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Supporting Information

Multifunctional pseudohalide-based ionic liquid doping promotes efficient and stable perovskite solar cells

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Experiment section

Materials

The Tin (IV) oxide (SnO_2, 15% in H_2O colloidal dispersion is purchased from Alfa Aesar. Lead iodide (PbI_2, 99.99%), Lead chloride ($PbCl_2$, 99.99%), and Cesium iodide (CsI, 99.99%) are purchased from Xi’an Polymer Light Technology Corp. Lead bromide ($PbBr_2$, 99.99%), Cesium bromide (CsBr, 99.99%), Methylammonium iodide (MAI, 99.9 %), Formamidinium iodide (FAI, 99.9%), and spiro-OMeTAD (99.86%) are purchased from Advanced Election Technology Co. Ltd. The N,N-Dimethylformamide (DMF, 99.8%), isopropanol (IPA, 99.5%) and chlorobenzene (CB, 99.5%) are purchased from Sigma-Aldrich. All materials are purchased without further purification.

Device fabrication

The indium tin oxide (ITO) substrates were cleaned sequentially with detergent, deionized water, and ethanol in an ultrasonic wave for 20 min, respectively. The substrate was treated with UV-ozone for 20 min before depositing SnO_2. The diluted SnO_2 solution (5%) was spin-coated on the ITO substrates at 4000 rpm for 30 s, then the substrates were annealed at 150 °C for 30 min on a hot plate. After cooling down to room temperature, the substrates were treated with UV-ozone for 5 min. After that, the substrates were transferred into a nitrogen-filled glove box. The perovskite films were fabricated by a two-step process. 1.36 M PbI_2, 0.24 M $PbCl_2$, and 0.08 M CsI were dissolved in the DMF and stirred for 3 h at 70 °C. 70 mg MAI and 30 mg FAI were dissolved in 1 mL IPA with 10 μL DMF added. For the $TEAPF_6$ doped precursor, the $TEAPF_6$ with different concentrations was added to the PbX_2 solution. PbX_2 precursor solution was spin-coated onto SnO_2 substrates at 3000 rpm for 45 s. Then, 200 μL MAI:FAI solution was spin-coated onto the PbX_2 at 3000 rpm for 45 s, immediately. Then the samples were thermally annealed on a hot plate at 100 °C for 10 min. After cooling to room temperature, the spiro-OMeTAD was spin-coated on the top of the perovskite layer at 4000 rpm for 45 s. The spiro-OMeTAD solution was prepared by dissolving 72.5 mg spiro-OMeTAD, 17.5 μL Li-TFSI solution (520 mg/mL in acetonitrile), 28.8 μL FK209 solution (300 mg/mL in acetonitrile), and 28.8 μL 4-tertbutylpyridine (tBP) in 1 mL chlorobenzene. Finally, 100 nm Ag was deposited on the top of spiro-OMeTAD by thermal evaporation as the electrodes. The area of the device is 7.5 mm^2 defined by shadow mask.

Characterization

The XRD spectra were performed by Bruker D8 Advance XRD. The UV-vis absorption spectra were measured by Perkin-Elmer Lambda 950 spectrophotometer. The PL and TR-PL spectra were measured by the Pico Quant Fluotime 300 with a 510 nm picosecond pulsed laser. The SEM images were measured by SEM JSM-7800F. XPS measurements were measured by the Escalab 250Xi with a source of monochromatic Al-Ka (1486.6 eV). The current-voltage curves of devices were tested by Keithley 2400 source meter under AM 1.5G irradiation with a luminous power of 100 mW cm^{-2}. The EQE spectra were measured by the SCS10-X150 systems (Zolix instrument. Co. Ltd). TPC spectra were measured by a digital oscilloscope (Tektronix, D4105) with a sampling resistor of 50 Ω under a 532 nm (1000 Hz, 3.2 ns) pulse laser. TPV spectra were measured by the same system with a sampling resistor of 1 MΩ under a 405 nm (50 Hz, 20 ms) pulse laser. The C-V and EIS spectra were measured by an electrochemical workstation (Jiangsu Donghua Analysis Instruments Co., Ltd, DH7001).

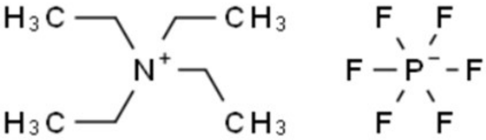

Figure S1. The chemical structure of TEAPF$_6$ ILs.

