Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information for

N-methyl-2-pyrrolidone as an Excellent Coordinative Additive with a Wide Operating Range for Fabricating High-Quality Perovskite Films

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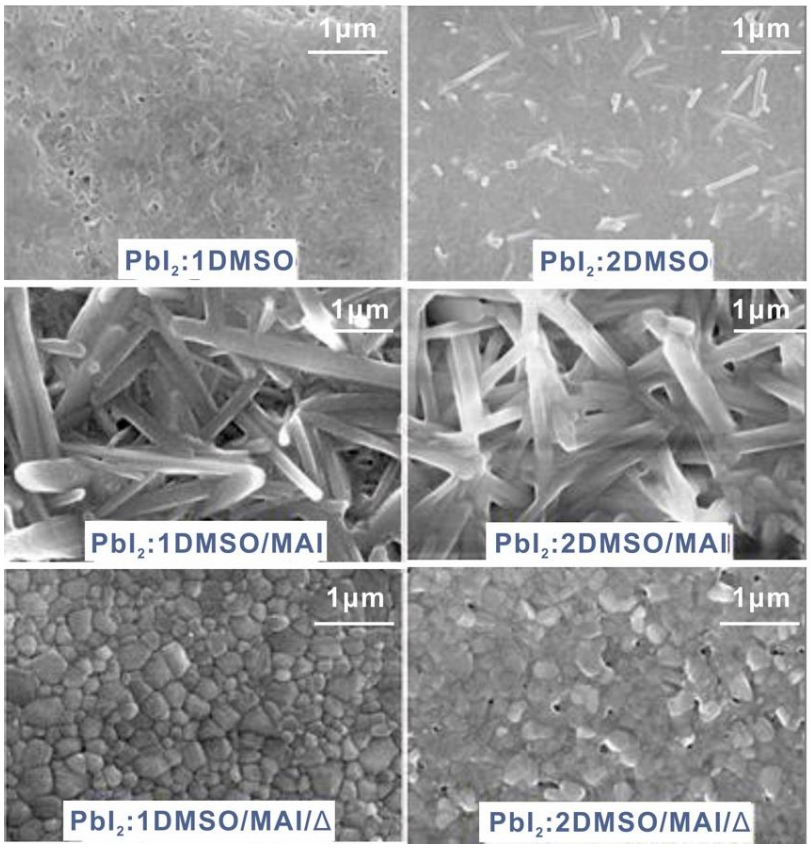

Figure S1. SEM images of PbI_2 precursor films and the reaction with MAI before and after annealing (Δ) prepared with PbI_2/DMSO molar ratios of 1:1 and 1:2.

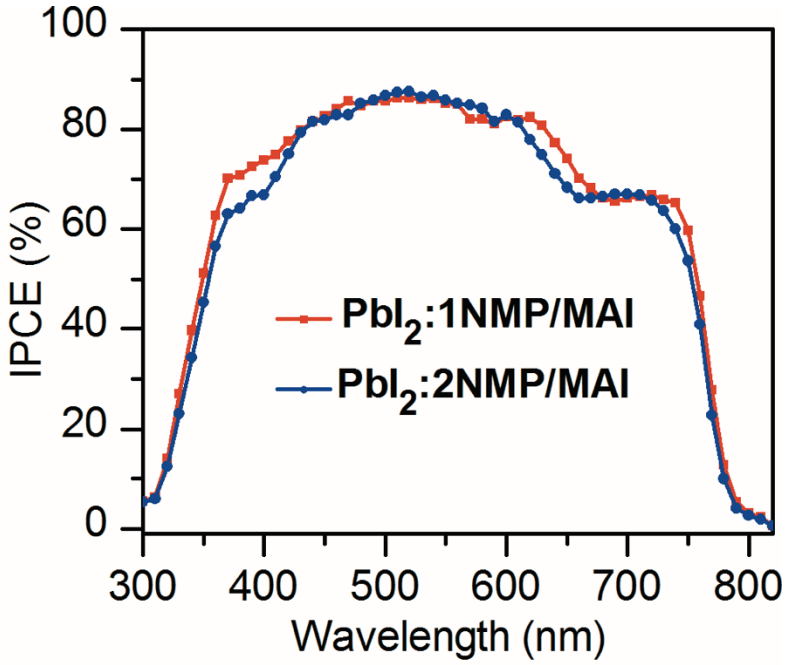

Figure S2. Best IPCE characteristics of perovskite films prepared with PbI_2/NMP molar ratios of 1:1 and 1:2.

