Supplementary information

for the manuscript

Enhancing the MA-free mixed halide perovskite efficiency and stability through bi-solvent engineering approach

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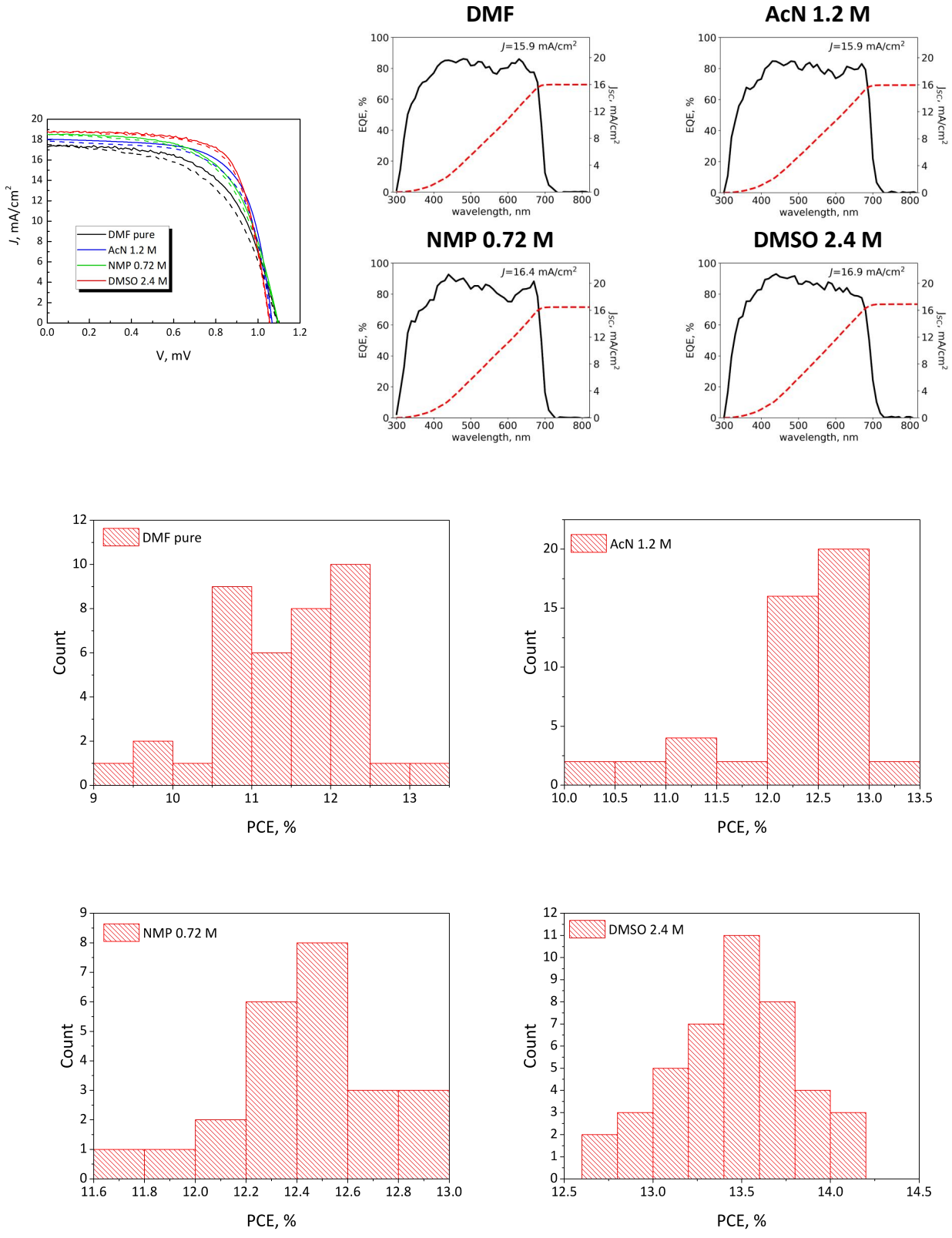


Figure S1. J-V curves for the best solar cells based on various solvent combinations utilized for perovskite layer production, EQE for average representative solar cell samples and PCE statistics. The reduced value of current measured by EQE occurs because of extreme degradation of perovskite material under the laser exposure during the measurement.

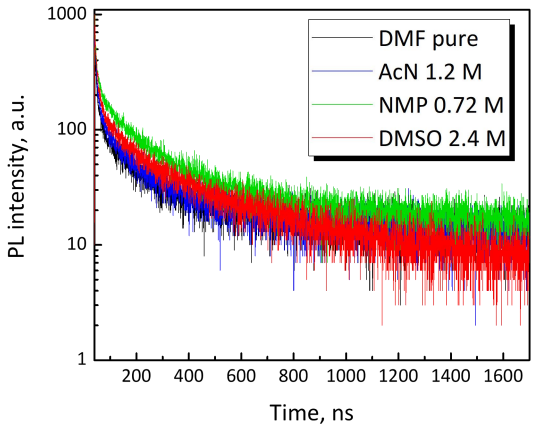


Figure S2. TRPL decays for perovskite films on glass substrates processed from various solvent combinations.

