Supplementary Information

Sustainable Solvent Selection for the Manufacture of Methylammonium Lead Triiodide ($MAPbI_3$) Perovskite Solar Cells

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Solvent	Health and Safety Information	B.P (°C)	F.P (°C)	Cost* (GPB/L)	Global and harmonized system of classification and labelling of chemicals (GHS) Hazard statements	Operational Exposure Limits (OEL)		Commercial Consideration	
						STEL	TWA	Advantages	Disadvantages
Dimethylformamide (DMF)	• Candidate for immediate substitution from Sanofi, GSK, and Pfizer [1–4] • GHS02, GHS07, GHS08 • Known Reprotoxic Effects • REACH registration as SVHC	153	58	£81.90	H226-H312 + H332-H319-H360D P201-P210-P261-P280-P308 + P313-P370 + P378 [5]	30 mg/m^3 or 10 ppm[5]	15 mg/m^3 or 5 ppm [5]	• Has been used to produce the highest efficiency devices in labs. • High donicity & dielectric constant, moderate vapour pressure and relatively low B.P.	• Synthesised by a distillation which is highly energy inefficient. • Toxic substance which requires expensive equipment and processing.
Dimethyl sulfoxide (DMSO)	• Known to permeate the skin enhancing the absorption of chemical species[6]	189	89	£108.00	H227 P210, P280 [7]	N/A	N/A	• One of the least concerning of the currently used organic solvents[8] rated as problematic by the IMI-CHEM21 study, GSK, and Sanofi[1,3,9].	• Percutaneous absorption, especially in a lead based solution could render use of this chemical more hazardous.
γ – butyrolactone (GBL)	• GHS05, GHS07 • REACH Registration	204	98	£50.00	H302-H318-H336 P261-P280-P305+P351+P338 [10]	N/A	N/A	• Reduced toxicological impact. • Found application in carbon based printable PSCs due to low coordinating ability and strong scaffold infiltration.	• GBL is a precursor to regulated drug GHB. Legality issues are a major barrier to any potential commercialisation.
Acetonitrile (ACN) with methylamine (MA)	• Methylamine – Highly flammable substance • Acetonitrile – REACH Registration; GHS02, GHS07	82	5.5	£105.00	H225-H302+H312+H332-H319 P210-P280-P305+P351+P338 [11] H220-H280-H315-H318-H332-H335 P210-P280-P305+P351+P338+P310-P377-P410+P403 [11]	ACN – 102 mg/m^3 or 60 ppm[11] MA – N/A	ACN – 70 mg/m^3 Or 40 ppm [11] MA – N/A	• Good potential method for pilot scale manufacturing. • ACN is an economically viable solvent.	• Safety issues associated with the storage of flammable MA. • Requirement of additional step bubbling MA through solution.
Dimethylacetamide (DMAC)	• Reproductive Toxicity • GHS07, GHS08 • REACH Registration as SVHC	165	69	£31.90	H312-H332-H319-H360D P201-P261-P280-P305+P351+P338-P308+P313 [12]	72 mg/m^3 or 20 ppm[12]	36 mg/m^3 Or 10 ppm [12]	• Has been used in conjunction with NMP to formulate highly efficient perovskite films without annealing requirements.	• Toxicity, and health and safety concerns. • Recommended for substitution by several solvent selection guides with a focus on green solvent use[1–4,13].
N-methyl-2-pyrrolidone (NMP)	• Reproductive Toxicity • REACH Registration • 1907/2006 (SVHC)	202	91	£107.00	H315, H319, H335, H360D P201, P280, P305+P351+P338 [14]	80 mg/m^3 or 20 ppm[14]	40 mg/m^3 or 10 ppm[14]	• Superior coordination ability and fluid properties allow highly efficient films at room temperature.	• REACH registration as SVHC. • Some uses of NMP are restricted under Annex XVII of REACH[15].

Table S1 - Previously used solvents for successful $MAPbI_3$ deposition. B.P – boiling point, F.P – flash point , STEL – short terms exposure limit, TWA – time weighted average (8 hour exposure).

Table S2 - Reference data for the Hansen solubility parameter (HD) used to identify candidates as DMF alternative aprotic polar solvents for perovskite ($CH_3NH_4PbI_3$) film deposition.

Perovskite Precursor Solute	δD ($MPa^{1/2}$)	δP ($MPa^{1/2}$)	δH ($MPa^{1/2}$)				
Lead iodide (PbI_2)[16]	17.76	21.41	14.46				
Solvent				**HD**[17]	**HD** *(this work)*	**Gutmann Donor Number**[18] **(kcal/mol)**	**Dielectric Constant**
dimethylformamide (DMF) [17]	17.4	13.7	11.3	1.8	8.4	26.6	38.25
dimethylsulfoxide (DMSO) [17]	18.4	16.4	10.2	1.8	6.7	29.8	47.00
diethylformamide (DEF) [17]	16.4	11.4	9.2	5.0	11.6	30.9	29.02
2-methylpyrazine (2-MP) [17]	18.3	12.3	10.5	2.9	10.0	Unknown	Unknown
γ-butyrolactone (GBL) [17]	18.0	16.6	7.4	3.7	8.6	18	41.70
acetonitrile (ACN) [17]	15.3	18.0	6.1	7.6	10.3	14.1	36.64
dimethyl carbonate (DMC) [17]	15.5	8.6	9.7	8.1	14.4	17.2	3.17
dimethylacetamide (DMAc) [19]	16.8	11.5	10.2	4.2*	11.0	27.8	38.85
dihydrolevoglucosenone - Cyrene [20,21]	18.8	10.6	6.9	6.2*	13.4	Unknown	37.30
dimethylpropyleneurea (DMPU) [19]	17.8	9.5	9.3	5.7*	13.0	33.0	36.12
2-methyltetrahydrofuran (2-MeTHF)[22]	16.9	5.0	4.3	12.1*	19.4	18.0	7.53

*calculated using the same assumed parameters and method as Wang *et al.* (2017) [17]

Table S3 - Profilometry results for evaluated solvent systems. 3 readings were taken per film with the average thickness calculated as the mean value.