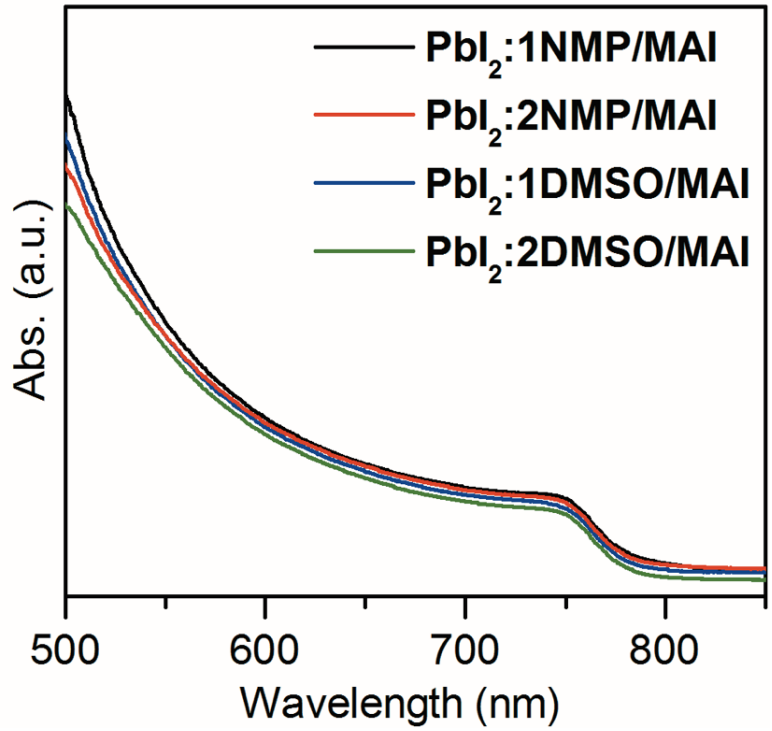

Figure S3. UV-vis absorption spectra of perovskite films prepared with different PbI_2/NMP ratios.

