ADVANCED ENERGY MATERIALS

Supporting Information

for *Adv. Energy Mater.,* DOI: 10.1002/aenm.201903365

CsI-Antisolvent Adduct Formation in All-Inorganic Metal Halide Perovskites

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Table S1: Properties of chosen antisolvents[1,2]

	DMSO	CB	Tol	DEE	Anisole	EtOAc	MeOAc
Boiling Point [^{o}C]	189	131	111	35	154	77	57
Vapor Pressure [Pa]	56	1587	2933	52702	472	9732	23065
Hildebrand [MPa$^{1/2}$]	26.7	19.6	18.2	15.8	19.5	18.1	18.7
Hansen – Polar [MPa$^{1/2}$]	16.4	4.3	1.4	2.9	4.1	5.3	7.2
Gutmann's donor number [kcal/mol]	29.8	3.3	0.1	19	9	17.1	16.3

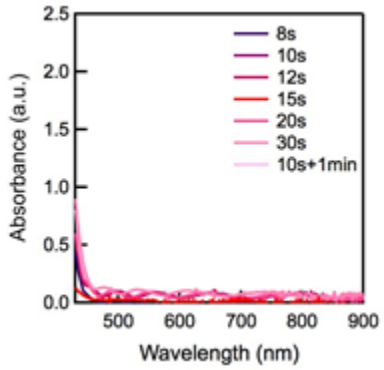

Figure S1: UV-Vis absorbance of CB as-quenched films where the antisolvent was added at different times.

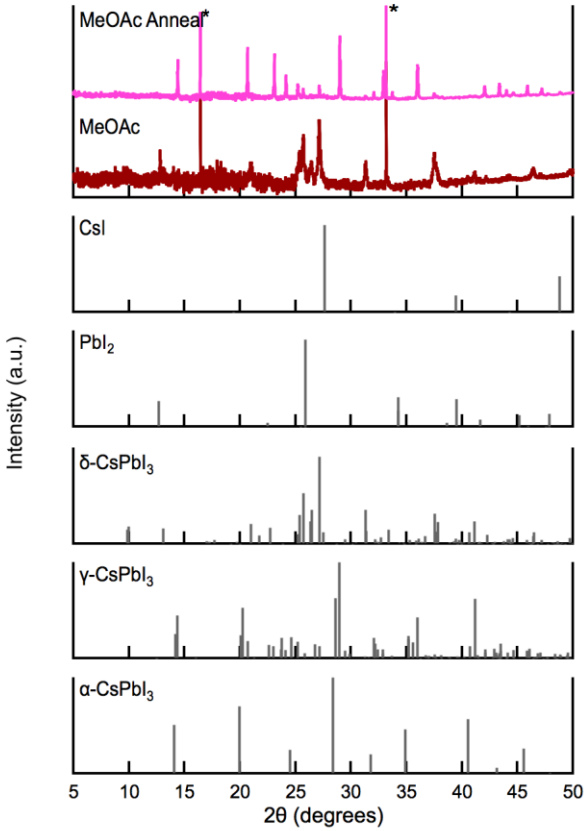

Figure S2: XRD of as-quenched (red) and annealed at 330 ^{o}C (pink) MeOAc films with relevant ICSD XRD spectra of CsI, PbI_2, δ-$CsPbI_3$, γ-$CsPbI_3$ and α-$CsPbI_3$.

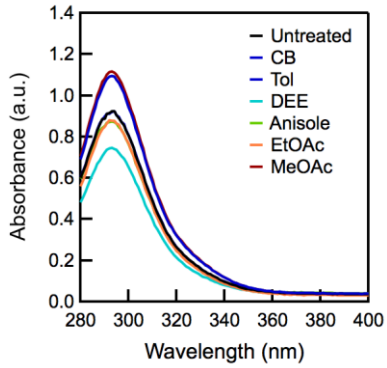

Figure S3: UV-Vis of NMR samples made up of 5 as-quenched films dissolved in deuterated DMSO for untreated (black), CB (purple), Tol (dark blue), DEE (turquoise), anisole (green), EtOAc (orange) and MeOAc (red) antisolvent treatments.

Table S2: Residual DMSO and DMF amounts in each as-quenched film, normalized to the PbI_2 UV-Vis peak.