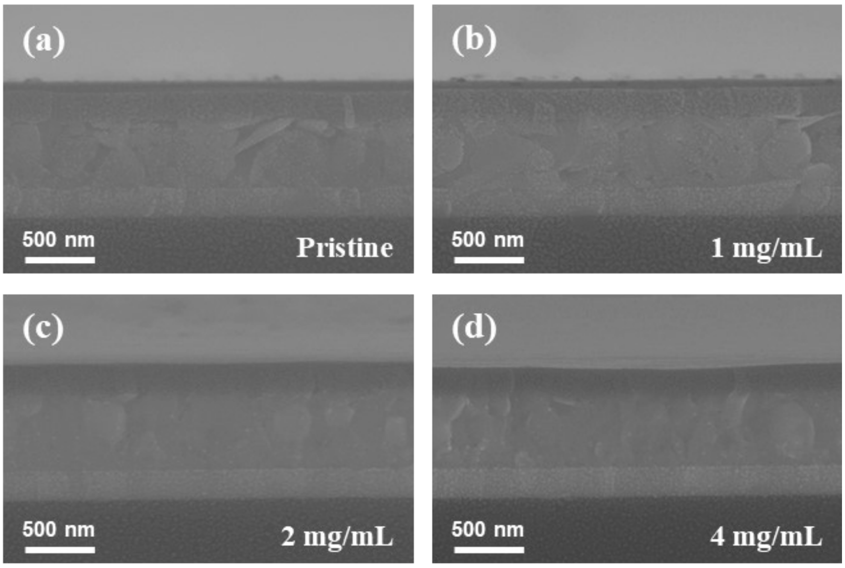

Figure S2. Cross-section SEM images of perovskite films with different concentrations of TEAPF$_6$.

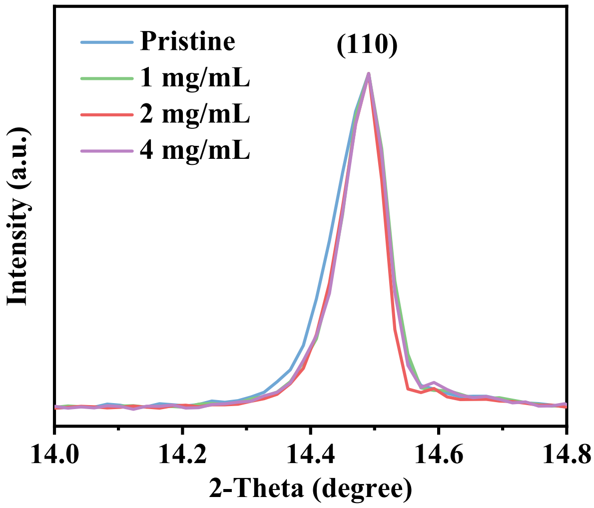

Figure S3. The FWHM of (110) peak of perovskite films in Figure 1e.

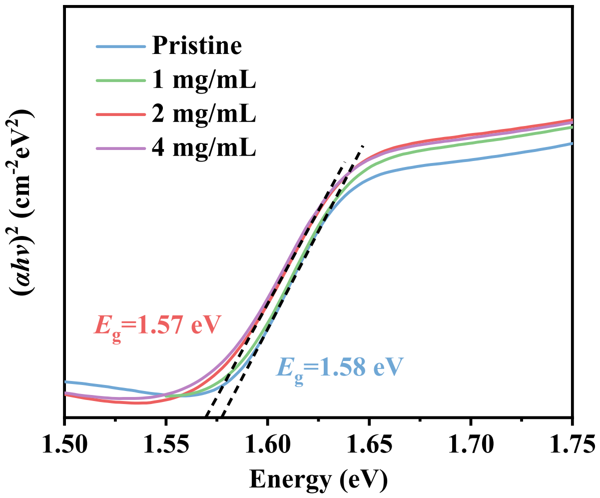

Figure S4. Tauc plots of perovskite films with different concentrations of $TEAPF_6$.

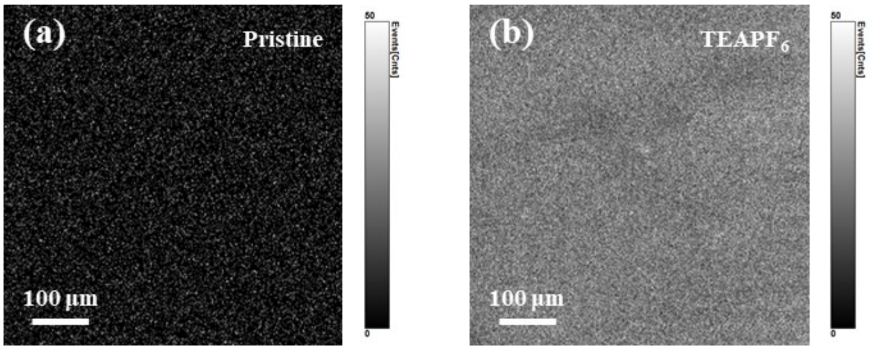

Figure S5. PL mappings of (a) pristine and (b) $TEAPF_6$ doped perovskite films.