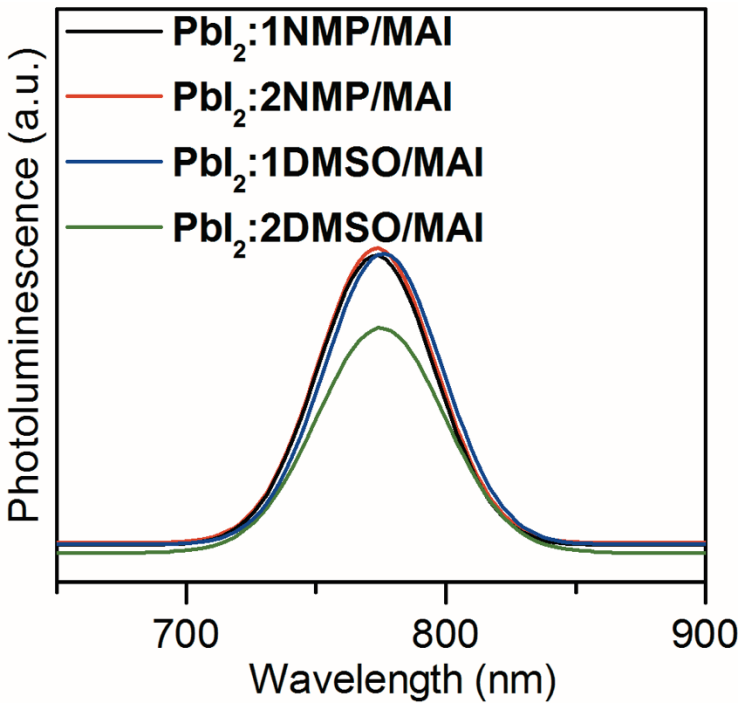

Figure S4. Steady-state photoluminescence spectra of perovskite films prepared with different PbI_2/NMP ratios. The quality of perovskite films made from NMP showed no dependence on PbI_2/NMP ratio, however, the PbI_2/DMSO ratio obviously affected the the quality of as-prepared perovskite films.

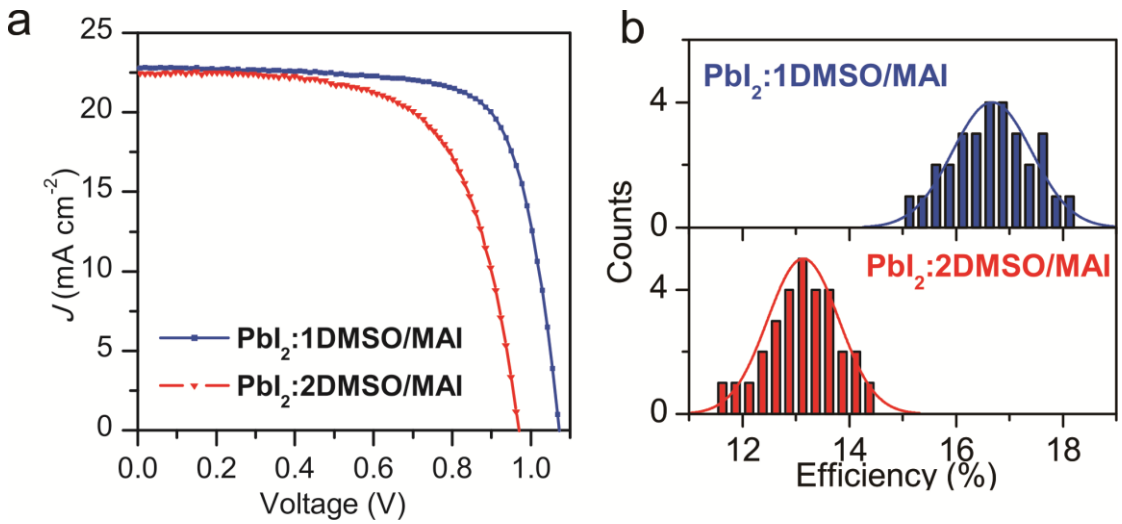

Figure S5. (a) Best *J-V* characteristics and (b) histograms of efficiencies among 30 cells of PSC devices with PbI_2:DMSO molar ratios of 1:1 and 1:2.

