Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary information

Exploring the formation of formamidinium-based hybrid perovskites by antisolvent methods: *in situ* GIWAXS measurements during spin coating

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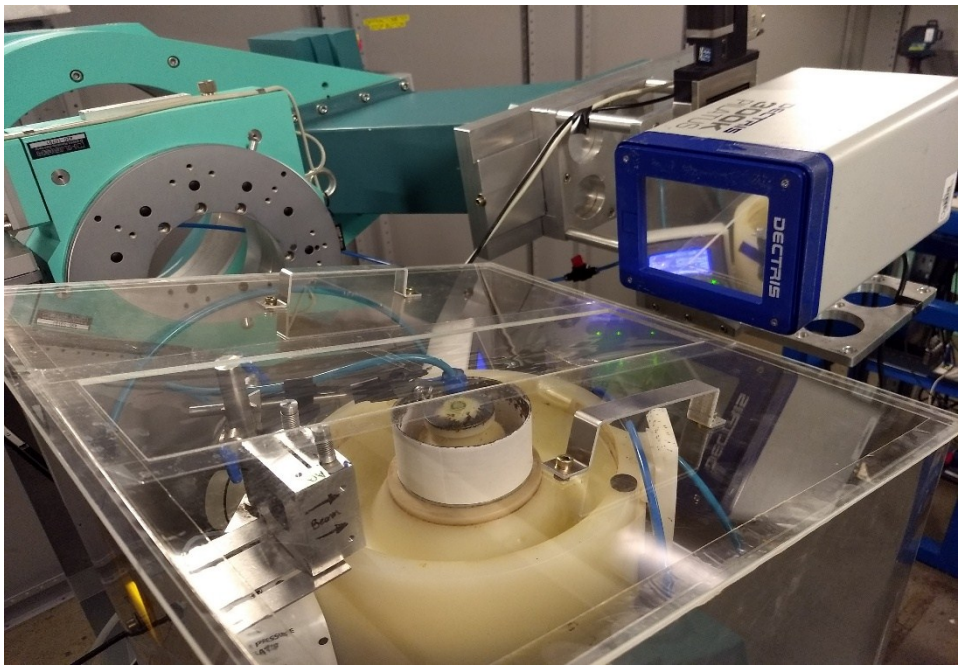

Figure S1: Photograph of the setup at XRD2/LNLS beamline.