Solvent System	Recorded Thicknesses / nm	Average Film Thickness / nm
Control (DMF/DMSO)	368	366 ± 3 nm
	363	
	366	
Candidate A 40% DMSO, 30% DMPU, 20% 2-MeTHF, 10% EtOH	475	487 ± 18 nm
	505	
	482	
Candidate B 40% DMSO, 30% DMPU, 15% 2-MeTHF, 15% EtOH	484	492 ± 8 nm
	496	
	497	
Candidate C 40% DMSO, 40% DMPU, 10% 2-MeTHF, 10% EtOH	370	365 ± 8 nm
	357	
	368	

Table S4 - Full width at half maximum for each film based on XRD peak analysis along with 110/310 peak intensity ratio

	110 FWHM	**220 FWHM**	**310 FWHM**	**110/310 Intensity Ratio**
Control	0.09796	0.13680	0.14950	4.02
Candidate A	0.09834	0.11705	0.13913	6.16
Candidate B	0.09663	0.13319	0.15377	6.16
Candidate C	0.11234	0.14174	0.16608	5.93

Figure S1 - Candidate A SEM images at A) 5,000× B) 10,000× C) 15,000× D) 30,000×

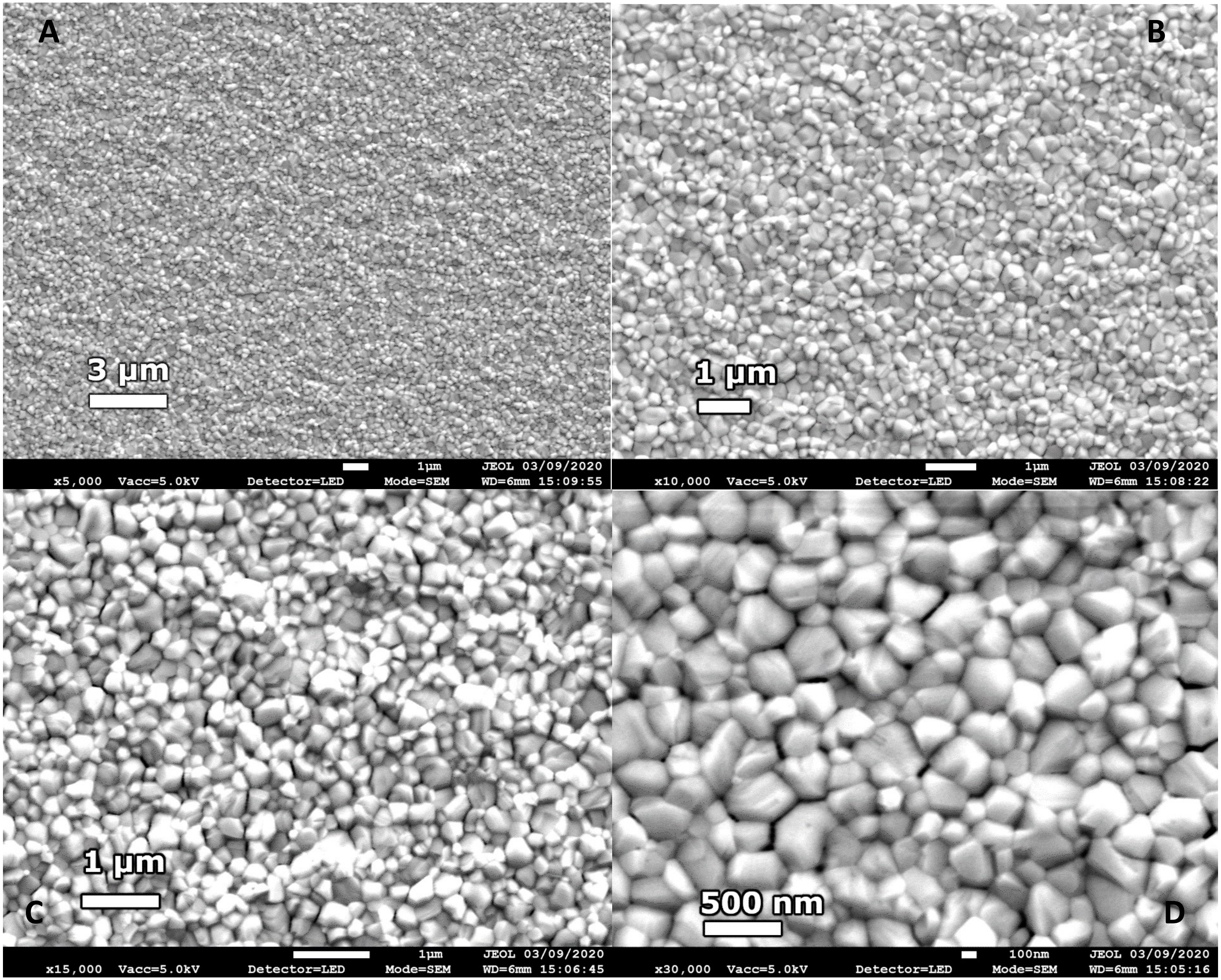


Figure S2 – Control SEM images at A) 5,000× B) 10,000× C) 15,000× D) 30,000×

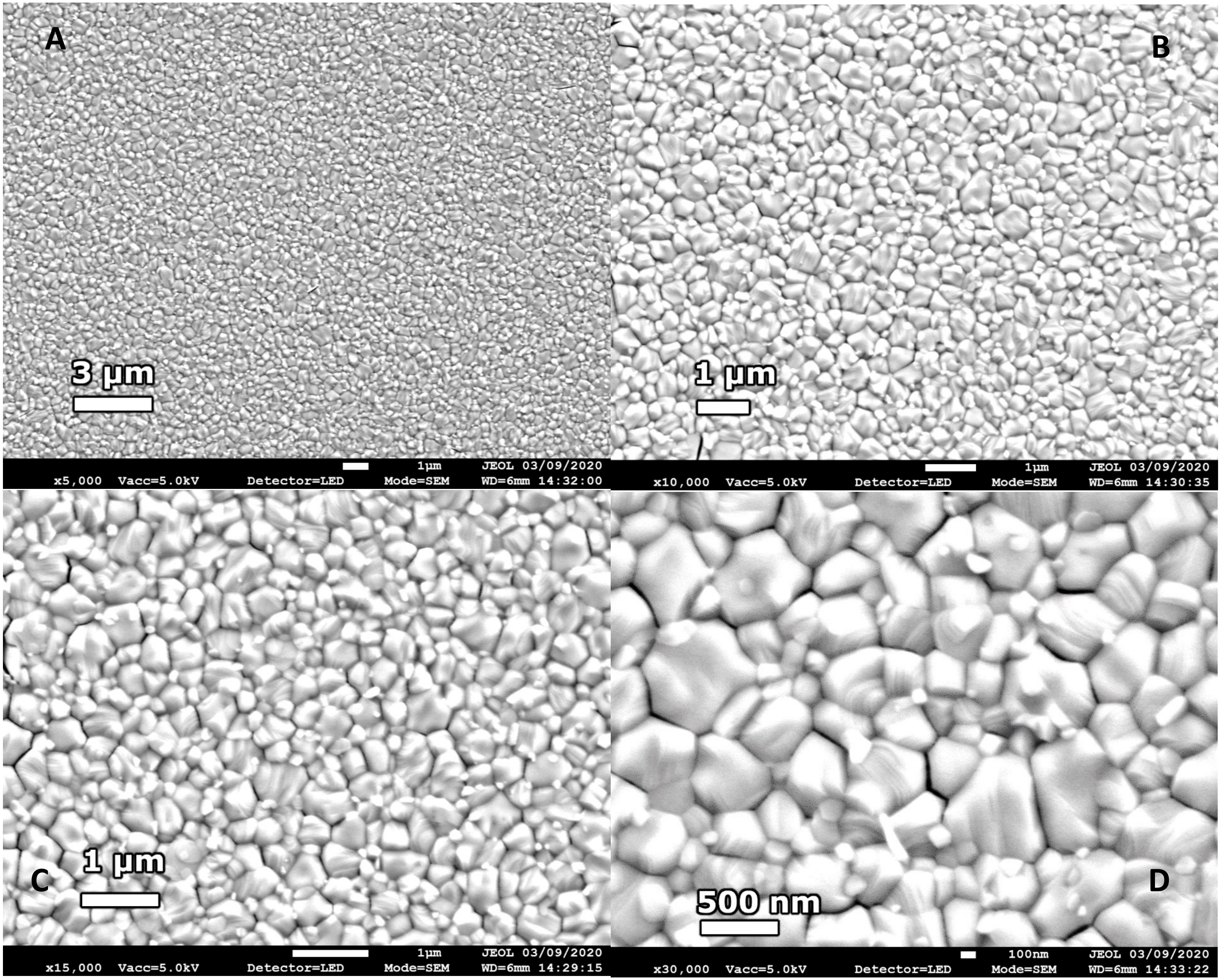


Figure S3 – Candidate B SEM images at A) 5,000× B) 10,000× C) 15,000× D) 30,000×

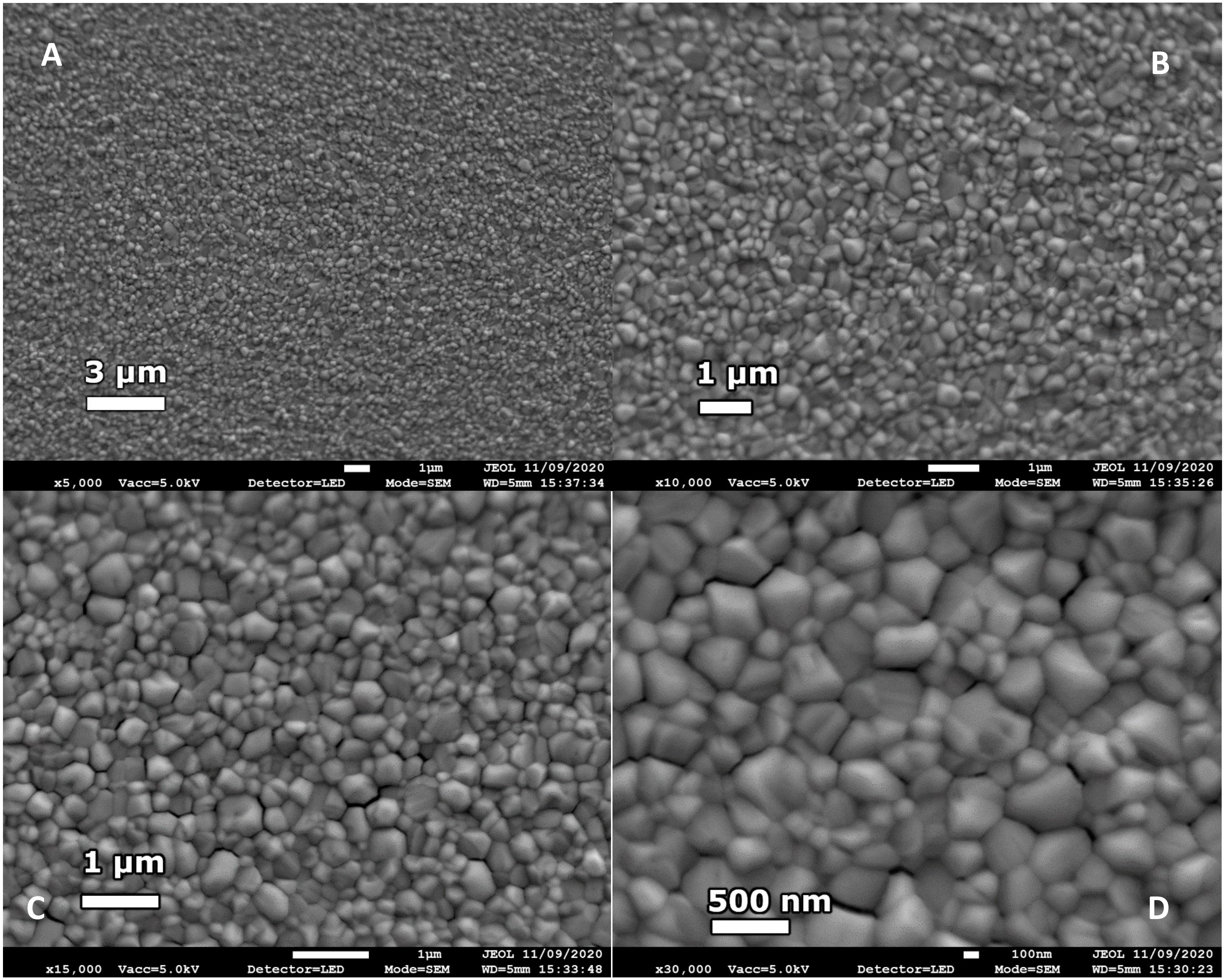
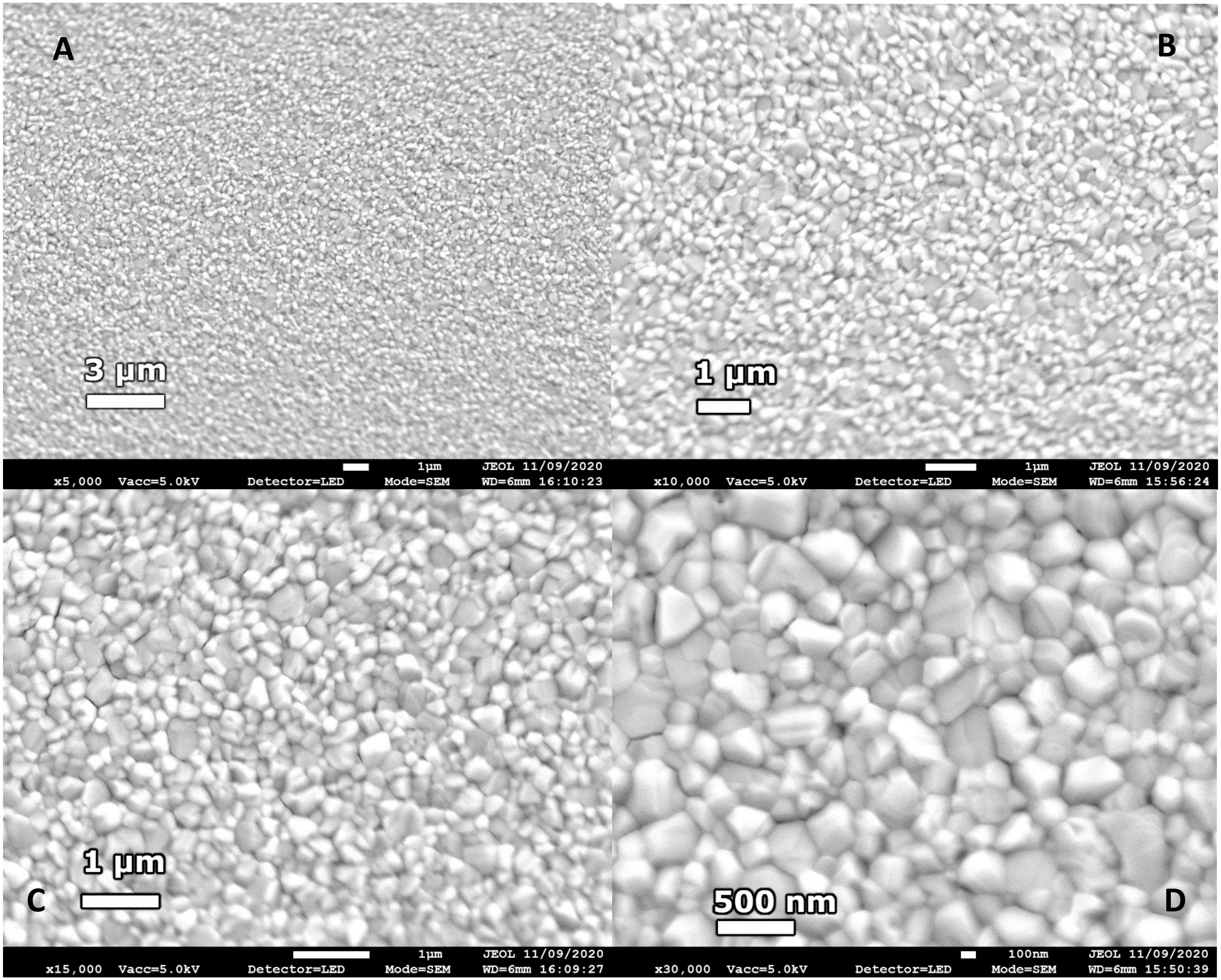


