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Electronic Supplementary Information

Enabling Room-Temperature Processed Highly Efficient and Stable 2D Ruddlesden−Popper Perovskite Solar Cells with Eliminated Hysteresis by Synergistic Exploitation of Additive and Solvent

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Experimental Section

Materials. PbI_2 and CH_3NH_3I were purchased from Maituowei Ltd. (China). phenethylamine was purchased from Energy Chemical. All other chemicals were purchased from J&K Scientific, Ltd. (China). All the reagents were used as received.

Fabrication of 2D perovskite films. The pristine $(PEA)_2MA_3Pb_4I_{13}$ precursor solutions (40 wt%) were prepared by mixing PbI_2, HI, CH_3NH_3I and PEA at a stoichiometric ratio of 4:2:3:2 in DMF. For the preparation of the precursors of PEA + NH_4Cl, PEA + DMSO and PEA + NH_4Cl + DMSO samples, additional 5 mg of NH_4Cl, 30 μL of DMSO and both of them were added to the pristine precursor (1 mL), correspondingly. All the 2D perovskites films were obtained by spin-coating the precursor solutions at 3000 rpm for 60 s at room temperature.

Characterization. Optical absorption spectra of samples were acquired on Agilent 8453 UV-Visible spectrophotometer. Steady-state photoluminescence was measured using a FluoroMax$^{@}$-4 spectrofluorometer (HORIBA JOBIN YVON, Inc., Edison, NJ) with the excitation beam at 500 nm. The PL intensity was then corrected by absorbed photon numbers at the exciting light wavelength. X-ray diffraction pattern data for 2θ values were collected with a Bruker AX D8 Advance diffractometer with nickel filtered Cu Kα radiation (λ = 1.5406 Å). Field-emission scanning electron microscopy images coupled with energy-dispersive X-ray elemental analysis were acquired on Philips XL-30 field-emission gun at an accelerating voltage of up to 30 kV. Grazing incidence wide-angle X-ray scattering (GIWAXS) experiments were carried out at the Shanghai Synchrotron Radiation Facility (SSRF). Samples were prepared on Si substrates using the same preparation conditions as for devices. The data were obtained with an area CCD detector of 3072 by 3072 pixels resolution (225 mm by 225 mm) at beamline BL14B1. The monochromated energy of the X-ray source was 10 keV. The X-ray wavelength was 1.2378 Å and the incidence angle was 0.15°. Transient absorption (TA) experiments were performed by using a femtosecond pump-probe setup in nitrogen atmosphere. Laser pulses (800 nm, 80 fs pulse length, 1 kHz repetition rate) were generated by a regenerative amplifier (Spitfire XP Pro) seeded by a femtosecond oscillator (Mai Tai SP, both Spectra Physics). The pump pulses at 400 nm were generated by a BBO crystal as a second harmonic of the laser. The used excitation photon fluxes are 3×10^{12} and 1.5×10^{14} photons/cm^2/pulse. For the probe, we used the super-continuum generation from a thin CaF_2 plate. The mutual polarization between pump and probe beams was set to the magic angle (54.7°) by placing a Berek compensator in the pump beam. The probe pulse and the reference pulse were dispersed in a spectrograph and detected by a diode array (Pascher Instruments). In order to avoid photo-damage, the sample was moved to a fresh spot after each time delay point. Global SVD analysis was performed with the Glotaran software package (http://glotaran.org). These methods yield more accurate fits of rate constants because they treat the full data set as a whole. A simple sequential decay model with various components is chosen for every fitting. Time-resolved photoluminescence (TRPL) spectra were obtained using a streak camera (Hamamatsu, C6860). The laser source is an amplified titanium/sapphire laser providing 800 nm 35-fs pulses at 2 kHz which is then frequency doubled for 400 nm excitation. The absolute PL quantum yield (PLQY) was measured by using a standard spectrometer with integrating sphere (Horiba) using the same fs pulse laser as in TA and TRPL measurement.