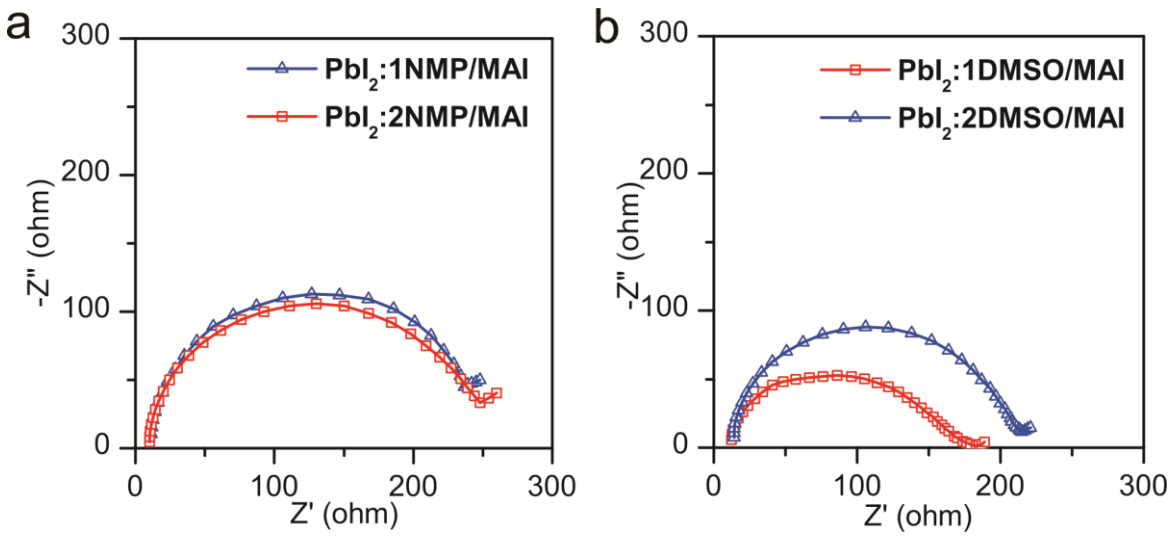

Figure S6. Electrical impedance spectroscopies (EIS) at 0 V bias under one sun illumination on whole devices with different perovskite layers: (a) PbI_2:1NMP and PbI_2:2NMP; (b) PbI_2:1DMSO and PbI_2:2DMSO. These impedances refer to the charge recombination rates in perovskite films.

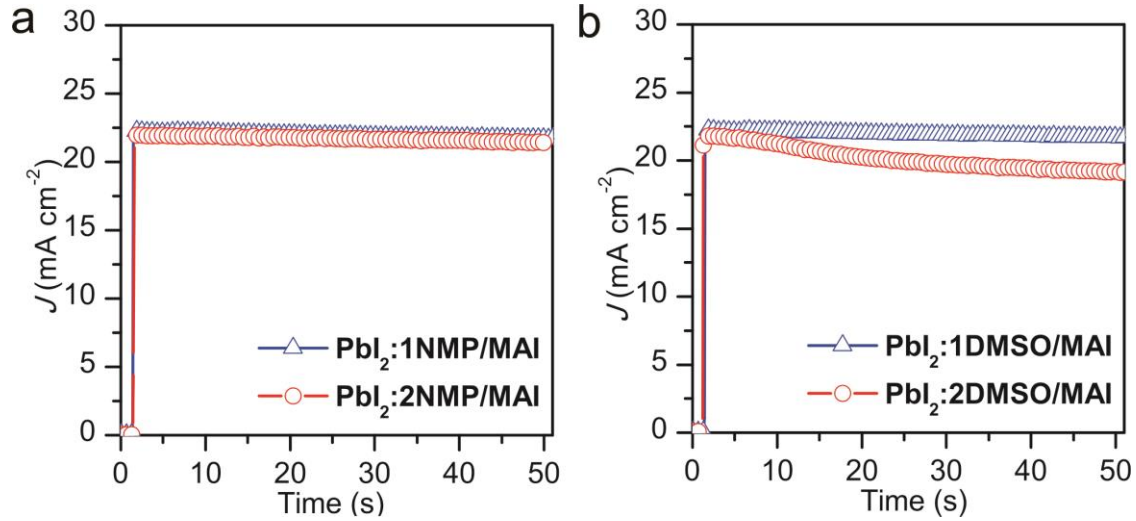

Figure S7. Stabilized outputs of current density measured as a function of time for devices fabricated with (a) PbI_2:1NMP and PbI_2:2NMP at their maximum power points (0.89 V bias and 0.88 V bias, respectively) and (b) PbI_2:1DMSO and PbI_2:2DMSO at their maximum power points (0.88 V bias and 0.82 V bias, respectively). The output of PbI_2:1NMP, PbI_2:2NMP and PbI_2:1DMSO devices maintained stable over 50 s, which was in good agreement with the *J-V* tests. In contrast, the PbI_2:2DMSO devices continuously degraded probably due to the presence of pinholes in the perovskite film (Figure S1).