Figure S4 – Candidate C SEM images at A) 5,000× B) 10,000× C) 15,000× D) 30,000×



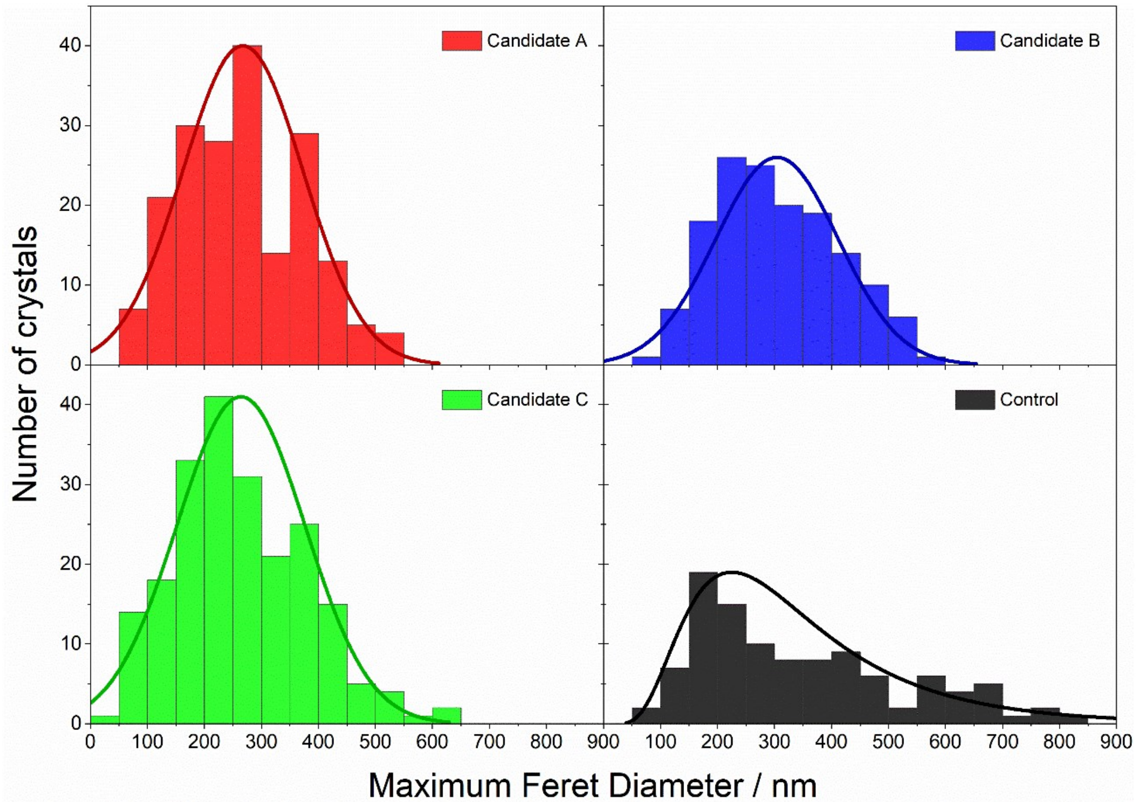


Figure S5 - Crystal size distribution histograms taken from the Zen Blue Intellesis analysis of the maximum Feret diameter for each sample. Normal distribution curves have been superimposed onto candidates A, B, and C, with a lognormal distribution applied over the control graph.