Device Fabrication and Measurements. ITO substrates were cleaned sequentially in an ultrasonic bath with deionized water, acetone, and isopropyl alcohol for 20 min, respectively, and then dried under nitrogen. The substrates were oxidized in UV-ozone for 20 min before use. The PEDOT:PSS layers were spin-coated on the patterned substrates at 3000 rpm for 60 s and annealed at 130 °C for 30 min. The substrates coated PEDOT:PSS were transferred to a N_2 filled glovebox for making the active layers. After the formation of the perovskite layer, a solution of PCBM in chlorobenzene was spin-coated at 3000 rpm for 50 s. Finally, Bphen and Al electrode of 3 nm and 80 nm were thermally deposited with a rate of 0.5 and 1 Å/s, respectively. The active area as defined shadow mask is ~0.09 cm^2. The sample was mounted inside a nitrogen-filled sample holder with a quartz optical window for subsequent measurements. The light *J–V* curves were measured on a Keithley 2400 source meter unit under AM 1.5G light illumination with a Newport-Oriel (Sol3A Class AAA Solar Simulator, 94043A) solar simulator operating at an intensity of 100 mW cm^{-2}. The light intensity was calibrated by a certified Oriel reference cell (91150V) and verified with a NREL calibrated, filtered silicon diode (Hamamatsu, S1787-04). The *J–V* profiles were obtained under both forward (−0.5 V → +1.5 V) and reverse (+1.5 V → −0.5 V) scans. External quantum efficiency (EQE) spectra were measured on a commercial EQE set-up (QE-R, Enli Technology Co., Ltd). A calibrated silicon diode with a known spectral response was used as a reference.

Results and Discussion

Table S1 XRD parameters of PEA based 2D perovskites

Sample	**2-Theta**	**d(A)**	**FWHM**
PEA	14.102	6.2749	0.168
	28.449	3.1347	0.307
PEA + NH4Cl	14.144	6.2567	0.201
	28.551	3.1238	0.351
PEA + DMSO	14.224	6.2214	0.218
	28.633	3.1150	0.367
PEA + NH4Cl + DMSO	14.183	6.2393	0.150
	28.612	3.1173	0.222

Table S2 Analysis of biexponetial fit parameters for TRPL kinetics data of PEA-perovskites with different treatment

Sample	**τ1 (ns)**	**b1**	**τ2 (ns)**	**b2**	**<τ> (ns)**
PEA	2.68	0.54	17.15	0.46	9.34
PEA + NH4Cl	2.39	0.46	17.01	0.54	10.28
PEA + DMSO	2.12	0.31	36.93	0.69	26.14
PEA + NH4Cl + DMSO	1.82	0.44	61.11	0.56	35.02

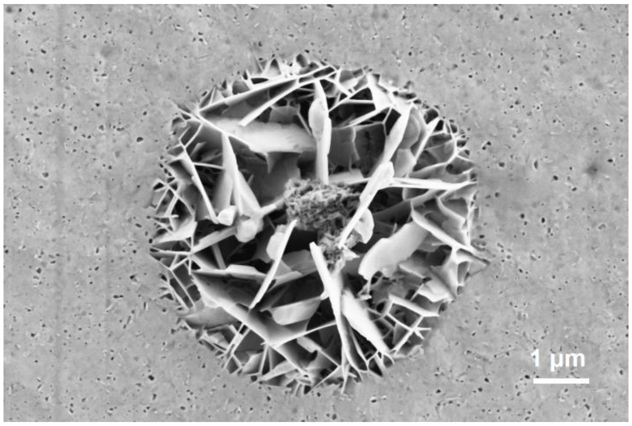

Fig. S1 Top-view FE-SEM micrograph of cracked PEA film. Scale bar = 1 μm.

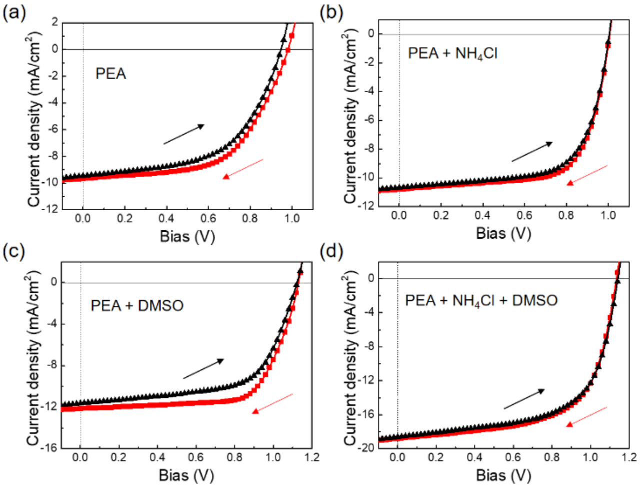

Fig. S2 Representative current density−voltage (J–V) characteristics of devices based on (a) PEA, (b) PEA + NH_4Cl, (c) PEA + DMSO and (d) PEA + NH_4Cl + DMSO under AM 1.5G simulated light at forward and reverse scans, respectively.