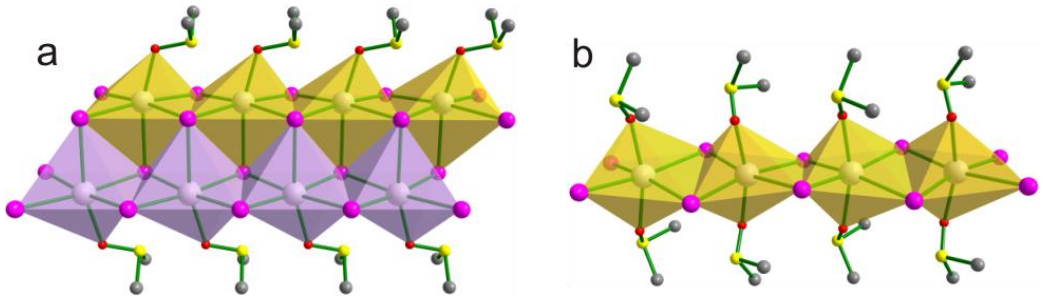

Figure S8. Crystal structure of (a) PbI_2·DMSO and (b) PbI_2·2DMSO.

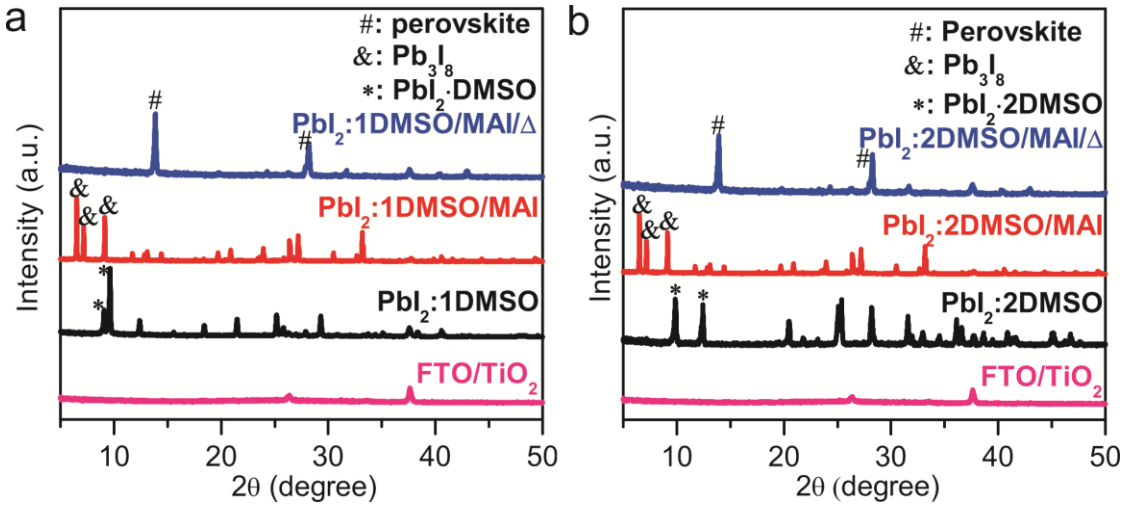

Figure S9. XRD patterns of the precursor films and the perovskite films (before and after annealing Δ) in the case of (a) PbI_2:1DMSO and (b) PbI_2:2DMSO.