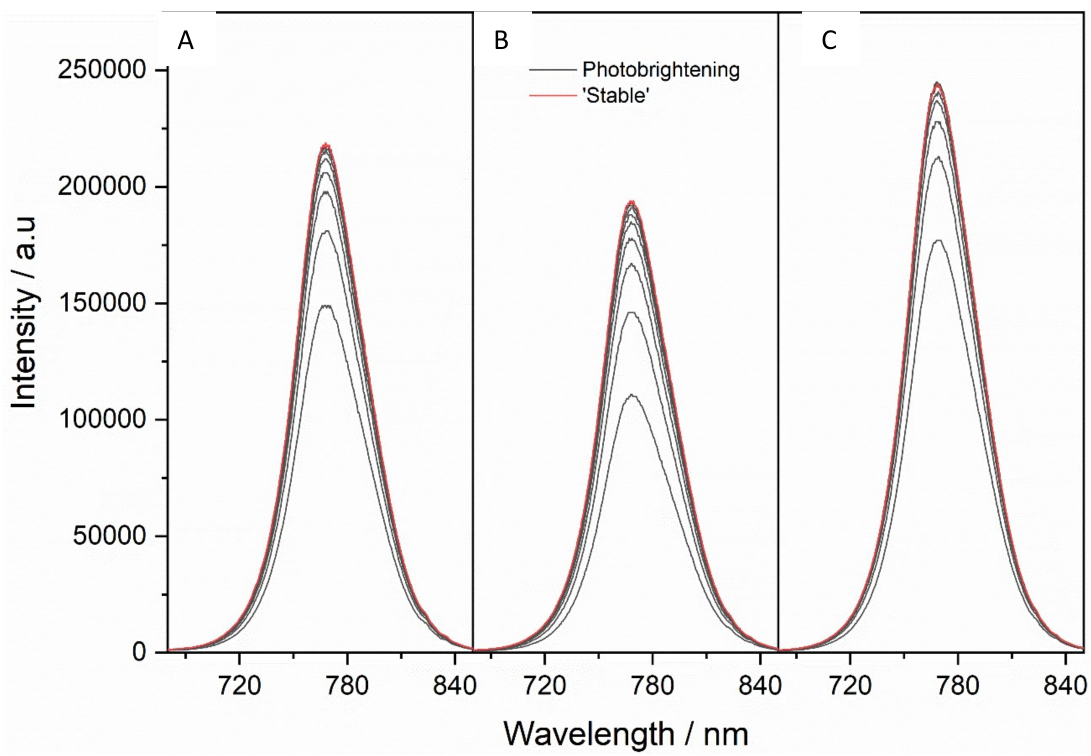


Figure S6 – Steady state photoluminescence (SSPL) for the candidate A average curve and standard deviation spread displayed in figure 5. The PL of all samples increased during measurement (attributed to the phenomenon of photobrightening). The sample was exposed to 450 nm excitation light during the 2.5 minute break between scans before commencement of the subsequent scan. This trend evolution can be seen in the data with the intensity increasing per measurement over time until a plateau is reached as evidenced by multiple overlapping curves, this was the final scan deemed 'stable'. A – A total of 9 scans before the 'stable' scan (highlighted red) B - A total of 9 scans before the 'stable' scan (highlighted red) C – A total of 10 scans before the 'stable' scan (highlighted red).

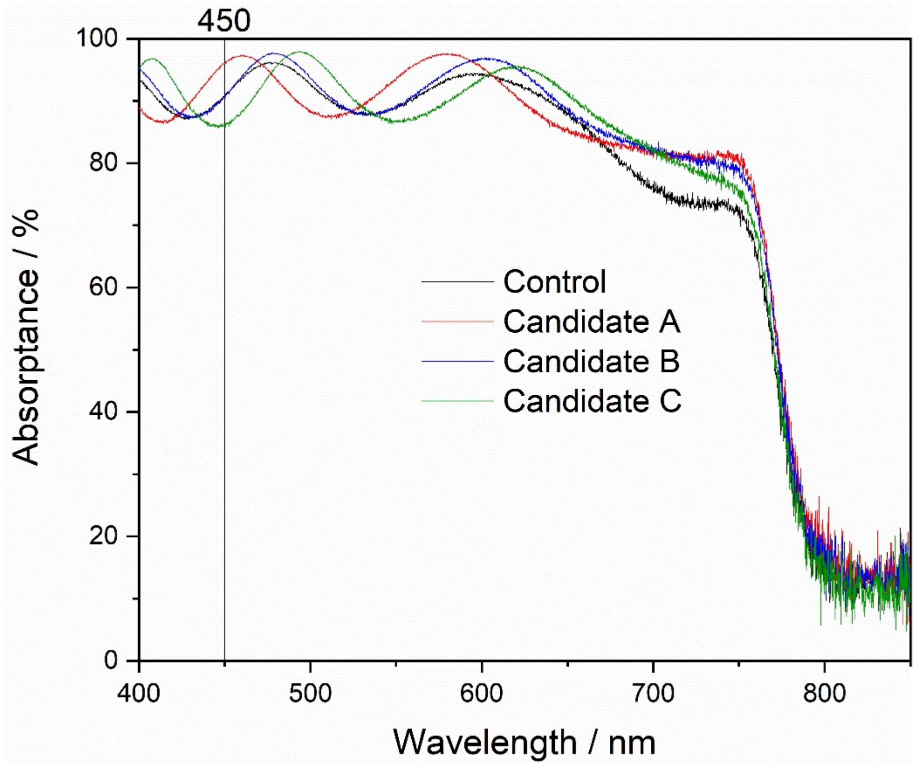


Figure S7 – Absorptance spectra of films deposited from each candidate solution and the control. Interference fringes in the absorptance below 600 nm attributed to the PMMA capping layer. SSPL excitation wavelength of 450 superimposed to highlight absorptance differences.

Table S5 – Crystal grain parameters for each candidate solution taken from image analysis on the Zen Blue Intellesis module software.

	Average Area / nm^2	**Average Perimeter / nm**	**Average Roundness**	**Average Diameter / nm**	**Average Max Feret Diameter / nm**
Control	73949	1111	63%	272	346
Candidate A	39429	882	61%	208	267
Candidate B	50758	1054	62%	238	304
Candidate C	38269	880	59%	203	264