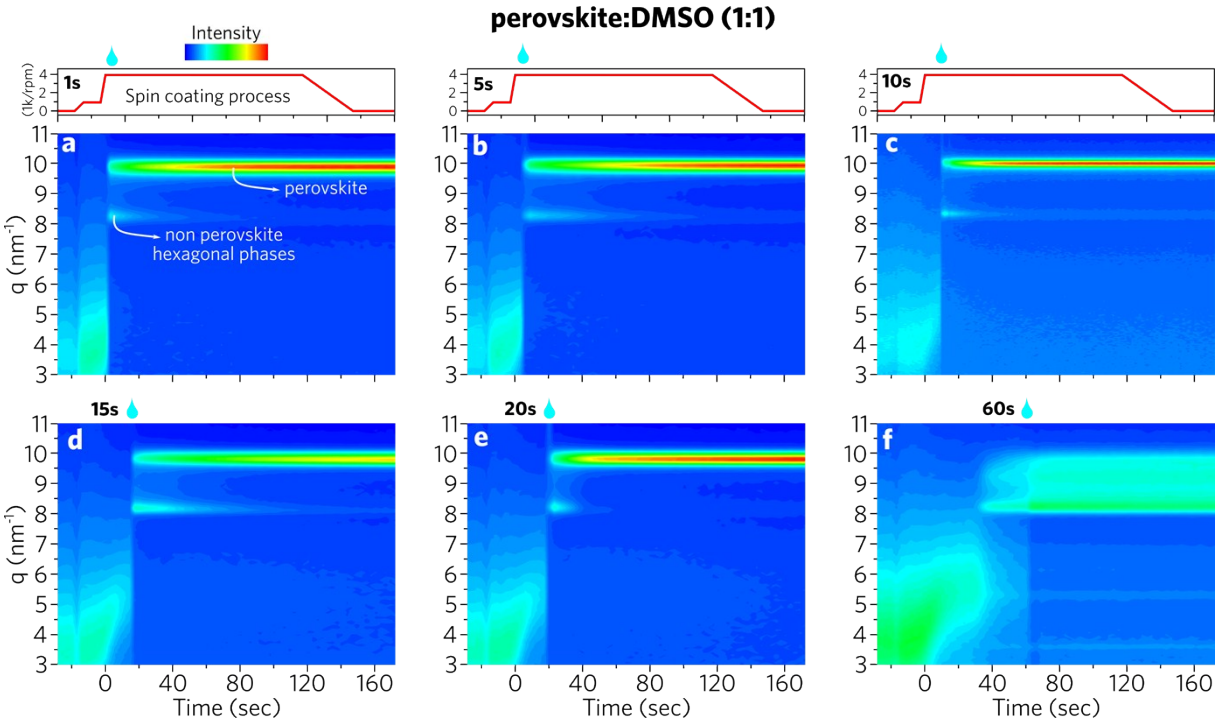

Figure S2: Scattering maps during spin coating for 1:1 PVSK:DMSO ratio at 20% rH in the CsFA perovskite with antisolvent drip time at (a) 1, (b) 5, (c) 10, (d) 15, (e) 20 and (f) 60s

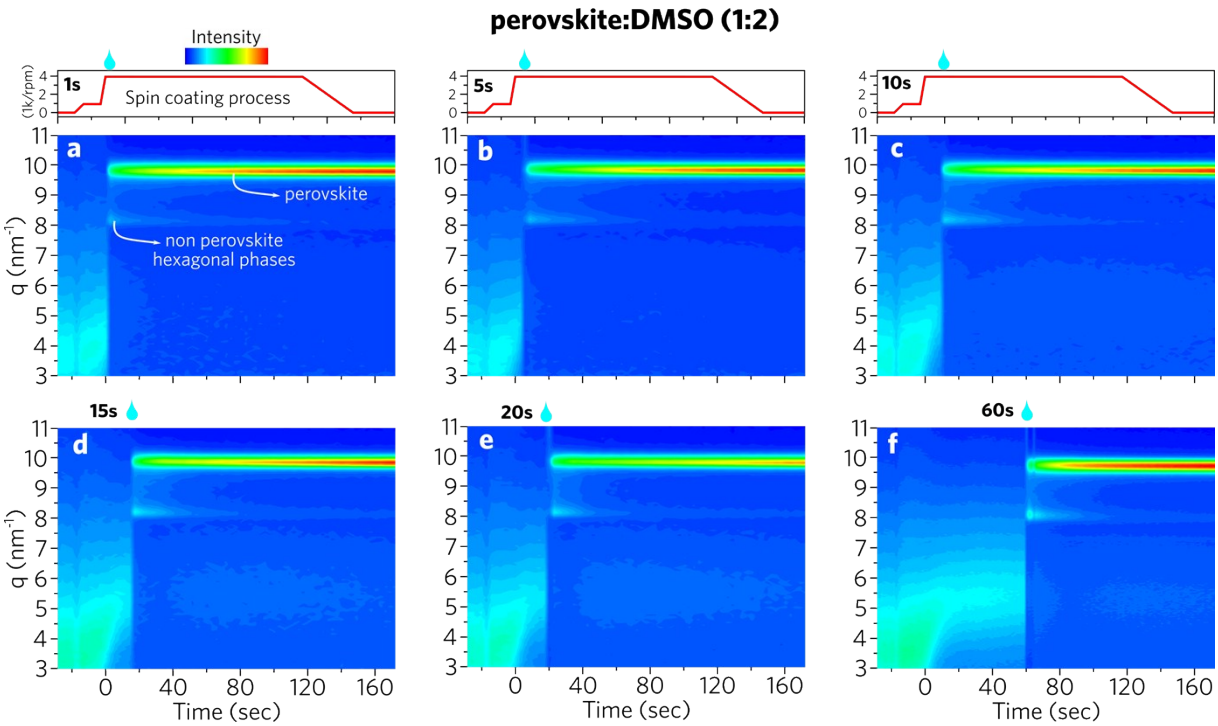

Figure S3: Scattering maps during spin coating for 1:2 PVSK:DMSO ratio at 20% rH in the CsFA perovskite with antisolvent drip time at (a) 1, (b) 5, (c) 10, (d) 15, (e) 20 and (f) 60s