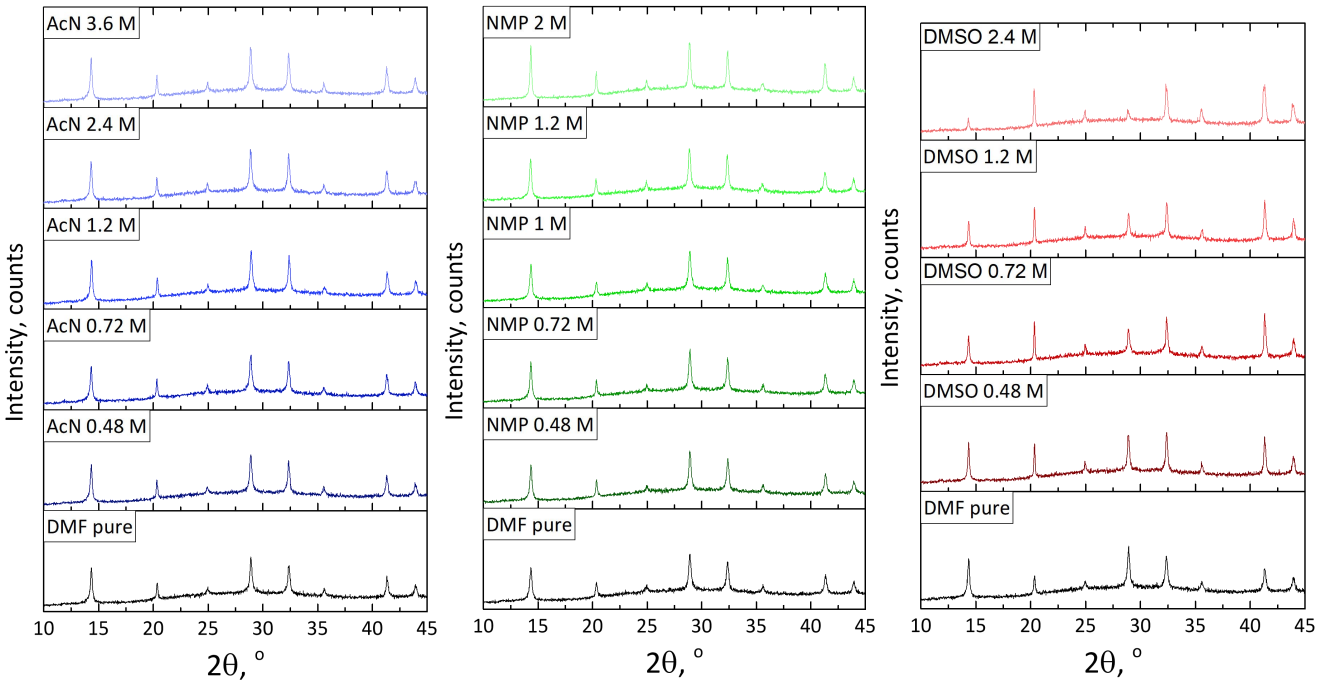
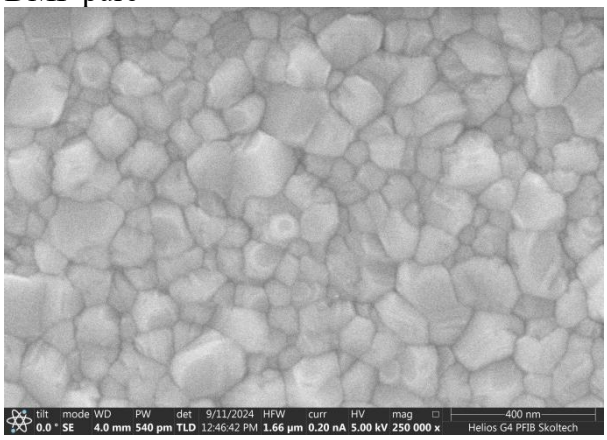
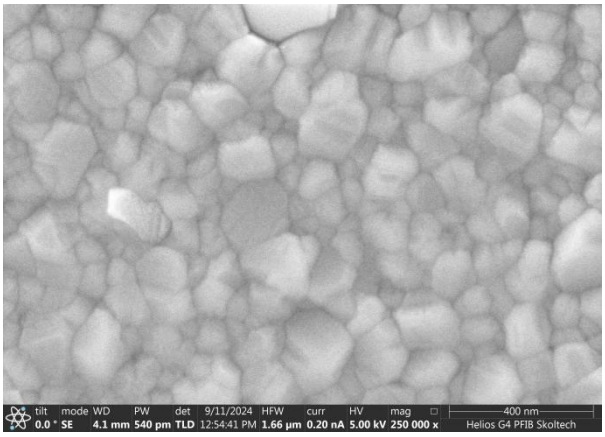


Figure S3. XRD evolution for various co-solvent concentrations.

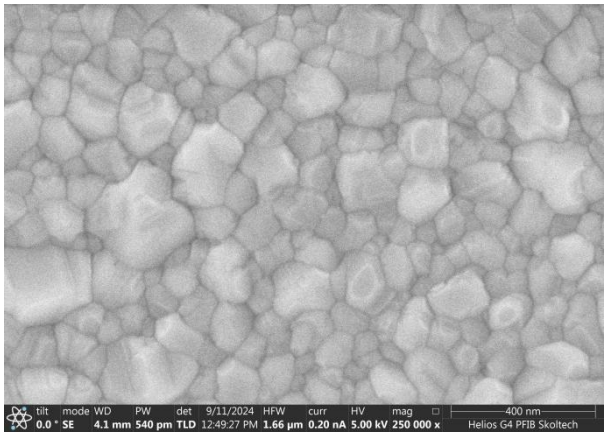
DMF pure



AcN 1.2 M



NMP 0.72 M



DMSO 2.4 M

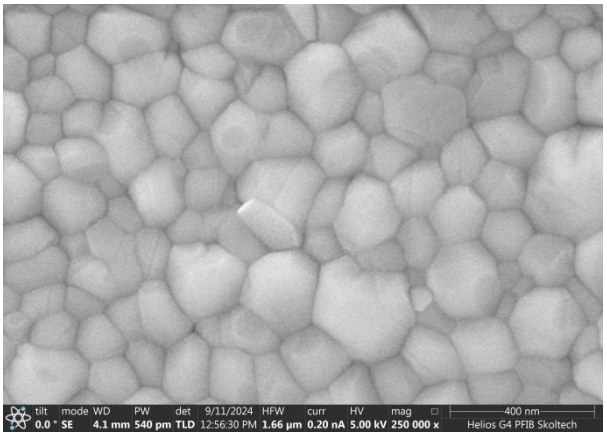


Figure S3. SEM analysis of perovskite film surfaces.