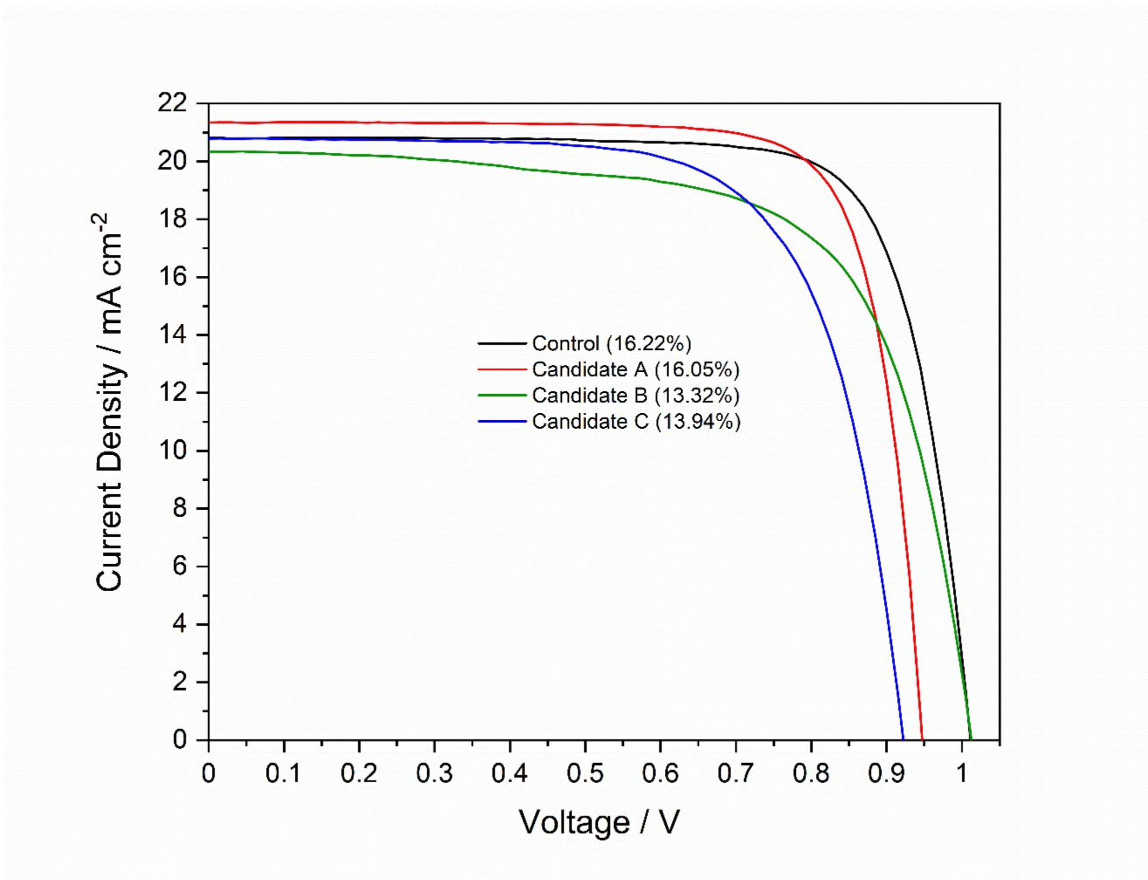


Figure S8 – Champion J-V curves attained for each evaluated solvent system (A, B, C, Control)

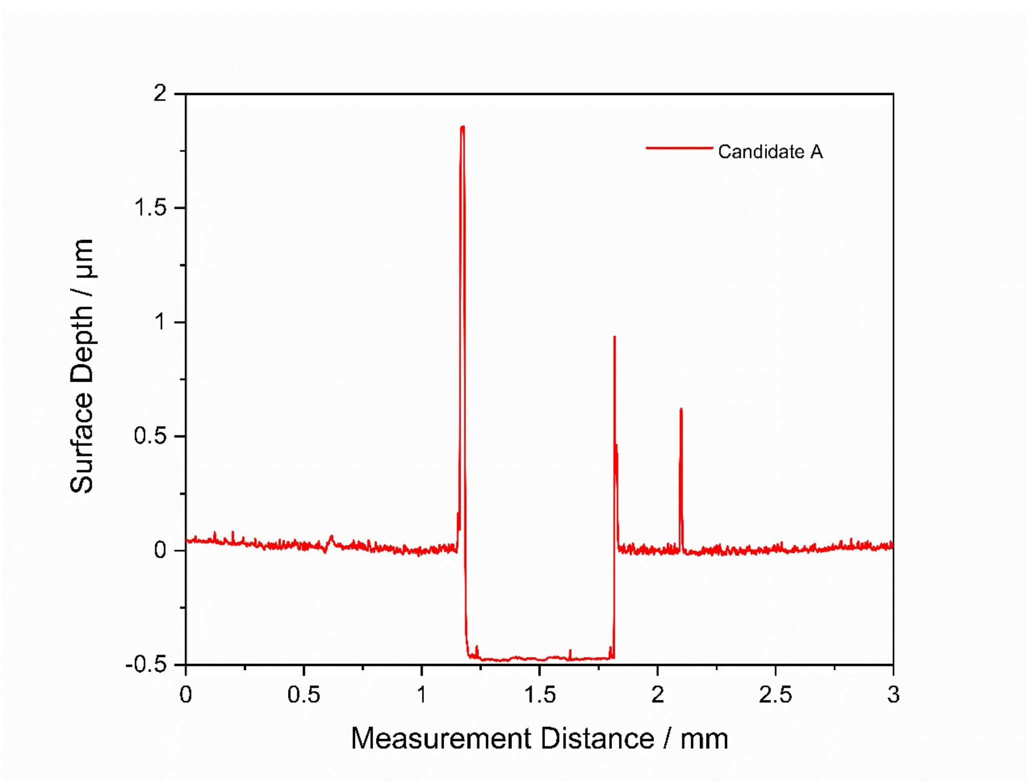


Figure S9 – Profilometry data for a candidate A film showing a film thickness ~500nm. Three measurements were taken corresponding to left side, centre, and right side.