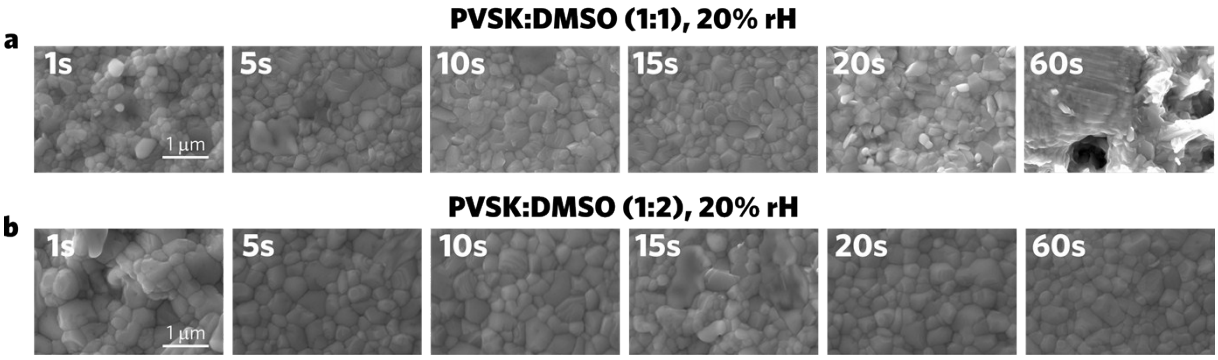

Figure S4: SEM images after thermal annealing of the samples prepared at 20% of rH with (a) 1:1 and (b) 1:2 PVSK:DMSO ratios at different anti-solvent dripping times.