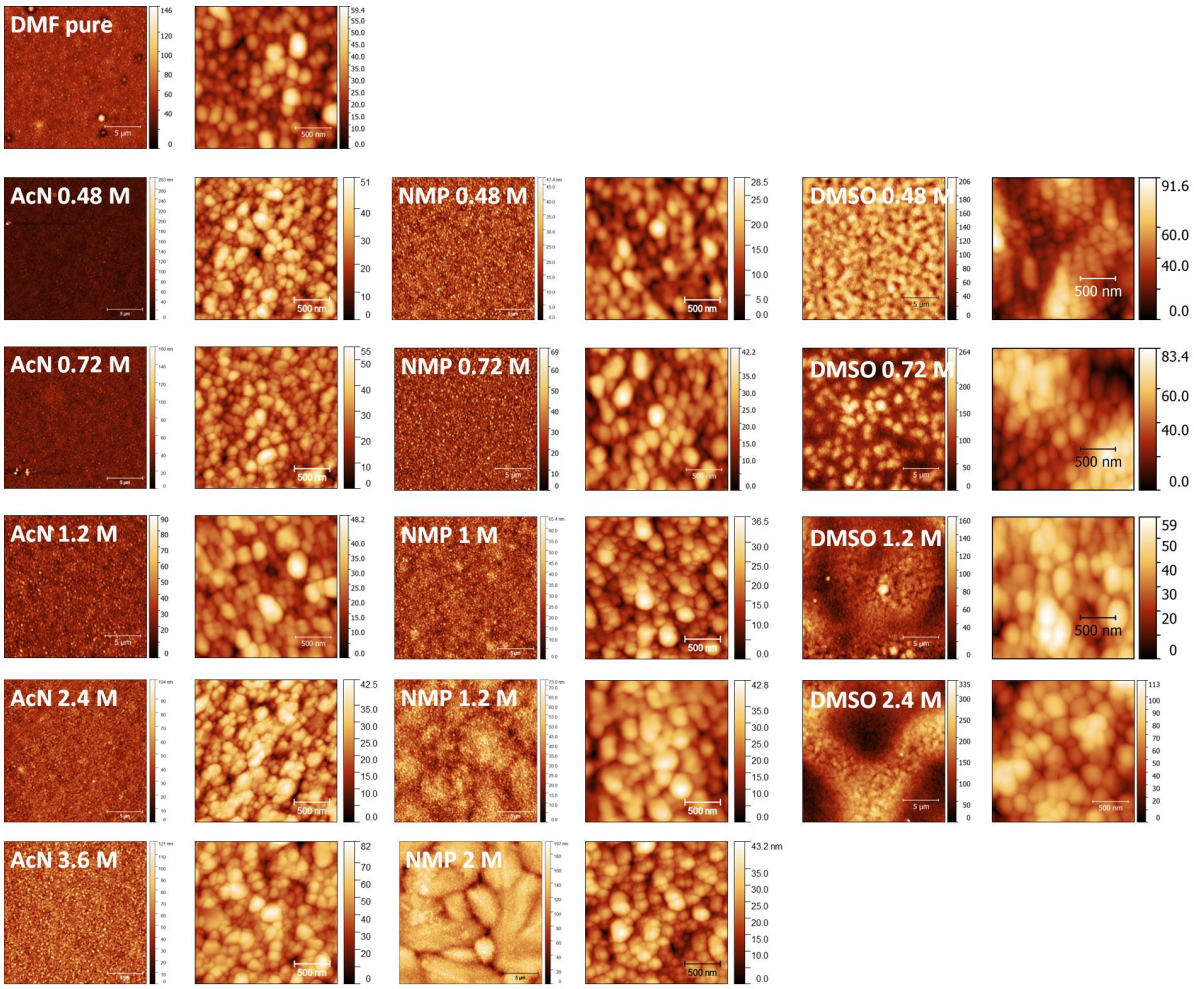


Figure S5. AFM profiles of perovskite thin films processed from various solvent combinations