	Untreated	CB	Tol	DEE	Anisole	EtOAc	MeOAc
DMF	2.180	2.141	1.101	1.718	1.979	1.731	2.295
DMSO	32.865	28.362	17.488	21.713	23.077	15.605	9.685

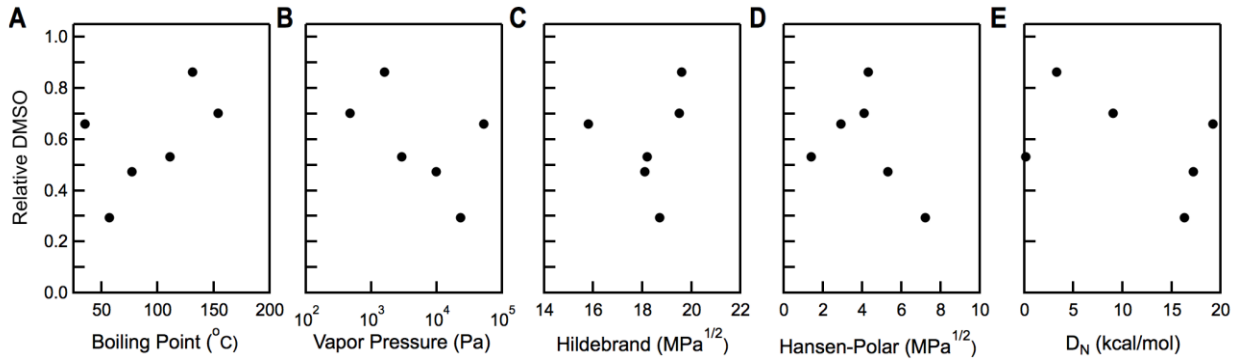

Figure S4: Relative DMSO amount compared to various antisolvent parameters, **A**) boiling point, **B**) vapor pressure, **C**) Hildebrand parameter, **D**) polar Hansen parameter, **E**) Gutmann's donor number (D_N).

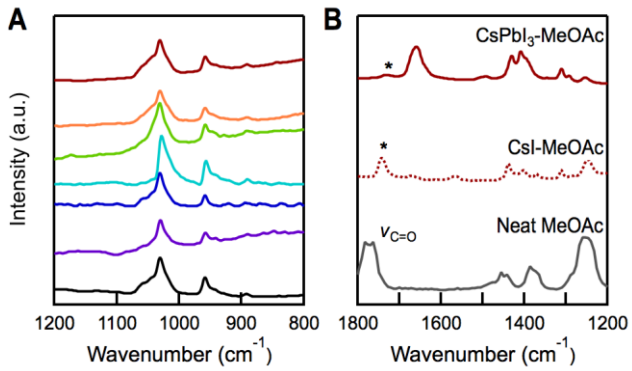

Figure S5: FTIR spectra of **A**) DMSO-CsI complex in the as-quenched films for untreated (black), CB (purple), Tol (dark blue), DEE (turquoise), anisole (green), EtOAc (orange) and MeOAc (red) antisolvent treatments. **B**) MeOAc complex with $CsPbI_3$ (solid red) and CsI (dashed red) as compared to a neat MeOAc (grey) FTIR spectra with * denoting MeOAc. The neat MeOAc FTIR spectra was obtained from the NIST spectral database.

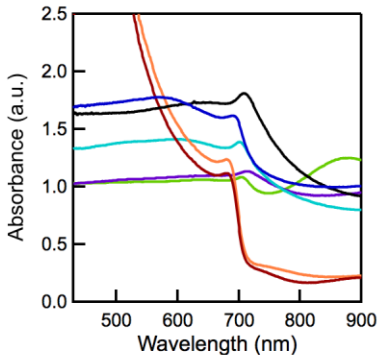

Figure S6. UV-Vis absorbance spectra of annealed films for untreated (black), CB (purple), Tol (dark blue), DEE (turquoise), anisole (green), EtOAc (orange) and MeOAc (red) antisolvent treatments.