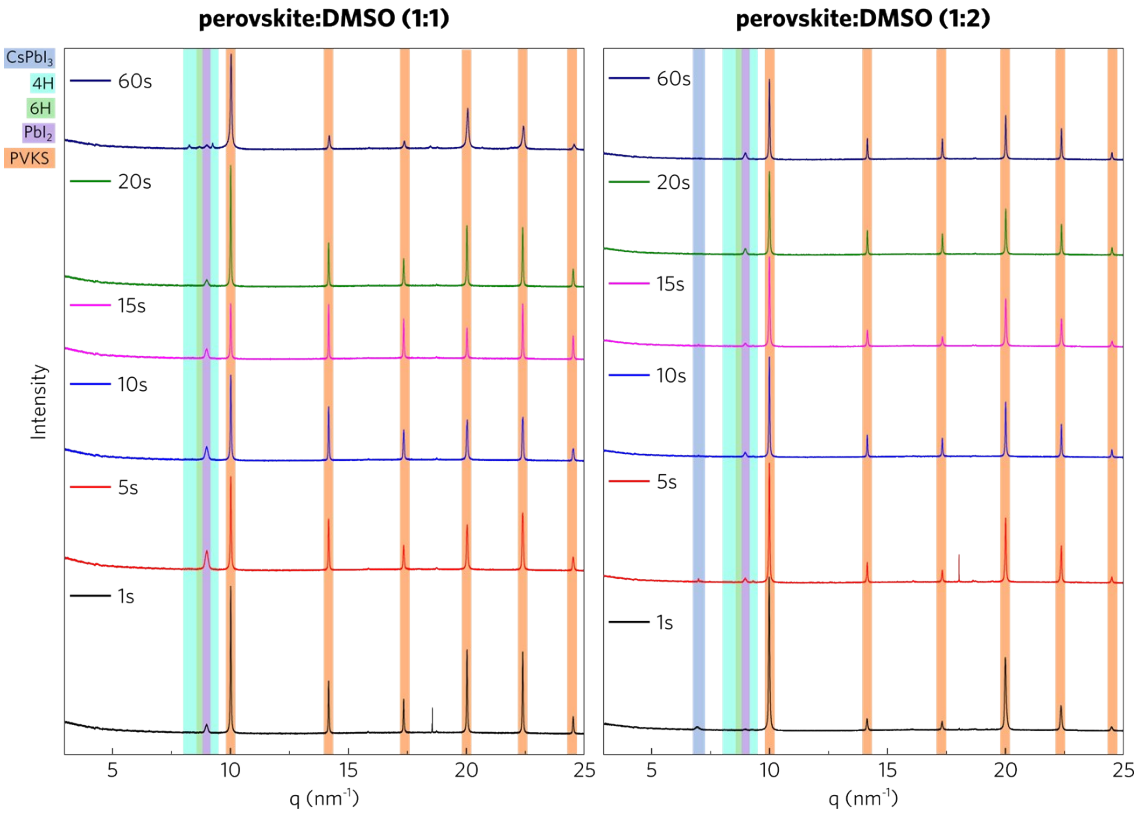

Figure S5: X-ray diffraction patterns of CsFA perovskite prepared at 20% of rH after thermal annealing.

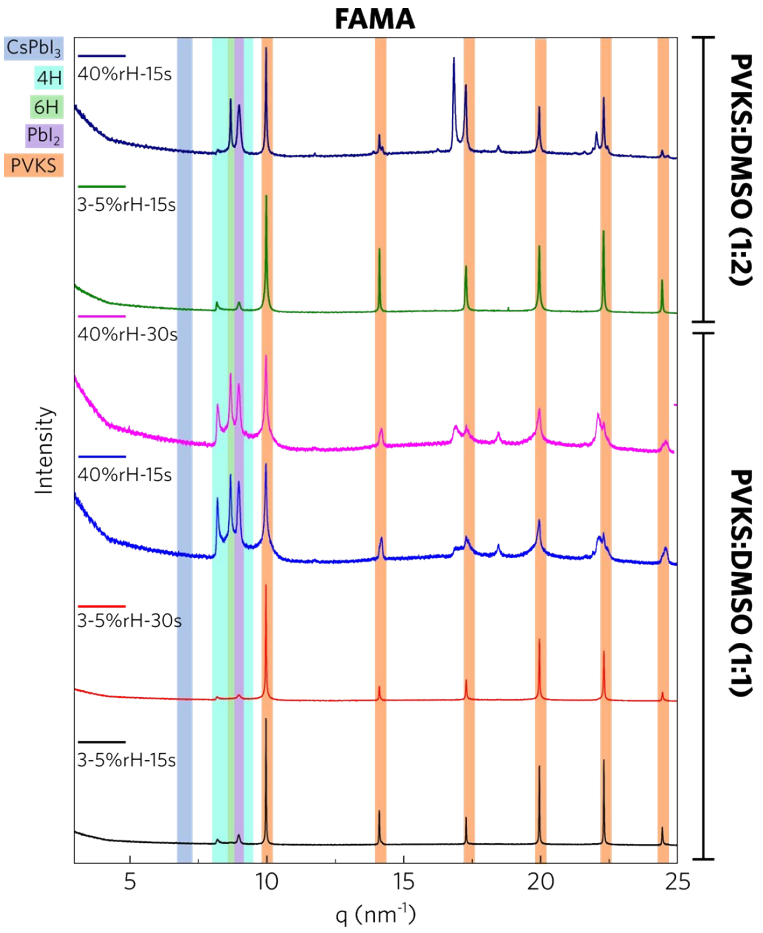

Figure S6: X-ray diffraction patterns of MAFA perovskites prepared at 3-5% and 40% of rH after thermal annealing.