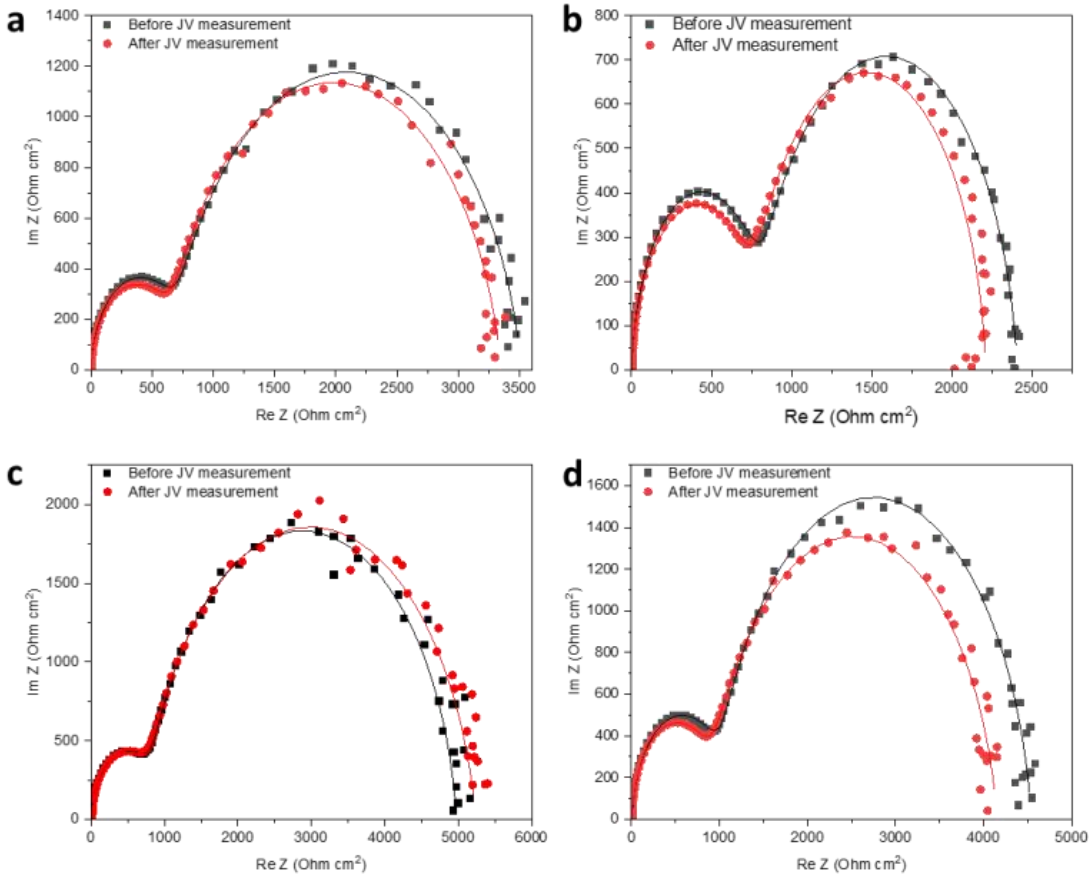


Figure S6. Nyquist plots of dark impedance spectra for PSCs with the active layer deposited from DMF (a), DMF:DMSO (b), DMF:NMP(c), and DMF:AcN (d).

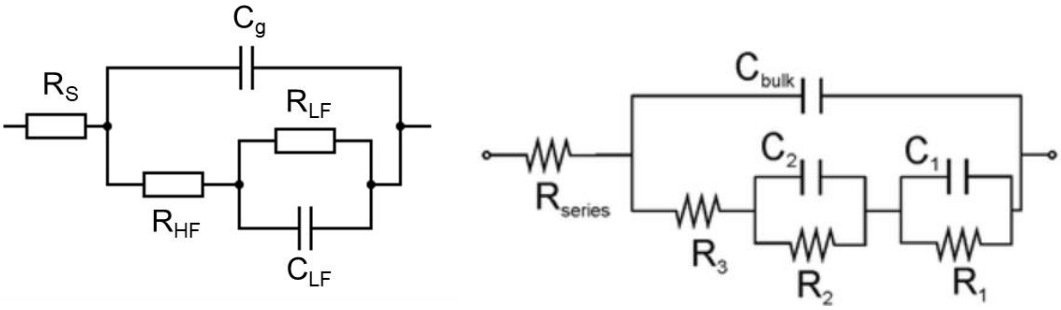


Figure S7. Equivalent circuits used for the fitting of impedance spectroscopy data obtained for perovskite solar cells. For the majority of Nyquist plots the left circuit was implemented, except the DMSO 2.4 M at 100 mW/cm^2 curve where the third semicircle appeared. For DMSO 2.4 M at 100 mW/cm^2 curve the right circuit was used for the fit.

Table 1. Parameters of the solar cells calculated from the 100 mW/cm^2 and 3 mW/cm^2 fitted Nyquist plots.

Solvent	R_S, Ohm	C_g, F	R_{HF}, Ohm	R_{LF}, Ohm	R_{rec}, Ohm	C_{LF}, F	R_{MF}, Ohm	C_{MF}, F
100 mW/cm^2								
DMF	26.2	1E-8	71	23	95	6.4E-4	-	-
AcN	22.9	2.1E-8	30	15	45	5.65E-4	-	-
NMP	22.3	1.6E-8	118	24	142	5.16E-4	-	-
DMSO	16.8	1.2E-8	108	15	123	4.6E-4	36	4.9E-7
3 mW cm^{-2}								
DMF	24.9	2.7E-8	509	53	562	2.3E-5	-	-
AcN	16.8	1.9E-8	387	91	478	1.2E-4	-	-
NMP	16.9	3.3E-8	722	310	1032	2.7E-5	-	-
DMSO	11.2	2.3E-8	785	236	1021	6.7E-5	-	-

Table 2. Parameters of the solar cells calculated from the dark fitted Nyquist plots.

	C_g, F cm^{-2}	R_{HF}, Ohm cm^2	R_{LF}, Ohm cm^2	C_{LF}, F cm^{-2}
DMF				
Before JV	$1.8*10^{-7}$	758	2758	$5.4*10^{-6}$
After JV	$2.0*10^{-7}$	715	2632	$5.3*10^{-6}$
DMF:DMSO				
Before JV	$1.4*10^{-7}$	852	1556	$6.1*10^{-6}$
After JV	$1.8*10^{-7}$	822	1391	$4.8*10^{-6}$
DMF:NMP				
Before JV	$1.7*10^{-7}$	934	4046	$2.5*10^{-6}$
After JV	$1.2*10^{-7}$	861	4368	$2.9*10^{-6}$
DMF:AcN				
Before JV	$1.6*10^{-7}$	1090	3456	$3.7*10^{-6}$
After JV	$1.3*10^{-7}$	985	3168	$4.4*10^{-6}$

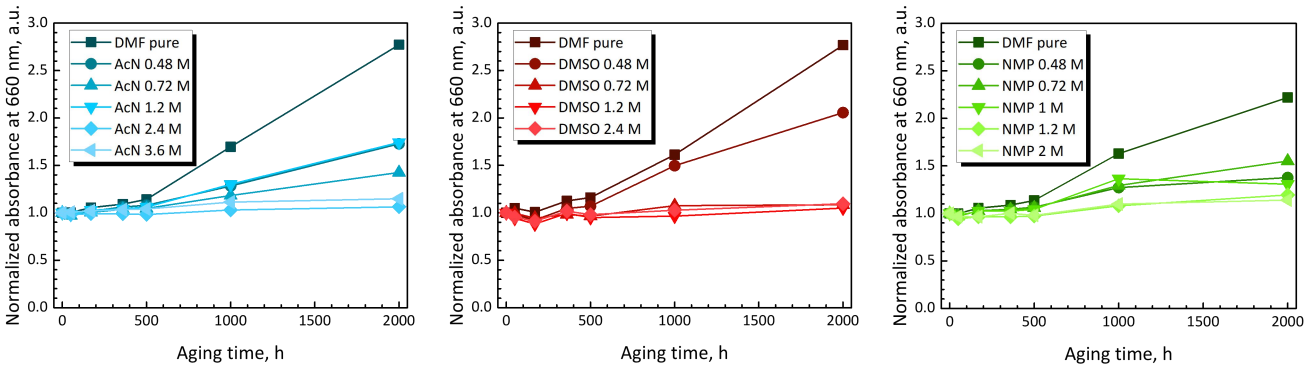


Figure S8. Relative normalized stability of perovskite thin films covered with PTAA/VO_x calculated by UV-Vis at 660 nm wavelength.

