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Li Dopant Inducing Moisture Sensitive Phase Degradation of All-inorganic $CsPbI_2Br$ Perovskite

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Supplementary Information

Experiment Details

Materials: The CsI, PbI_2 and $PbBr_2$ were purchased from Alfa Aesar. The PMMA and DMF was purchased from Sigma-Aldrich. The $HPbI_{3+x}$ (x=0.1-0.2) were prepared by mixing PbI_2 and 57% w/w hydroiodic acid (molar ratio 1:1.4) in DMF and then stirring for 2h.[35] The excess HI was used to ensure the complete conversion of PbI_2 into $HPbI_{3+x}$. The precipitates were recovered by evaporating the solutions at 70 °C. Finally, the resulting solid was centrifuged and washed four times with copious diethyl ether until supernatant turned to colorless. The collected powders were stored in oven at 50 °C.

Device preparation: The patterned TEC-15 FTO substrate was coated with a compact TiO_2 layer by spray pyrolysis using 0.2 M Ti(IV) bis (ethyl acetoacetate)-diisopropoxide in 1-butanol solution at 450 °C. The coated substrate was then annealed at 450 °C for one hour. The 0.5 M perovskite $CsPbI_2Br$ in N,N-Dimethylformamide (DMF) was prepared by mixing stoichiometric CsI, $HPbI_{3+x}$ and $PbBr_2$ with 2:1:1 molar ratio. Then the precursor solution was spun onto the c-TiO_2/FTO substrate at 3000 rpm with accelerating rate of 3000 rpm/s for 30 s, following by annealing at 150 °C for 4 minutes to form inorganic perovskite film. The TiO_2 coated substrates were subject to preheating at 70 °C in order to increase the surface coverage of the inorganic perovskite. PMMA (10mg/ml, chlorobenzene) was spun onto the perovskite film to form PMMA layer. Then the annealed perovskite films was spin-coated with a HTM layer consisting 0.1 M Spiro-MeOTAD, 0.035 M bis(trifluoromethane) sulfonamide lithium salt (Li-TFSi) and 0.12 M 4-tert-butylpyridine (tBP) in chlorobenzene/acetonitrile (10:1, v/v) solution at 4000 rpm for 20 s. Referring to the other work for PTAA[34], non-doping PTAA (10mg/ml in toluene) was spun onto the annealed perovskite. A 100-nm thick Ag layer was deposited by thermal evaporation.

Moisture stability evaluation: PMMA (10 mg/ml, chlorobenzene) was spun onto the perovskite film to form PMMA layer.The relative humidity level of the drybox was controlled by the entrance ratio of dry air in and moisture air. The a-$CsPbI_2Br$ films were kept in the corresponding box to study phase changes.

Characterization: The crystal structures of the perovskite films were measured by X-ray diffraction (XRD, Shimadzu XRD-6100 diffractometer with Cu Kα radiation). The absorption spectra of the perovskite films were characterized by a Cary-60 UV-vis spectrophotometer. The morphologies of the perovskite films were characterized using SEM (JEOL JSM-7800F Prime). The photocurrent-voltage (J-V) characteristic of perovskite solar cells was measured with a Keithley 2401 source meter with a scan rate of 0.05 V/s under simulated AM 1.5G illumination using Enlitech's 3A light source.