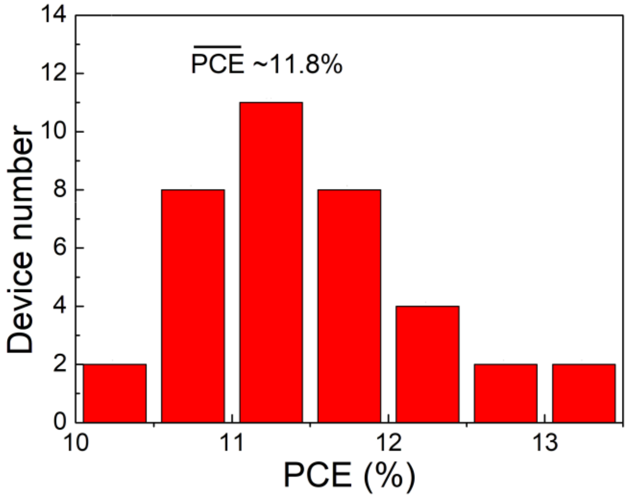

Fig. S3 The distribution of PCEs over 37 devices based on PEA + NH_4Cl + DMSO perovskites.

Table S3 Hysteresis Index of optimal PEA + NH_4Cl + DMSO perovskite based solar cells with different scan rates

Scan speed (mV/s)	Hysteresis Index (%)
20	0.021
50	0.036
100	0.011
200	0.003

Note: Hysteresis Index = $\frac{\int_{SC}^{OC}(J_{RS}(V)-J_{FS}(V))dV}{\int_{SC}^{OC}(J_{RS}(V))dV}$

Refer to: Lee, J.-W.; Kim, S.-G.; Bae, S.-H.; Lee, D.-K.; Lin, O.; Yang, Y.; Park, N.-G. The Interplay between Trap Density and Hysteresis in Planar Heterojunction Perovskite Solar Cells. *Nano Lett.* **2017**, *17*, 4270−4276.

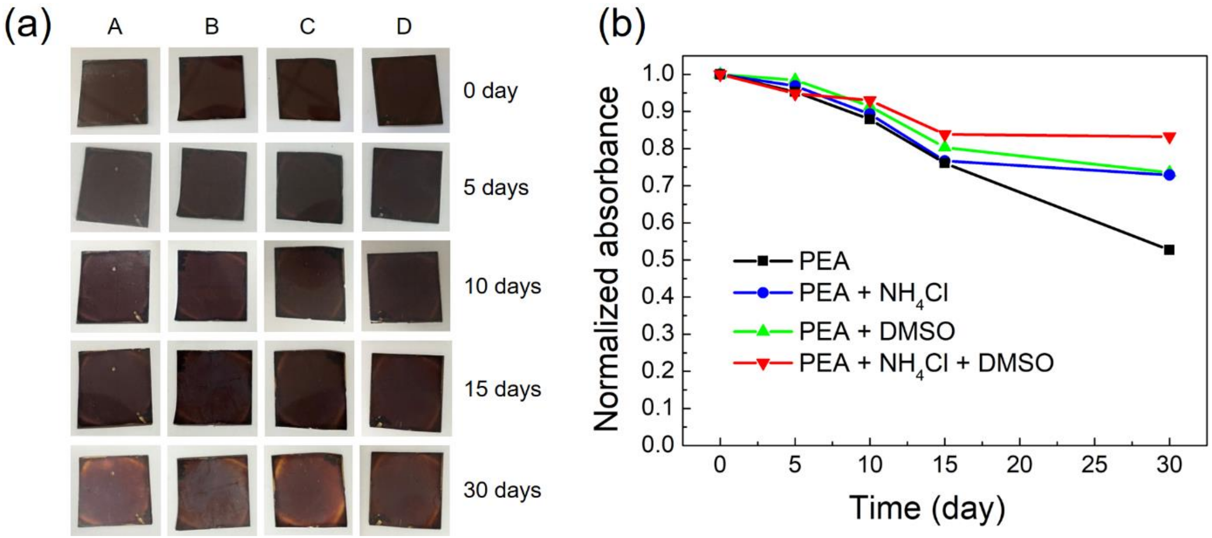

Fig. S4 (a) Photographs and (b) normalized absorbance (at 420 nm) of the film samples stored in an environmental chamber with RH 60% and at 30 °C for up to 30 days. A: PEA, B: PEA + NH_4Cl, C: PEA + DMSO, D: PEA + NH_4Cl + DMSO.