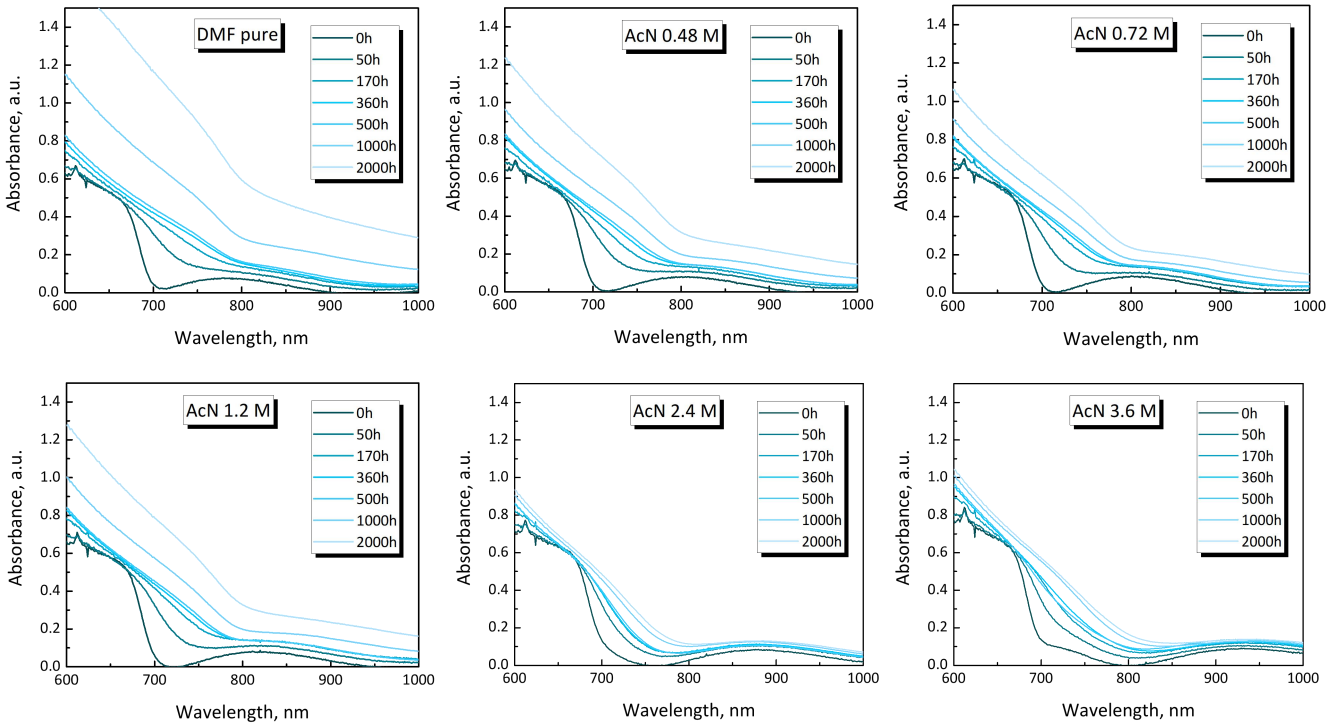


Figure S9. Evolution of UV-Vis spectra of perovskite films covered with PTAA/VOx for various AcN co-solvent concentrations.

