Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

for

Solvent Engineering Towards Controlled Grain Growth in Perovskite Planar Heterojunction Solar Cells

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1. Experimental details

Materials and preparation of precursor solutions: Lead iodide (PbI_2), anhydrous *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and toluene were purchased from Sigma-Aldrich and used without further purification. Methylammonium iodide (MAI) was synthesized according to the literature[1]. The precursor solution was prepared by dissolving 1.25 M MAI and PbI_2 mixture (molar ratio 1:1) in pure DMF, DMSO or DMF:DMSO mixed solvent at 1:3 volume ratio at 70 ^{o}C.

Device fabrication: PEDOT:PSS was spin-coated on cleaned ITO substrates at 4000 rpm for 30 s after UV-ozone treatment for 15 min, and dried at 115 ^{o}C for 20 min. The $MAPbI_3$ precursor solution were spin-coated on top of PEDOT:PSS layer at 1000 rpm for 10 s and 5000 rpm for 5-30 s. Toluene (200 µl for DMF and 400 µl for DMF/DMSO mixture solvent) was dripped at the center of the substrate with different delay time during the 5000 rpm spin-coating process. After solvent treatment, the films were transferred onto a hotplate and annealed at 100 ^{o}C for 15 min. After cooling down to room temperature (RT), 40 mg ml^{-1} dichlorinebenzene (DCB) solution of PCBM was spin-coated on top of perovskite films at 1800 rpm for 30 s, and dried at 80 °C for 20 min. Finally, 8 nm thick bathocuproine (BCP) and 100 nm thick Al were thermal evaporated with a mask under high vacuum (2×10^{-6} Pa). The active device area is 0.09 cm^{-2}.

Characterization: The X-ray diffraction (XRD) spectra of the perovskite films were measured using a Rigaku diffractometer with Cu Kα radiation (1.5405 Å). Crystallographic data for compound $[CH_3NH_3]_2Pb_3I_8\cdot 2DMSO$ was collected using a Siemens SMART platform diffractometer (monochromatized Mo $K_{\alpha1}$ radiation; λ=0.71073Å) equipped with an APEX II CCD area detector. The data was integrated and unit cell was refined using the SAINT program[2]. An absorption correction was applied using Bruker Apex2 software package [3]. The structure was solved by direct methods and refined by full-matrix least-squares calculations on F^2. All calculations were made with using the SHELXTL programs package.[4] The FTIR spectra were recorded on a Thermo Scientific spectrophotometer (Nicolet iS5). The ultraviolet-visible (UV-Vis) absorption spectra were measured using an Agilent Technologies spectrophotometer (Cary 60). Atomic Force Microscopy (AFM) tests were performed using Bruker's Innova-IRIS AFM system in tapping mode. The current density-voltage (*J-V*) characteristics were measured using a Keithley 2400 source-meter under AM1.5G illumination at 100 mW cm^{-2} from a Newport solar simulator calibrated with a Si diode (KG-5 filter). The J-V curves were obtained through reverse scan (1.0 V to -0.2 V) and forward scan (-0.2 V to 1.0 V) with step size of 20 mV and the delay time between 50 and 400 ms. External quantum efficiencies (EQE) were measured by an EQE system in the AC mode (Enli Technology).

2. Simulated powder XRD pattern based on refined crystal structure of $MA_2Pb_3I_8 \cdot 2DMSO$

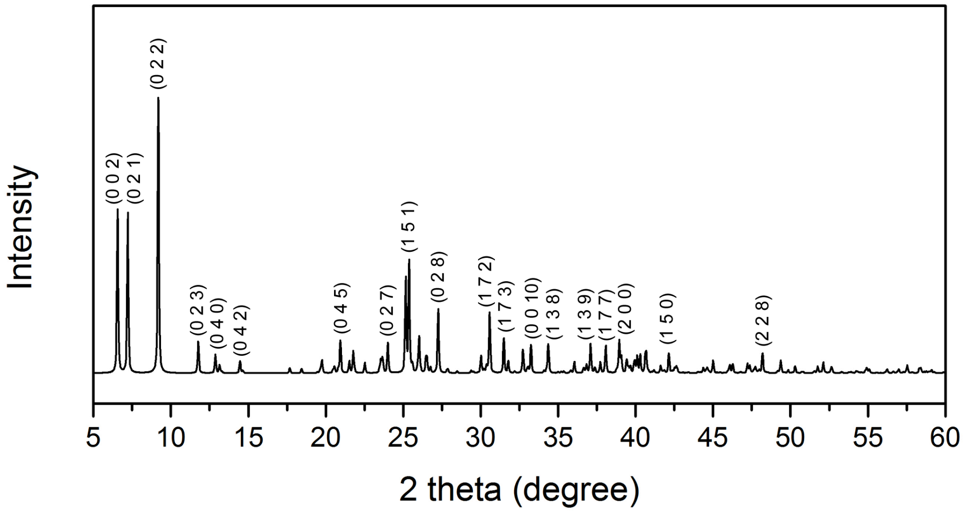

Figure S1. Simulated powder diffraction pattern of $MA_2Pb_3I_8 \cdot 2DMSO$.