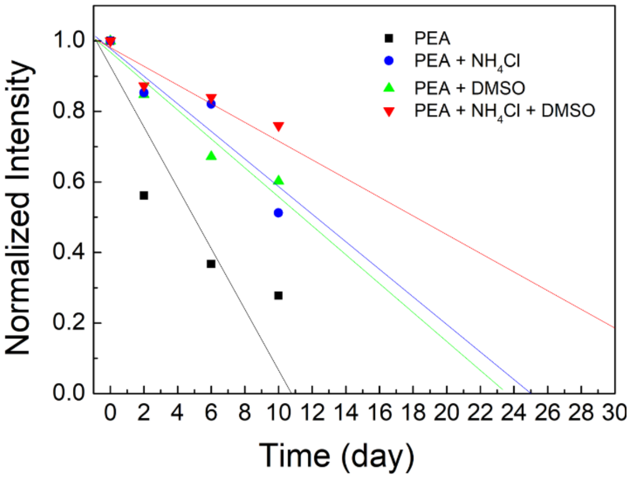

Fig. S5 Normalized XRD intensity at 14.1° and the corresponding fitting extension cords of the film samples stored in an environmental chamber with 60% RH and at 30 °C for 10 days.

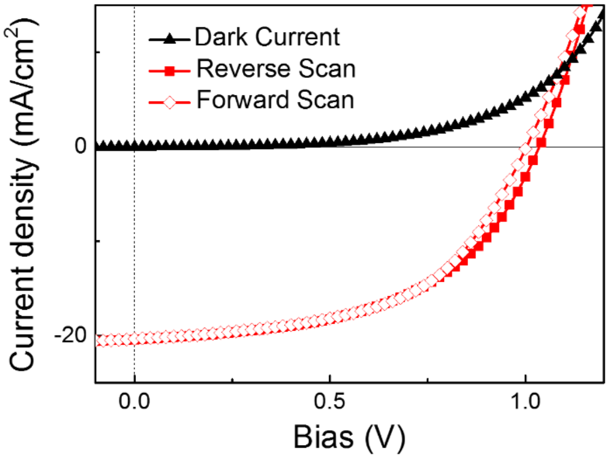

Fig. S6 J–V characteristics of the champion device based on the PEA + NH_4Cl + DMSO film after storage in an environmental chamber with a RH of 60% and 30 °C for 360 h in air.

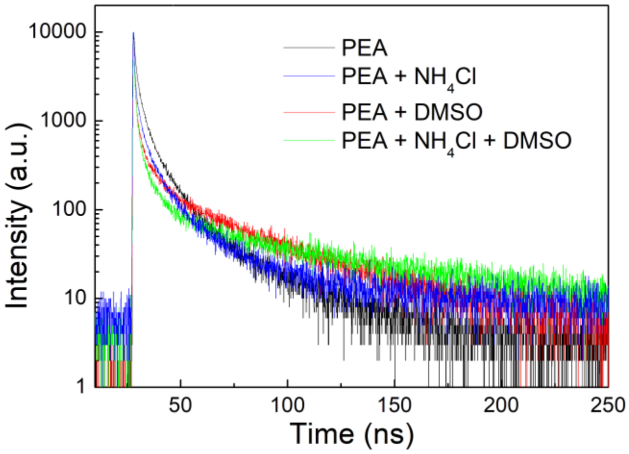

Fig. S7 TRPL decays (λ_{ex} = 505 nm) of PEA based 2D perovskites.

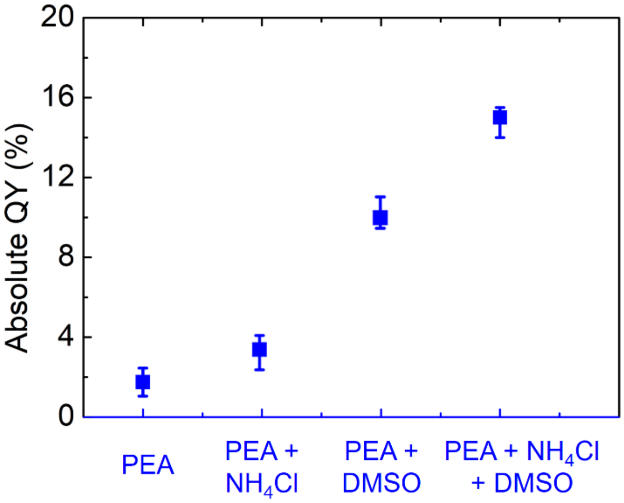

Fig. S8 Absolute PLQY values of four different PEA samples.