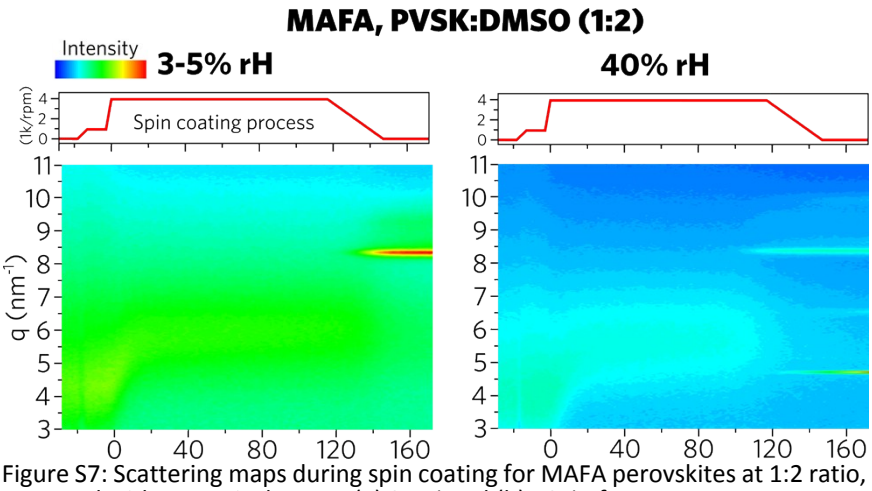

Figure S7: Scattering maps during spin coating for MAFA perovskites at 1:2 ratio, prepared without antisolvent at (a) 3-5% and (b) 40% of rH.

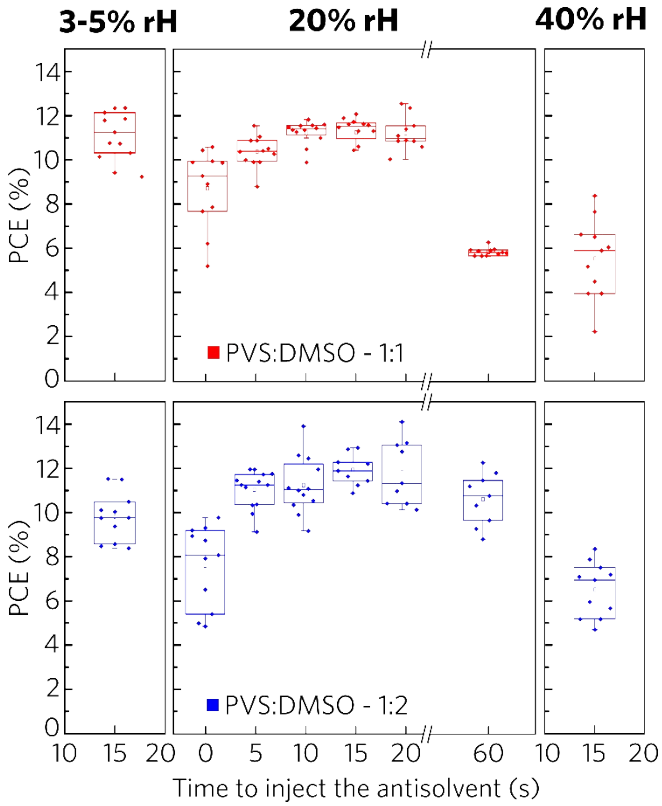

Figure S8: PCE of the CsFA perovskite prepared and thermal annealed in the same rH of GIWAXS experiments.

Table S1: Summary of the phases formed with non-chlorobenzene application

rH	3-5%		20%		40%	
PVSK:DSMO ratio	**1:1**	**2:1**	**1:1**	**2:1**	**1:1**	**2:1**
Perovskite (black phase)	√	√	----	√√	-----	----
Hexagonal phases	√	√	√	√	√√	√
Intermediates	-----	----	√	----	√√	√√

---- : not observed, √: observed, √√: more intense

Table S2: Summary of the phases formed with antisolvent dripping for CsFA perovskite at low (3-5%) and high rH (40%) during spin coating preparation and after thermal annealing.