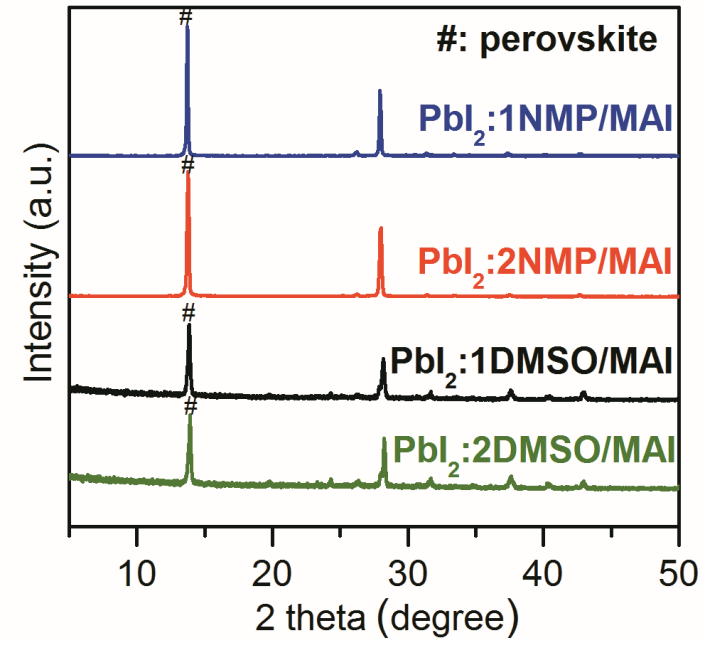

Figure S10. XRD patterns of the perovskite films deposited with PbI_2:1NMP, PbI_2:2NMP, PbI_2:1DMSO and PbI_2:2DMSO.

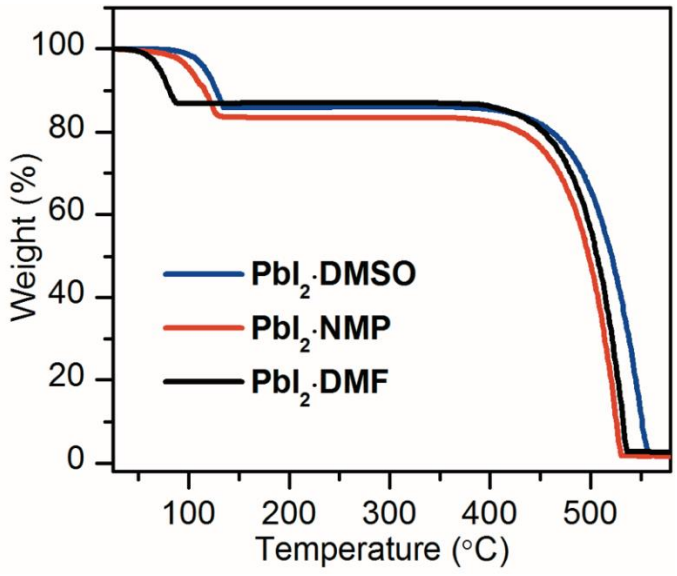

Figure S11. TGA curves of PbI_2·DMF, PbI_2·NMP and PbI_2·DMSO powder samples.

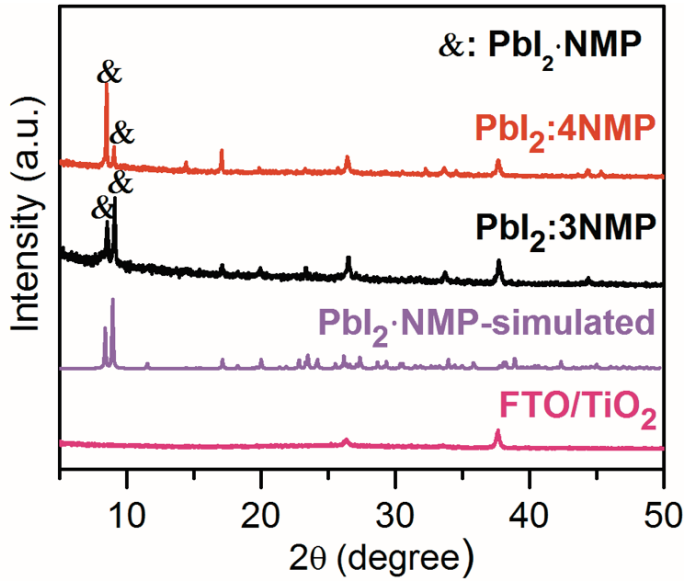

Figure S12. Comparison of simulated and experimental XRD patterns of precursor films prepared with PbI_2/NMP molar ratios of 1:3 and 1:4.