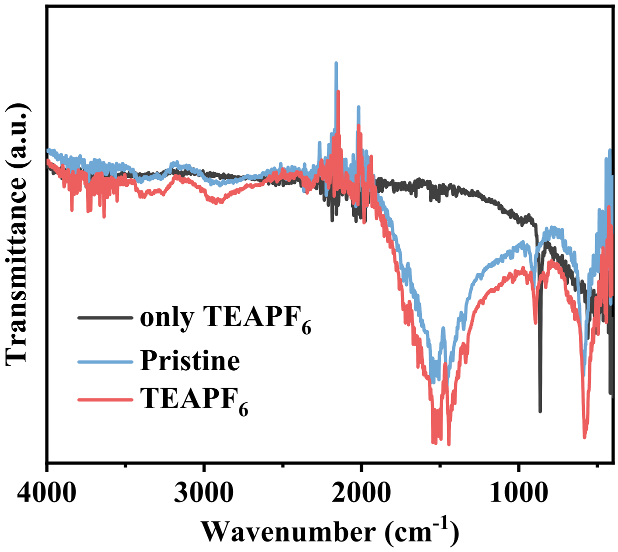

Figure S6. FTIR spectra of perovskite films without and with $TEAPF_6$ doping.

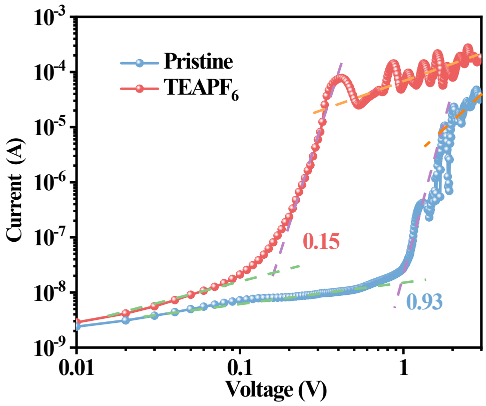

Figure S7. The dark *I-V* curves of the electron-only devices based on perovskite without and with $TEAPF_6$.

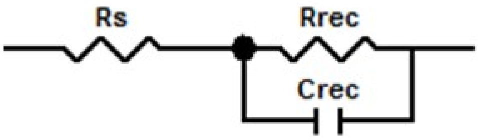

Figure S8. The equivalent circuit for fitting EIS curves.

Table S1. Fitting parameters of TR-PL curves of perovskite films without and with $TEAPF_6$.

Conditions	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
Pristine	0.84	9.46	0.16	80.35	52.95
1 mg/mL $TEAPF_6$	0.72	22.07	0.28	143.65	109.68
2 mg/mL $TEAPF_6$	0.53	35.62	0.47	204.70	176.87
4 mg/mL $TEAPF_6$	0.54	26.07	0.46	166.89	145.41

Table S2. The *J-V* parameters of PSCs with different concentrations of $TEAPF_6$.

Conditions		J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
Pristine	Average	22.96	1.09	0.77	19.27
	Best	23.89	1.10	0.77	20.23

1 mg/mL	Average	23.15	1.11	0.76	19.53
TEAPF$_6$	Best	24.15	1.11	0.79	21.28
2 mg/mL	Average	23.39	1.14	0.78	20.80
TEAPF$_6$	Best	24.26	1.15	0.79	22.13
3 mg/mL	Average	23.21	1.12	0.77	20.02
TEAPF$_6$	Best	23.89	1.14	0.79	21.52
4 mg/mL	Average	23.03	1.11	0.76	19.43
TEAPF$_6$	Best	23.19	1.14	0.76	20.09

Table S3. The *J-V* parameters of PSCs without and with TEAPF$_6$ in different scan directions.

Conditions	Scan directions	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)	HI (%)
Pristine	RS	23.33	1.11	0.77	19.94	21.65
	FS	23.07	1.11	0.61	15.62	
TEAPF$_6$	RS	23.84	1.14	0.79	21.47	14.23
	FS	23.41	1.14	0.69	18.41	

Table S4. Fitting parameters of the EIS curves of PSCs.

Conditions	R_{S} (Ω)	R_{rec} (Ω)	C_{rec} (F)
Pristine	60.93	2.08×10^{6}	6.45×10^{-9}
With TEAPF$_6$	41.48	3.09×10^{6}	5.82×10^{-9}