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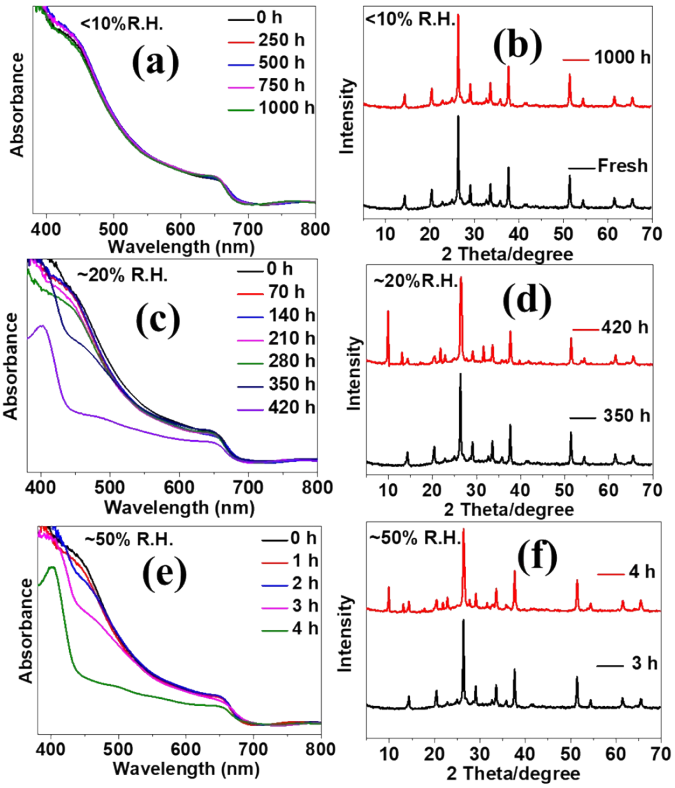

Fig. S1 (a, c, e) Evolution of UV-vis absorption and (b, d, f) XRD patterns of α-$CsPbI_2Br$ films exposed to different R.H. of <10%, ~20%, ~50% and different exposure times.

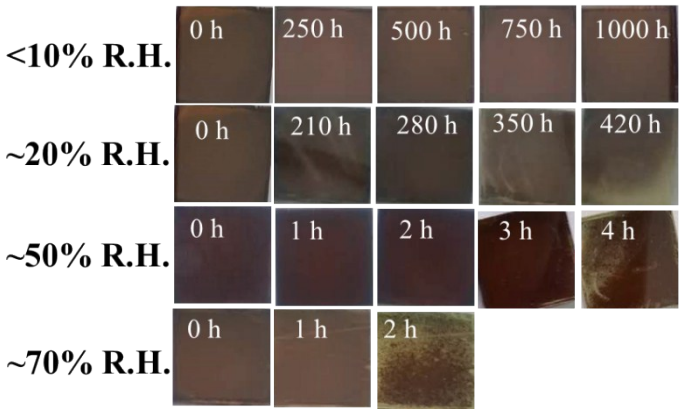

Fig. S2 Variation of color of the α-$CsPbI_2Br$ films exposed to different R.H. of <10%, ~20%, ~50%, and ~70%.