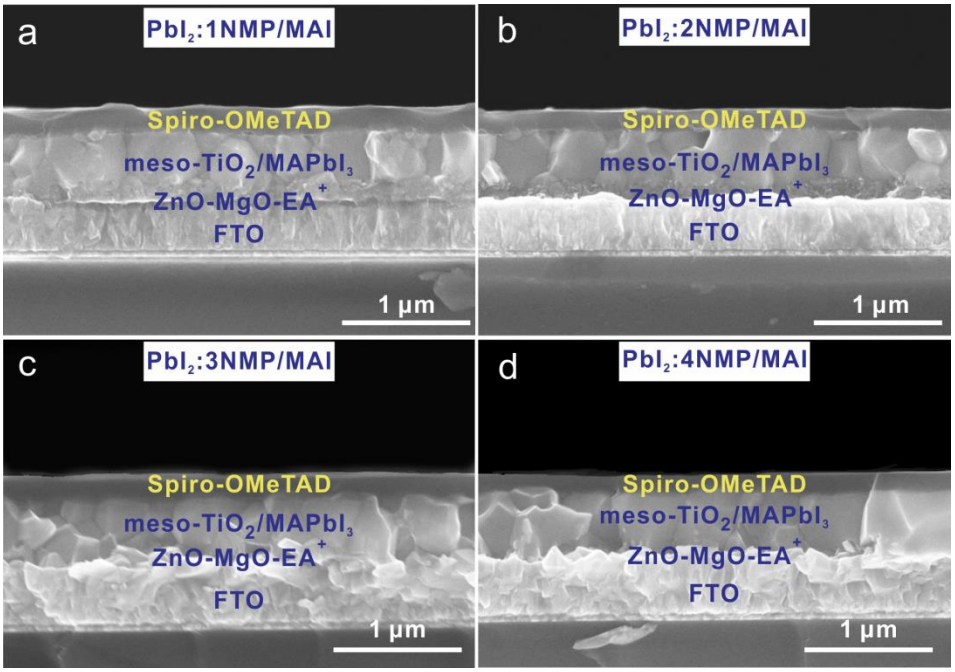

Figure S13. Cross-sectional SEM images of devices fabricated with PbI_2/NMP molar ratios of (a) 1:1, (b) 1:2, (c) 1:3 and (d) 1:4.

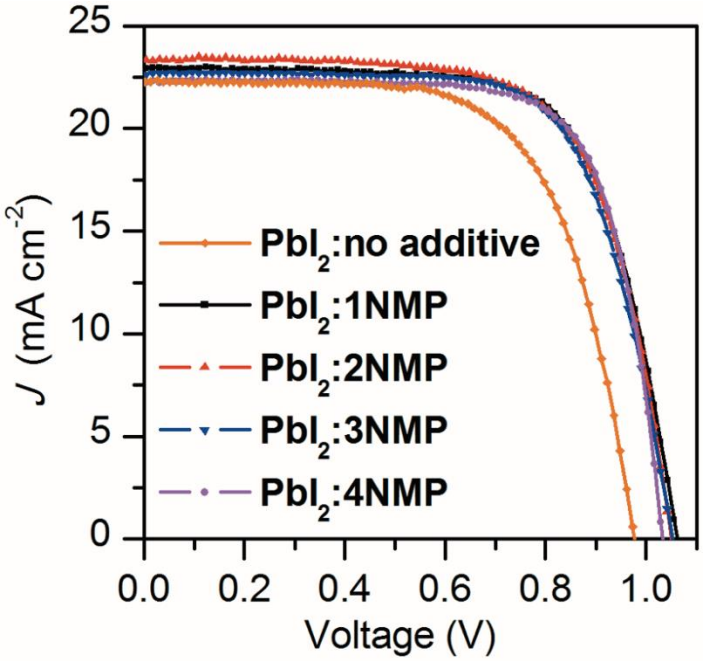

Figure S14. *J-V* characteristics of $MAPbI_3$ PSCs fabricated with different PbI_2/NMP ratios (from 1:0 to 1:4).