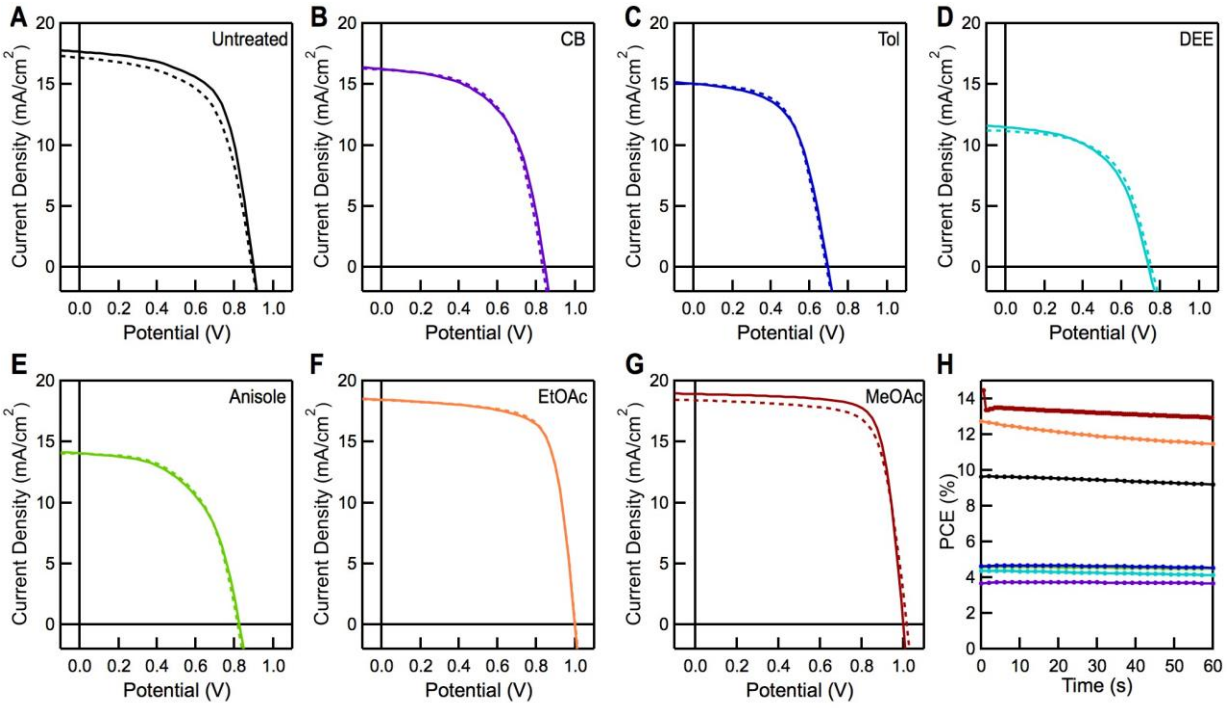

Figure S7: Champion JV curves for **A**) untreated, **B**) CB, **C**) Tol, **D**) DEE, **E**) Anisole, **F**) EtOAc, **G**) MeOAc and **H**) SPO.

Table S3: Average and champion device performance for each antisolvent

		Voc [V]	Jsc [mA/cm^2]	FF [%]	PCE [%]	SPO [%]
Untreated	Average +/- Stdev	0.809 +/- 0.083	16.71 +/- 0.96	55.0 +/- 7.1	7.56 +/- 1.70	
	Champion Device	**0.899**	**17.67**	**62.7**	**9.96**	**9.20**
Chlorobenzene	Average +/- Stdev	0.676 +/- 0.110	13.26 +/- 1.65	51.1 +/- 6.8	4.75 +/- 1.61	
	Champion Device	**0.844**	**16.25**	**56.6**	**7.77**	3.68
Toluene	Average +/- Stdev	0.593 +/- 0.120	11.30 +/- 3.07	47.8 +/- 7.3	3.30 +/- 1.37	
	Champion Device	**0.693**	**15.04**	**57.9**	**6.04**	4.55

Diethyl Ether	Average +/- Stdev	0.608 +/- 0.077	10.89 +/- 1.97	50.4 +/- 3.8	3.36 +/- 0.87	
	Champion Device	**0.739**	**11.47**	**53.9**	**4.56**	**4.14**
Anisole	Average +/- Stdev	0.686 +/- 0.107	13.15 +/- 0.91	52.4 +/- 5.3	4.82 +/- 1.18	
	Champion Device	**0.825**	**14.06**	**54.5**	**6.32**	4.49
Ethyl Acetate	Average +/- Stdev	0.903 +/- 0.091	17.74 +/- 0.96	60.1 +/- 8.7	9.84 +/- 2.64	
	Cha4pion Device	**0.999**	**18.44**	**71.7**	**13.20**	**11.47**
Methyl Acetate	Average +/- Stdev	0.951 +/- 0.056	18.60 +/- 0.51	72.9 +/- 4.1	12.95 +/- 1.43	
	Champion Device	**0.998**	**18.93**	**76.3**	**14.42**	**12.30**