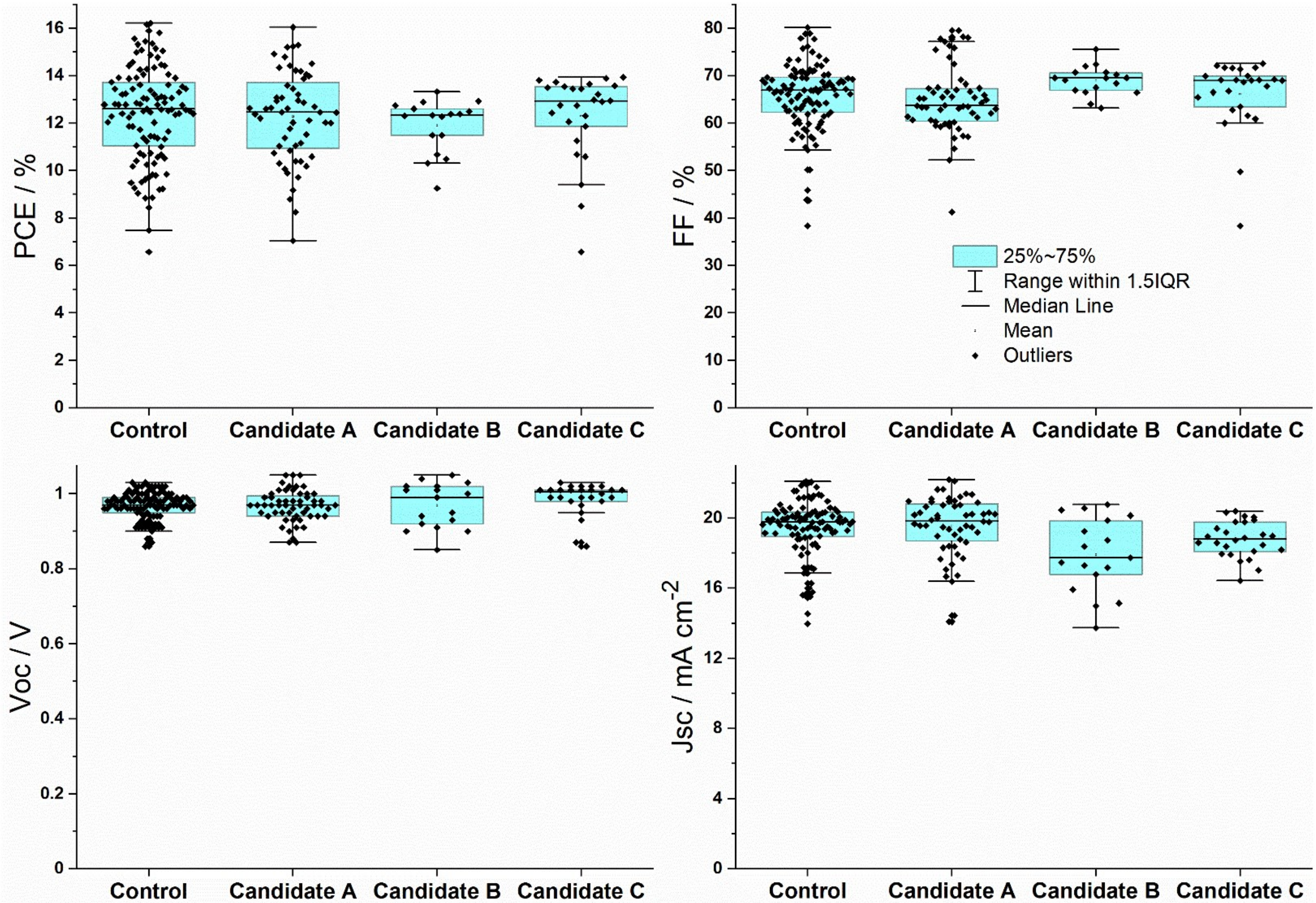


Figure S10 – Device performance box plots for power conversion efficiency (PCE), open circuit voltage (Voc), short circuit current (Jsc), and fill factor (FF).

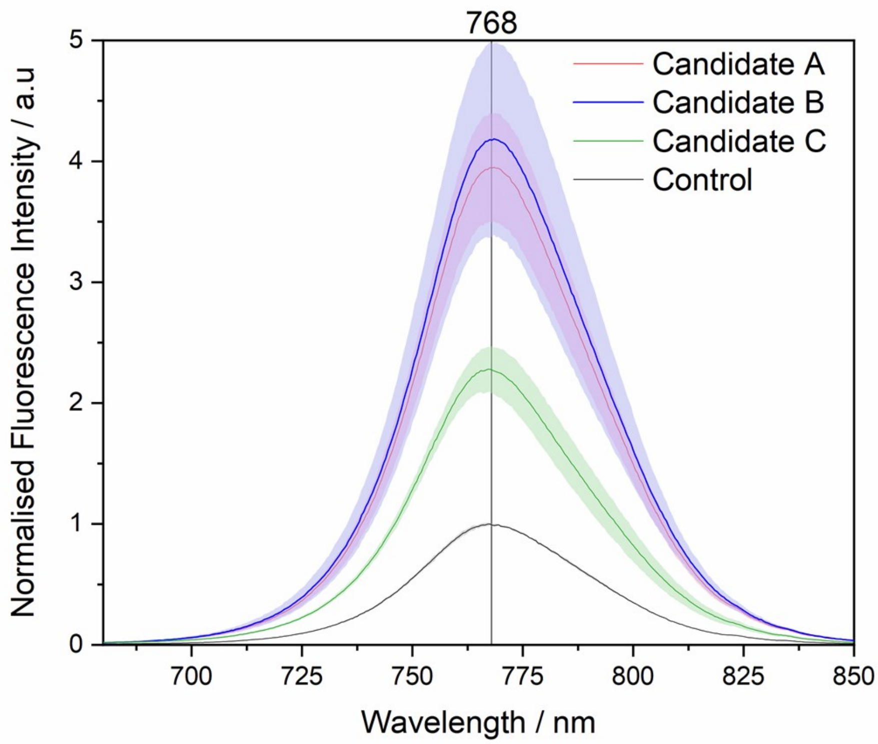


Figure S11 – Normalised fluorescence emission spectra (λ_{ex} = 450 nm) normalised relative to the control film with a superimposed line at 768 nm highlighting the close peak position of the curves deposited from each of the experimental solutions.

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