PVSK:DMSO ratio	**1:1**				**1:2**			
rH	3-5%		40%		3-5%		40%	
	Spin coating	After thermal annealing	Spin coating	After thermal annealing	Spin coating	After thermal annealing	Spin coating	After thermal annealing
Perovskite (black phase)	√√	√√	√√	√√	√√	√√	√√	√√
Hexagonal Phases	√√	---	√	---	√	---	√	√
PbI_2	---	√	---	√	---	√	---	√
$CsPbI_3$	---	√	---	---	---	---	---	√

---- : not observed, √: observed, √√: more intense

Table S3: Photovoltaic parameters CsFA perovskite prepared and thermal annealed in the same rH of GIWAXS experiments. Average of 10 solar cells for each condition. F = Forward Scan, R = Reverse Scan.

rH (%)	PVS:DMSO	Time to drip(s)		Voc (V)	Jsc (mA/cm^2)	FF (%)	n (%)
3_5	1_1	15	F	0.97±0.02	20.04±0.82	50.43±3.67	9.87±1.24
			R	0.99±0.02	18.48±0.89	60.93±2.58	11.20±0.99
3_5	1_2	15	F	0.97±0.01	19.22±1.17	49.04±4.83	9.19±1.23
			R	0.98±0.01	17.53±1.32	57.11±2.33	9.82±1.04
20	1_1	1	F	0.98±0.04	17.58±1.77	42.39±4.50	7.39±1.62
			R	0.99±0.04	15.98±2.06	54.36±3.28	8.73±1.77
20	1_1	5	F	0.97±0.02	18.69±0.58	46.78±4.35	8.45±0.91
			R	0.99±0.01	16.99±0.94	61.70±2.15	10.38±0.70
20	1_1	10	F	0.94±0.01	18.85±0.67	52.40±2.35	9.33±0.67
			R	0.98±0.01	18.11±0.62	63.28±1.29	11.24±0.54
20	1_1	15	F	0.95±0.01	19.36±1.41	52.03±3.00	9.51±0.76
			R	0.99±0.01	18.33±1.29	62.33±1.11	11.25±0.78
20	1_1	20	F	0.97±0.01	19.53±0.77	48.69±2.42	9.21±0.58
			R	1.00±0.01	18.19±0.85	62.02±2.80	11.22±0.77
20	1_1	60	F	0.86±0.01	13.69±0.32	39.02±1.52	4.60±0.21
			R	0.90±0.01	11.10±0.26	58.83±1.96	5.58±0.18
20	1_2	1	F	0.94±0.06	16.55±1.12	38.13±5.72	6.03±1.40
			R	0.97±0.05	14.63±1.40	52.70±6.80	7.62±1.84
20	1_2	5	F	0.96±0.02	19.06±0.74	49.72±3.12	9.11±0.88
			R	1.00±0.01	18.11±0.99	61.26±2.07	11.06±0.82
20	1_2	10	F	0.96±0.02	19.76±1.75	50.17±1.67	9.52±0.99
			R	0.98±0.02	19.06±1.67	59.87±3.27	11.24±1.30
20	1_2	15	F	0.96±0.01	21.18±0.92	48.34±1.91	9.88±0.59
			R	0.99±0.01	20.45±0.90	59.12±1.71	11.93±0.71
20	1_2	20	F	0.97±0.01	20.74±1.88	48.38±2.46	9.72±1.22
			R	1.00±0.01	19.70±1.89	60.09±2.01	11.82±1.46
20	1_2	60	F	0.97±19.28	19.28±1.74	47.47±3.07	8.88±1.31
			R	0.99±0.01	18.04±1.64	59.18±1.46	10.61±1.19
40	1_1	15	F	0.90±0.09	14.33±2.47	27.49±6.41	3.68±157
			R	0.94±0.08	10.98±2.27	52.51±6.01	5.54±1.80
40	1_2	15	F	0.90±0.03	15.71±1.92	32.03±4.94	4.61±1.30
			R	0.94±0.03	12.61±2.21	54.99±3.61	6.52±1.23