

Table S2. Photovoltaic parameters of control, DMIMBF₄, BMIMBF₄, and HMIMBF₄-modified devices.

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Control	24.76	1.139	75.90	21.41
DMIMBF ₄	24.81	1.163	76.78	22.15
BMIMBF ₄	24.87	1.166	78.12	22.67
HMIMBF ₄	24.94	1.179	79.37	23.34

Table S3. Photovoltaic parameters of control, HMIMI, and HMIMBF₄-modified devices.

	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Control	24.76	1.139	75.90	21.41
HMIMI	24.85	1.151	78.81	22.54
HMIMBF ₄	24.94	1.179	79.37	23.34

Table S4. Photovoltaic parameters of HMIMBF₄-modified for one-step and two-step devices.

	Method	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
Control	One-step	24.75	1.122	75.80	21.04
HMIMBF ₄		24.86	1.145	77.56	22.08
Control	Two-step	24.76	1.139	75.90	21.41
HMIMBF ₄		24.94	1.179	79.37	23.34

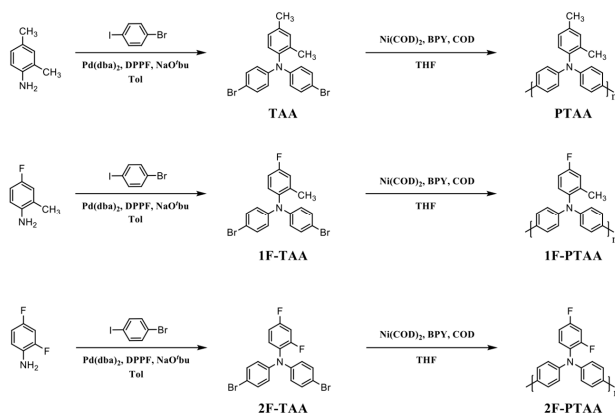


Figure S11. Synthesis path for poly(triarylamine)(PTAA) and fluorinated poly(triarylamine) (1F-PTAA and 2F-PTAA). (b) TGA curves of 1F-PTAA- and (c) J-V curves for 1F-PTAA-based ILs-assisted device. (d) Thermal stability results for both doped-Spiro-OMeTAD- and 1F-PTAA-based IL-assisted device at 80 °C in glovebox.

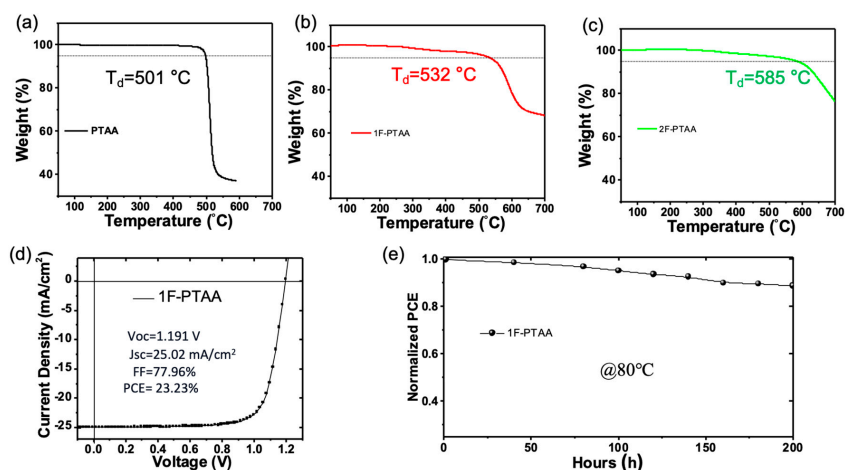


Figure S12. (a-c) TGA curves of PTAA, 1F-PTAA, and 2F-PTAA, and (d) J-V curve for 1F-PTAA-based IL-modified perovskite device. (e) Thermal stability results for 1F-PTAA-based IL-modified perovskite device at 80 °C in glovebox.