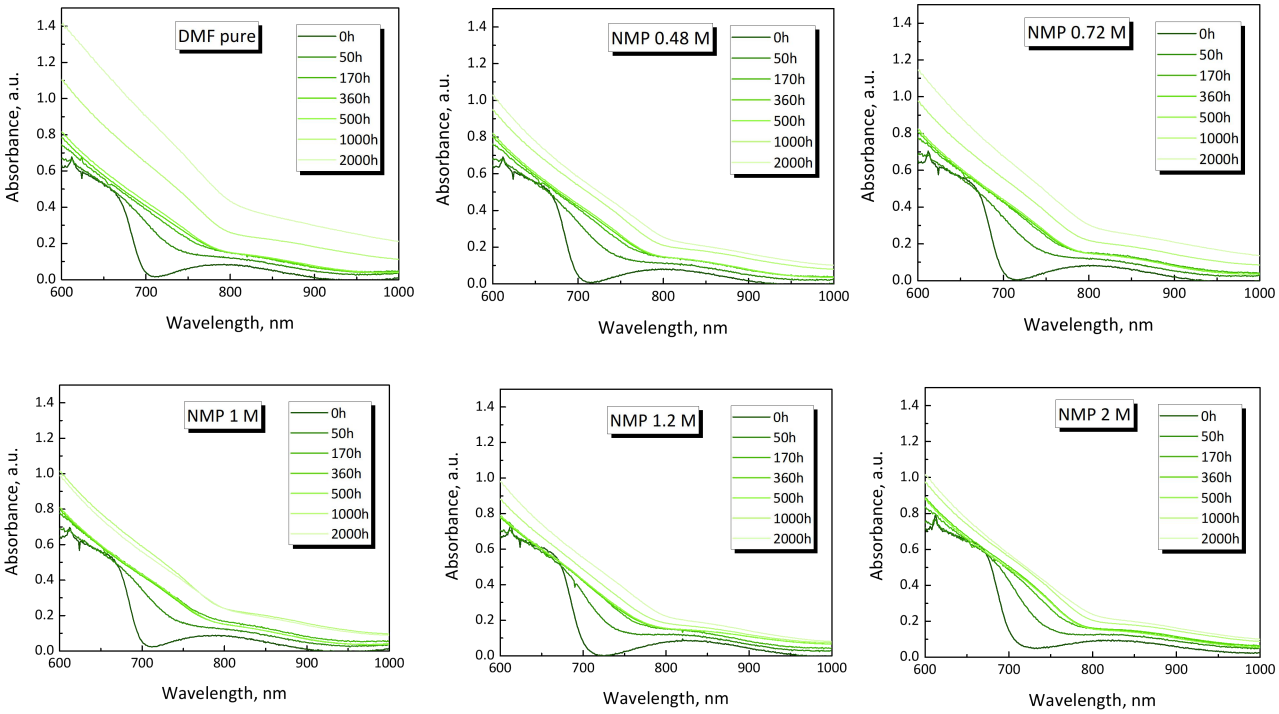


Figure S10. Evolution of UV-Vis spectra of perovskite films covered with PTAA/VOx for various NMP co-solvent concentrations.

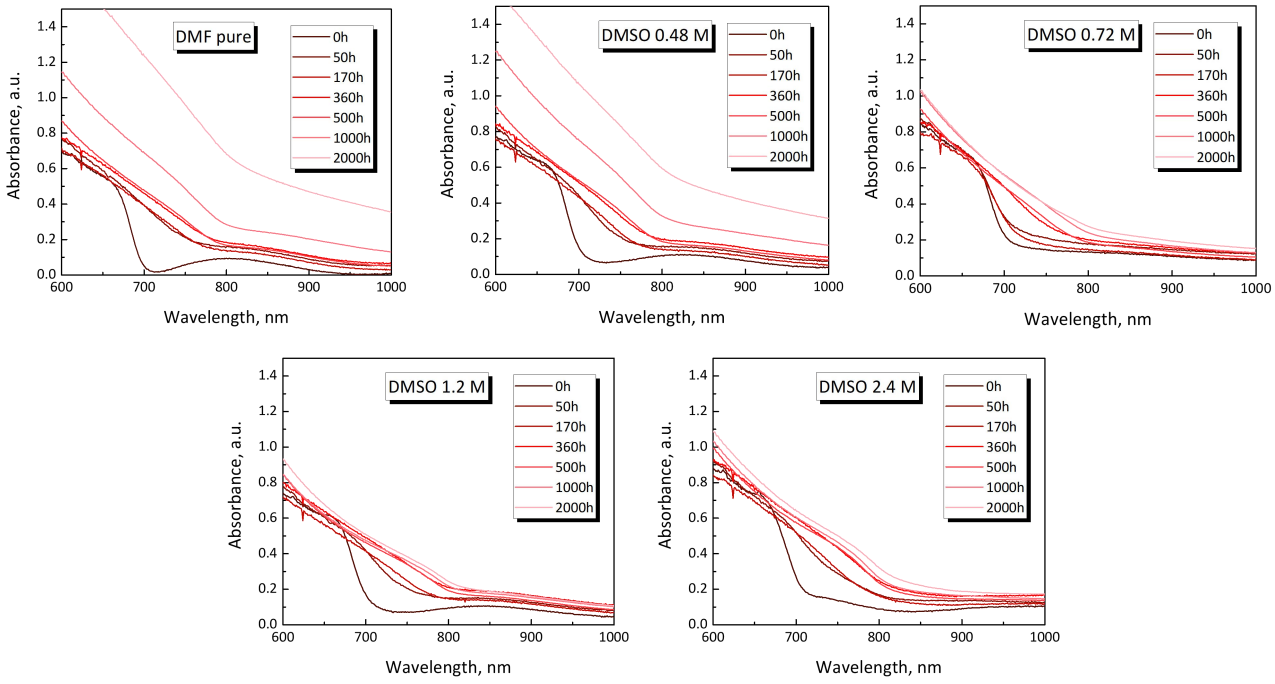


Figure S11. Evolution of UV-Vis spectra of perovskite films covered with PTAA/VOx for various DMSO co-solvent concentrations.