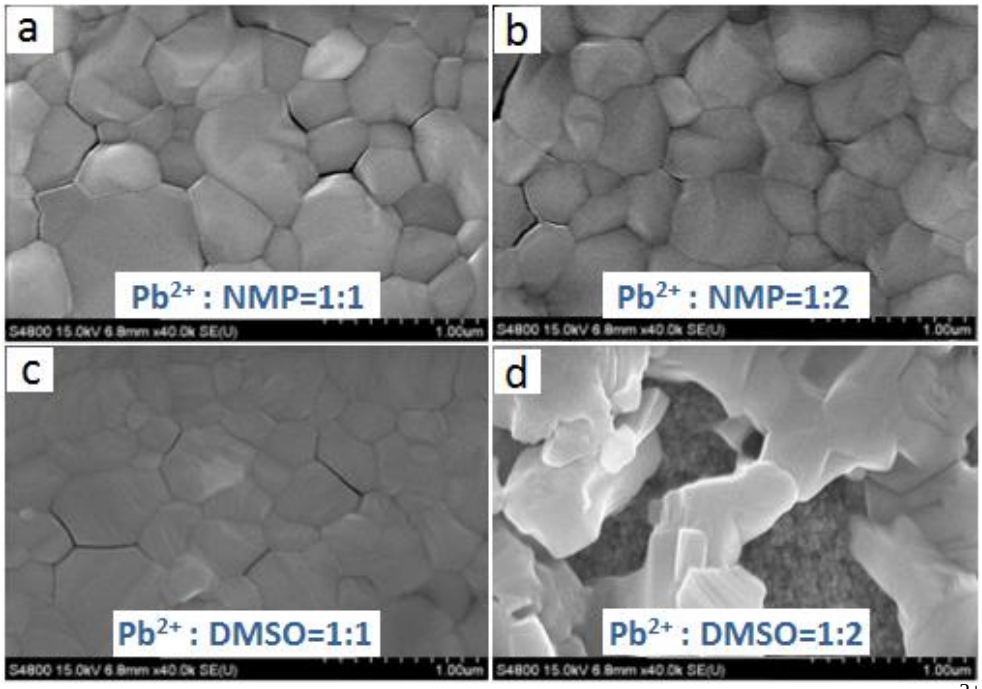

Figure S15. SEM images of Cs/FA/MA perovskite films prepared with Pb^{2+}/NMP molar ratios of (a) 1:1 and (b) 1:2 and Pb^{2+}/DMSO molar ratios of (c) 1:1 and (d) 1:2.

Table S1. Photovoltaic parameters of the champion cells with different molar ratios of PbI_2/NMP and different fabricated methods.

Devices	J_{sc}/mA·cm^{-2}	V_{oc}/V	*FF*/%	η/%	*Rs*/Ω·cm^{-2}
PbI_2:1NMP/MAI	23.5	1.07	75.6	19.1	3.41
PbI_2:2NMP/MAI	23.5	1.06	77.1	19.2	3.90
Pb^{2+}:1NMP/CsI-FAI-MABr	24.5	1.07	76.5	20.1	3.36
Pb^{2+}:2NMP/CsI-FAI-MABr	24.5	1.06	76.8	20.1	3.66

Table S2. Crystal data and structure refinement for PbI_2·NMP.

Complexes	PbI_2·NMP
Formula	$C_5H_9I_2NOPb$
M/g mol^{-1}	560.12
T/K	100.01(10)
Crystal system	Monoclinic
Space group	*P*2/*m*
a/Å	4.6337(2)
b/Å	19.1129(8)
c/Å	12.1265(5)
α/deg	90
β/deg	98.144(4)
γ/deg	90
V/$Å^3$	1063.13(8)
Z	4
d_{cal}/g cm^{-3}	3.499
Limiting indices	-5 <= h <= 6, -23 <= k <= 24, -15 <= l <= 11
Reflections collected / unique	2422/2177 [*R(int)* = 0.0655]
Goodness-of-fit on F^2	1.049
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0564 wR_2 = 0.1386