3. FTIR spectra of intermediate phase and crystalline perovskite

The presence of DMF or DMSO molecule in the intermediate phase film is confirmed by Fourier transform infrared spectroscopy (FTIR), as shown in Fig. S1. For sample A, the peak located at 1020 cm^{-1} is assigned to S=O stretching vibration. For thin film C, strong bands located at 1432 and 1377 cm^{-1} are assigned to symmetrical and asymmetrical C-H bending vibration and the band at 1637 cm-1 is assigned to C=O stretching vibration of DMF molecules. After thermal annealing, the intensities of peaks originated from DMF or DMSO significantly reduces, indicating the removal of solvent molecules and formation of $MAPbI_3$.

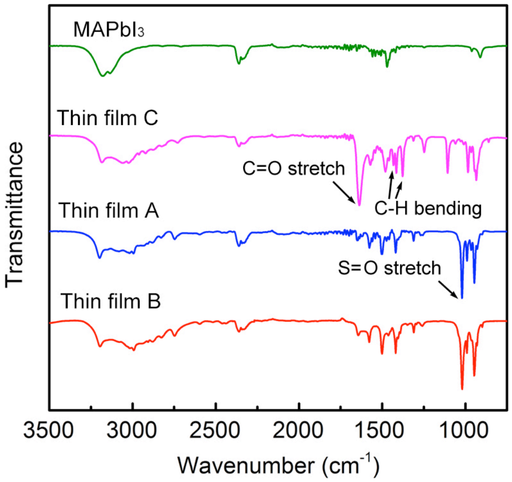

Figure S2. FTIR spectra of intermediate phase film obtaind with DMSO (Thin film A), DMF/DMSO (Thin film B), DMF (Thin film C), and annealed $MAPbI_3$ perovskite film on glass substrates.

4. I-V curves and J_{sc} and V_{oc} dependence on light intensity

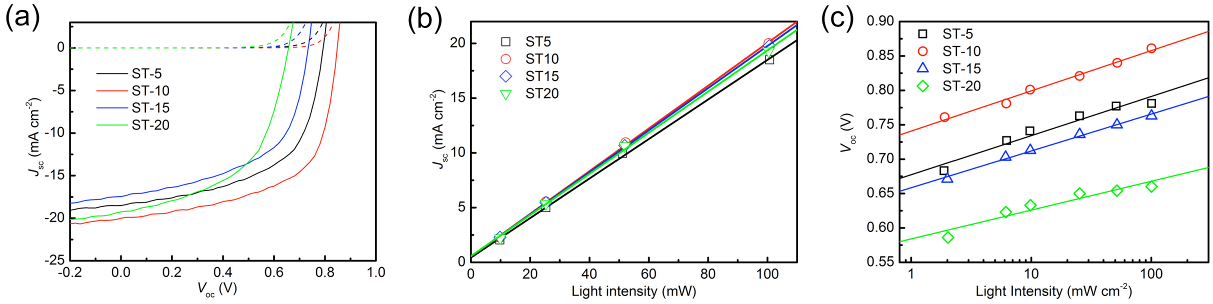

Figure S3. (a) J-V curves of the devices fabricated with different delay time under 1 sun illumination and in the dark; (b) J_{sc} dependence of the devices on light intensity (0.02-1.0 Sun); (c) V_{oc} dependence of the devices on light intensity (0.02-1.0 Sun).

5. Results of the single crystal X-ray investigations of $[CH_3NH_3]_2Pb_3I_8{\cdot}2DMSO$

Table S1. Crystal data and structure refinement for $[CH_3NH_3]_2Pb_3I_8{\cdot}2DMSO$