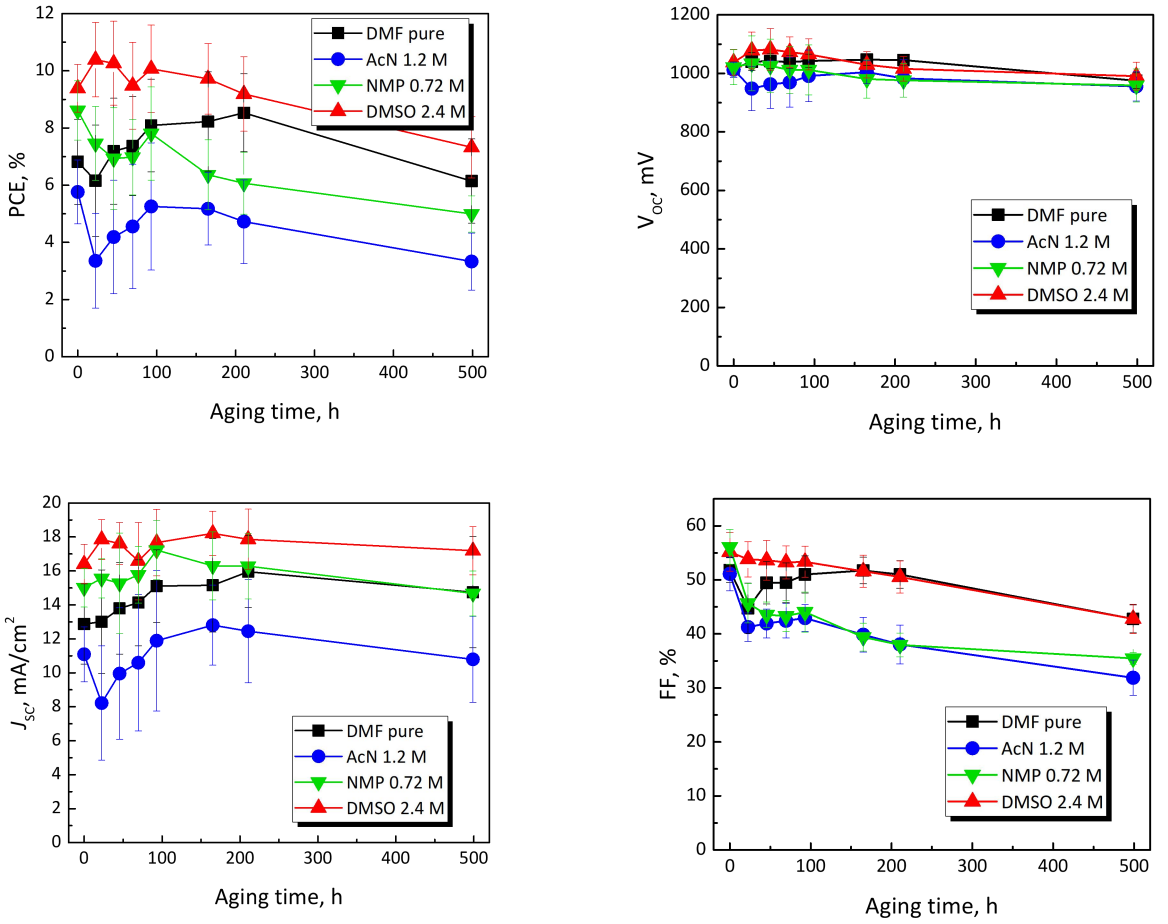


Figure S12. Evolution of solar cell parameters under the light exposure of 100 mW/cm^2

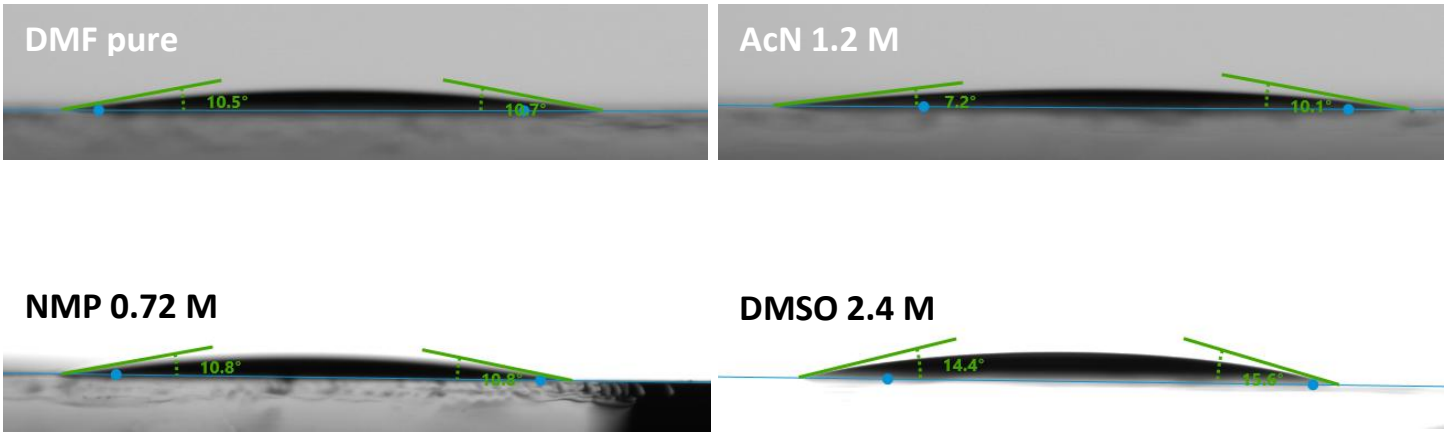


Figure S13. Photos of contact angle measured for perovskite solution droplets placed on ITO/SnO_2/PCBA substrates with calculated contact angle values.