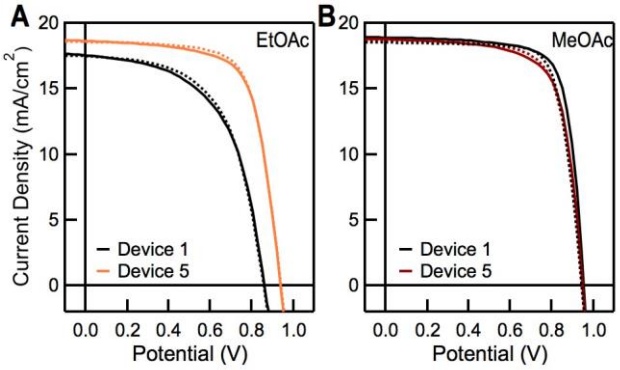

Figure S8: Performance of **A**) EtOAc and **B**) MeOAc with a clean (device 1) and solvent rich atmosphere (device 5).

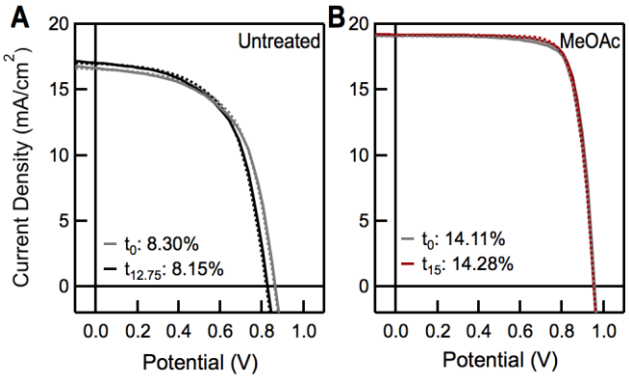

Figure S9. Performance of representative **A**) Untreated and **B**) MeOAc devices unaged ($t_{0,}$ grey) and aged in the dark in N_2 for > 12 hrs (t_x) and the reverse curve PCE. On average, there is a small decrease in PCE from 7.10 ± 1.67 % to 6.74 ± 2.11 % after storage for the untreated devices that was not seen for MeOAc devices which maintained PCE from 12.79 ± 0.89 % to 12.88 ± 0.75 %, although all decreases are within the standard deviation and thus not significant in this timeframe.

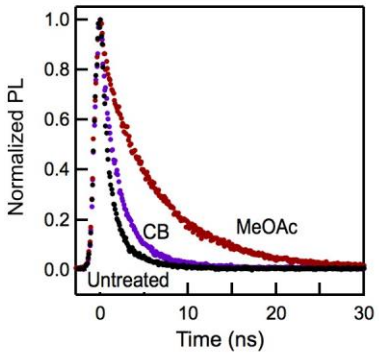

Figure S10: TRPL lifetimes of untreated (black, τ_{avg} = 1.4 ns), CB (purple, τ_{avg} = 2.2 ns) and MeOAc (red, τ_{avg} = 6.4 ns).

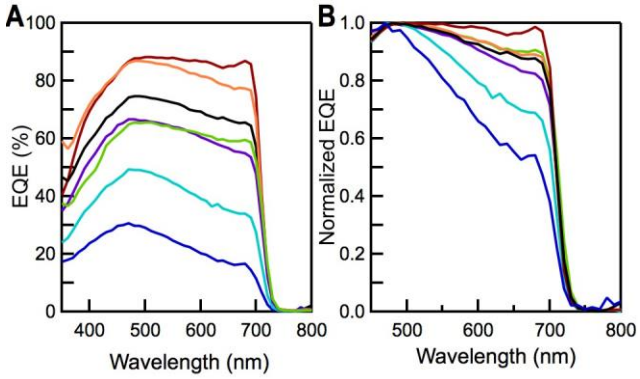

Figure S11: **A**) EQE and **B**) normalized EQE for devices made with untreated (black), CB (purple), Tol (dark blue), DEE (turquoise), anisole (green), EtOAc (orange) and MeOAc (red) antisolvent treatment.

References:

[1] F. Cataldo, *Eur. Chem. Bull* **2015**, *4*, 92.

[2] C. M. Hansen, in *The Three Dimensional Solubility Parameter and Solvent Diffusion Coefficient*, **1967**, pp. 13–30.