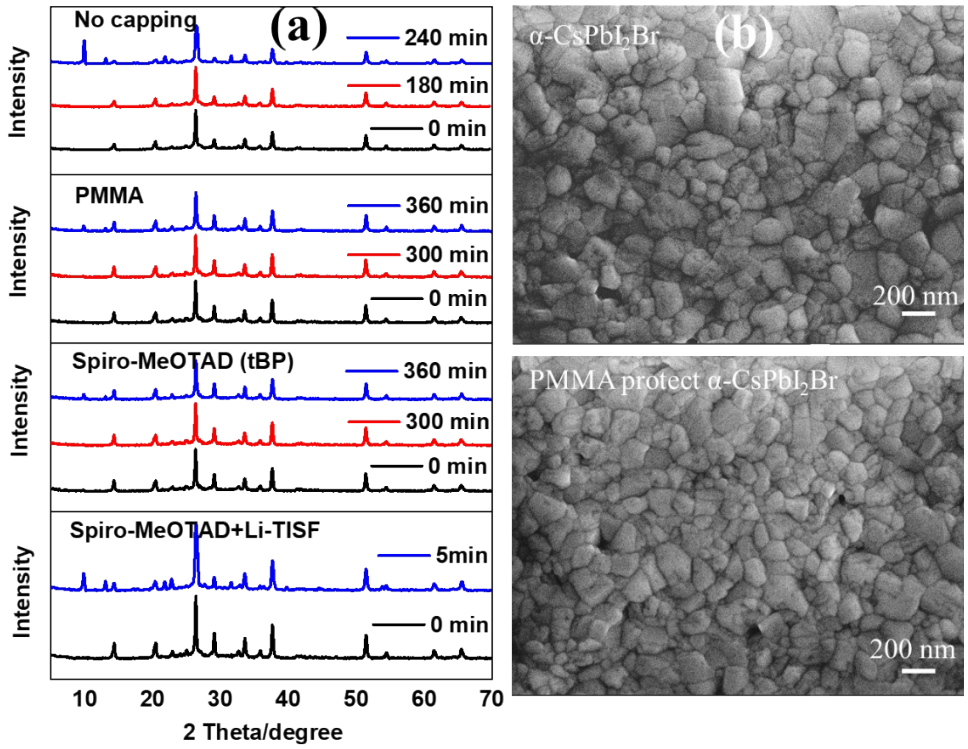

Fig. S3 (a) XRD patterns of $CsPbI_2Br$ films with and without PMMA, Spiro-MeoTAD (tBP), and Spiro-MeoTAD+Li-TISF capping. (b) SEM images of α-$CsPbI_2Br$ films (top) without PMMA capping and (bottom) with PMMA capping.

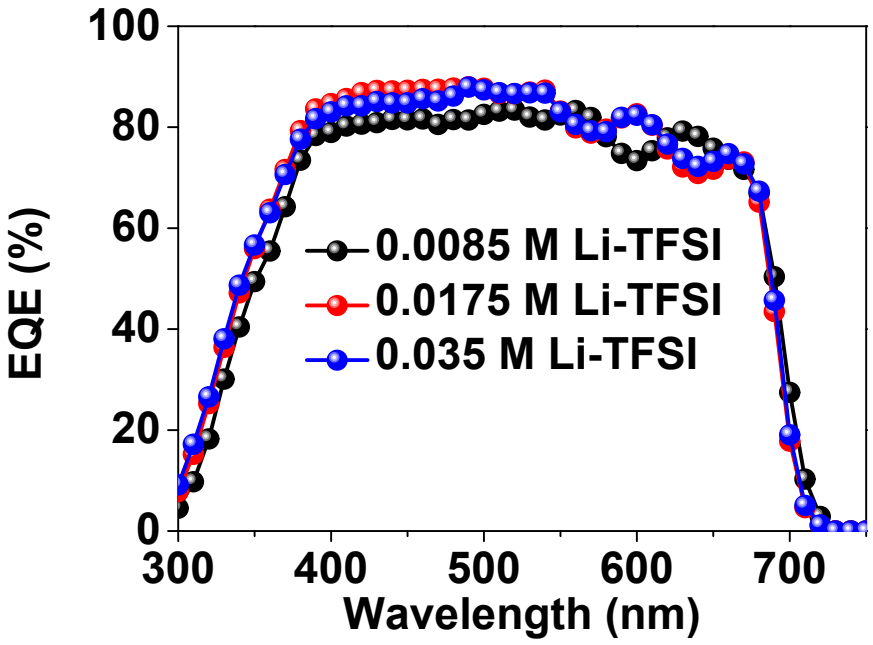

Fig. S4 IPCE of $CsPbI_2Br$ PSCs based on Spiro-MeOTAD with 0.0085 M Li-TFSI, 0.0175 M Li-TFSI, and 0.035 M Li-TFSI doping.

Table S1. Photovoltaic parameters of $CsPbI_2Br$ PSCs based on Spiro-MeOTAD with 0.0085 M Li-TFSI, 0.0175 M Li-TFSI, and 0.035 M Li-TFSI doping. The data were averaged from 32 devices.

	***J*sc (mA·cm^{-2})**	***V*oc (V)**	**FF**	**PCE (%)**
0.0085M	15.56±0.13	1.04±0.015	53±3	8.57±0.59
0.0175M	15.67±0.1	1.044±0.01	62.9±1.8	10.3±0.4
0.035M	15.7±0.09	1.06±0.01	72.35±2.2	12.04±0.37