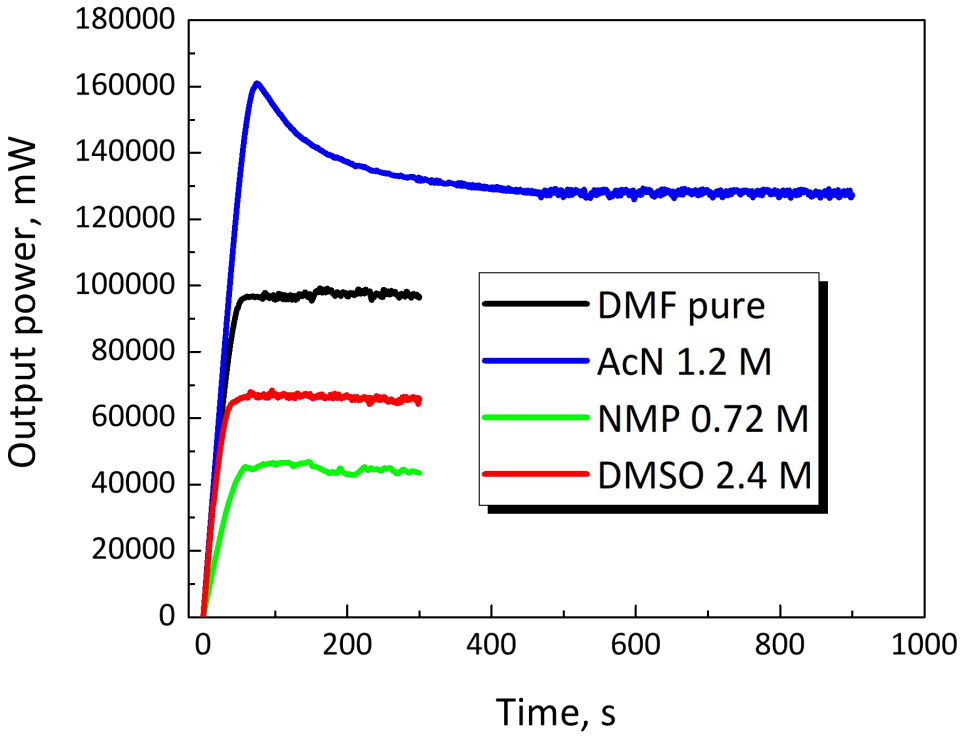


Figure S14. MPPT tracking for mini-modules with various perovskite layers

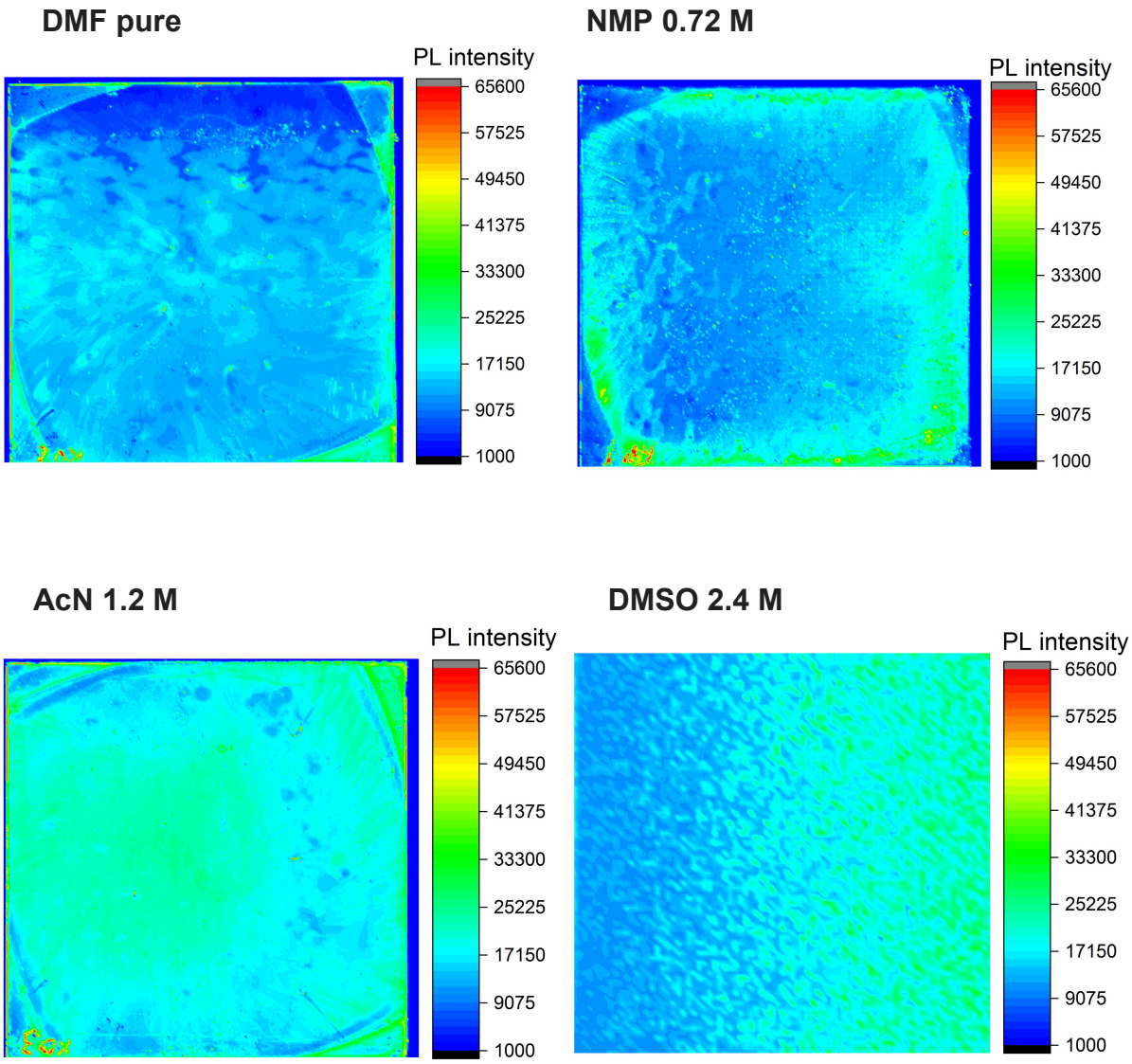


Figure S15. PL mapping for 5x5 cm perovskite films on glass substrates spincoated from various solvents

Table 3. Properties of all the implemented solvents

	Formula	Density	Boiling temperature	Dynamic viscosity	Dipole moment
DMF	$(CH_3)_2NC(O)H$	0.94 g/cm^3	153°C	0.92 mPa·s	3.82
AcN	CH_3CN	0.79 g/cm^3	82°C	0.35 mPa·s	3.92
NMP	$(CH_3)C_4H_6NO$	1.03 g/cm^3	202°C	1.65 mPa·s	4.09
DMSO	$(CH_3)_2OS$	1.10 g/cm^3	189°C	1.996 mPa·s	3.96

Table 4. Grain size distribution for all solvent systems, calculated from 2D AFM data. Data for the reference and optimized concentrations with best device efficiencies is highlighted green.

DMSO concentration	Avg grain size, nm	RMS, nm	**NMP** concentration	Avg grain size, nm	RMS, nm	**AcN** concentration	Avg grain size, nm	RMS, nm
DMF pure	117.28	113.62						
0.48 M	140.08	144.84	0.48 M	135.8	117	0.48 M	90.5	83.62
0.72 M	89.36	76.34	0.72 M	163.38	167.32	0.72 M	96.26	90.34
1.2 M	180.14	182.24	1.0 M	129.9	119.26	1.2 M	134.68	135.14
2.4 M	162.28	166.18	1.2 M	130.6	109.4	2.4 M	79.48	73.76
2.8 M	194.26	183.68	2.0 M	118.98	113.92	3.6 M	104.18	94.54