Identification code	$[CH_3NH_3]_2Pb_3I_8{\cdot}2DMSO$
Empirical formula	C6 H24 I8 N2 O2 Pb3 S2
Formula weight	1857.16
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$Cmc2_1$
Unit cell dimensions	a = 4.6212(13) Å, a= 90°. b = 27.484(8) Å, b= 90°. c = 26.923(7) Å, g = 90°.
Volume	3419.5(16) $Å^3$
Z	4
Density (calculated)	3.607 g/cm^3
Absorption coefficient	22.084 mm^{-1}
F(000)	3168
Crystal size	0.40 x 0.02 x 0.02 mm^3
Theta range for data collection	1.48 to 29.34°.
Index ranges	-4<=h<=6, -37<=k<=34, -36<=l<=32
Reflections collected	9176
Independent reflections	4384 [R(int) = 0.0841]
Completeness to theta = 25.00°	99.7 %
Absorption correction	Psi-scan
Max. and min. transmission	0.8401 and 0.6129
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4384 / 1 / 123
Goodness-of-fit on F^2	0.836
Final R indices [I>2sigma(I)]	R1 = 0.0538, wR2 = 0.1053
R indices (all data)	R1 = 0.1237, wR2 = 0.1217
Absolute structure parameter	0.42(1)
Extinction coefficient	0.00005(1)
Largest diff. peak and hole	1.395 and -1.390 e.$Å^{-3}$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for $[CH_3NH_3]_2Pb_3I_8 \cdot 2DMSO$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	5000	3623(14)	8214(14)	72(10)
C(1)	5000	3692(19)	7622(18)	96(17)
N(2)	5000	8658(16)	2797(16)	105(14)
C(2)	5000	8818(17)	2276(16)	63(11)
S(1)	1440(30)	4466(6)	8936(6)	58(4)
O(1)	0	4045(10)	8576(11)	66(8)
C(3)	0	5032(13)	8794(13)	46(9)
C(4)	0	4332(18)	9550(16)	73(14)
S(2)	8660(30)	8018(5)	1512(5)	50(4)
O(2)	10000	8402(10)	1882(8)	58(8)
C(5)	10000	8136(15)	942(14)	50(10)
C(6)	10000	7491(18)	1654(18)	87(16)
Pb(1)	5000	1217(1)	306(1)	39(1)
Pb(2)	0	105(1)	1348(1)	44(1)
Pb(3)	0	2350(1)	-745(1)	45(1)
I(1)	0	430(1)	96(1)	43(1)
I(2)	0	2018(1)	498(1)	44(1)
I(3)	5000	967(1)	1483(1)	44(1)
I(4)	5000	1492(1)	-844(1)	47(1)
I(5)	-5000	-628(1)	1046(1)	48(1)
I(6)	-5000	3113(1)	-512(1)	49(1)
I(7)	0	-142(1)	2444(1)	59(1)
I(8)	0	2542(1)	-1845(1)	60(1)

6. Photovoltaic parameters of devices fabricated using pure DMF based precursor solution

Table S3. Photovoltaic parameters of devices fabricated with pure DMF based precursor solution and different solvent treatment delay time.

Delay Time	V_{oc} / V	J_{sc} / mA cm^{-2}	FF	PCE / %
5 s	0.79±0.03	16.71±0.62	0.57±0.06	7.59±1.17
10 s	0.48±0.05	7.43±0.82	0.50±0.01	1.78±0.30
15 s	/	/	/	/

7. Photovoltaic performance of optimized device measured under different conditions

Table S4. Photovoltaic parameters obtained with different scan directions and scan rates of the solvent-assisted deposition method based device obtaining the highest PCE; Reverse: scan from 1.0 to -0.2 V, Forward: scan from -0.2 to 1.0 V.

Scan direction	Scan Rate/ms	V_{oc} / V	J_{sc} / mA cm^{-2}	FF / %	PCE / %
Reverse	50	0.85	20.2	62.68	10.83
Reverse	100	0.86	20.1	60.87	10.44
Reverse	200	0.86	19.7	60.39	10.18
Reverse	400	0.86	19.5	59.47	9.94
Average value	/	0.86	19.87±0.32	60.9±1.35	10.35±0.38
Forward	50	0.87	20.0	59.75	10.35
Forward	100	0.86	19.3	61.02	10.13
Forward	200	0.86	19.2	62.44	10.30
Forward	400	0.86	19.2	62.63	10.37
Average value	/	0.86	19.42±0.39	61.5±1.35	10.29±0.11

References

[1] L. Etgar, P. Gao, Z. Xue, Q. Peng, A. K. Chandiran, B. Liu, M. K. Nazeeruddin and M. Grätzel, *J. Am. Chem. Soc.*, 2012, **134**, 17396-17399.

[2] SAINT, version 7.60A; Bruker AXS Inc.: Madison, Wisconsin, USA, 2002-2014.

[3] APEX2, Version 2014. 5-0; Bruker AXS Inc.: Madison, Wisconsin, USA, 2014.

[4] Sheldrick, G. M. SHELXTL; Bruker AXS Inc.: Madison, Wisconsin, USA, 2005.