Supporting Information

Improved Morphology and Efficiency of n-i-p Planar Perovskite Solar Cells by Processing with Glycol Ether Additives

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Experimental Section

Device Fabrication

Patterned indium tin oxide (ITO) substrates were cleaned with detergent, deionized water, acetone, and IPA using sonication, followed by UV-O₃ cleaning for 10 min. A compact zinc oxide (ZnO) layer was deposited by spin coating at 5000 rpm using a 2.5 wt.% ZnO nanoparticle suspension in IPA (Avantama, N-10) solution. The CH₃NH₃PbI₃ absorber layer was deposited on top of ZnO by using a previously reported interdiffusion method. 1M PbI₂ solution was prepared from anhydrous DMF (Sigma Aldrich) by stirring over night at 70 °C. The PbI₂ layer was spun at 3500 rpm for 15 s and 40 mg/ml MAI (DyeSol) in IPA (Sigma Aldrich) solution at 70 °C was loaded on the PbI₂ layer. After a color change was observed, the MAI layer was spun at 3500 rpm for 15 s. The CH₃NH₃PbI₃ absorber layer was then washed with IPA using spin-coating prior to annealing at 100 °C. MAI solutions with different glycol ethers, ME, EE, and PE (Sigma Aldrich), were prepared by adding amounts from 10 to 50µl to 1 ml MAI solution. A Spiro-OMeTAD solution (80 mg/ml 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)9,9'-spirobifluorene, 30 µl 4-tert-Butylpyridine, 18 µl stock solution of 520 mg/ml lithium-bis(trifluoromethylsulfonyl)imide (Li TFSI) in acetonitrile (ACN) and 30 µl stock solution of 520 mg/ml Co dopant (FK 102 Co(III) TFSI salt) in ACN, dissolved in chlorobenzene) was spun on top of the perovskite layer at 2200 rpm for 30 sec. To conclude the device fabrication, 8 nm MoOx and 90 nm Ag contacts were thermally evaporated with deposition rates of 0.25 Å/sec and 3.00 Å/sec, respectively.

X-ray diffraction measurements

X-ray diffraction patterns were obtained using a Bruker D8 Advance X-ray diffractometer (Cu-K_{a1} radiation, λ =1.5406 Å) from 10° to 70° (20) with a scan speed of 3°/min.

Scanning electron microscopy

Surface and cross sectional images of the samples were investigated with a Carl Zeiss AURIGA® CrossBeam® Workstation using in-lens detectors. A 5 kV voltage was used to accelerate the electrons and the working distance was 5 mm.

Atomic force microscopy

Surface topography of the samples was analyzed using an Atomic Force Microscope NEXT (NT-MDT) in contact mode and $10 \times 10 \ \mu\text{m}^2$ scanning area.

Fourier transform infrared (FT-IR) spectroscopy

FT-IR measurements were done in ambient atmosphere on neat materials, precursor solutions, and thin film powder. Perovskite films were scratched off for measurements. A Bruker Tensor 27 FT-IR and OPUS Data Collection Program were used for the measurements, carried out in transmittance mode, and the data analysis, respectively.

Ultraviolet-visible absorption spectroscopy

The absorbance (*A*) spectra were obtained using a Cary 6000 UV-vis-NIR (Agilent Technologies) spectrophotometer equipped with an integrating sphere.

In situ UV-vis absorption measurements performed during perovskite absorber layer processing

In situ UV–vis absorption measurements were performed in a N_2 glove box using a home-built combination of a spin coater and UV-vis spectrophotometer (F20, Filmetrix). Measurements for spin coating of perovskite absorber layers were performed using a transmission mode with an integration time of 0.2 s per transmission spectrum. The integration time was set to 0.5 s during annealing of perovskite thin films. Afterwards, the UV–vis absorption spectra were calculated from transmission spectra.

Static and Time Resolved Grazing incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS measurements were conducted at the D-line at the Cornell High Energy Synchrotron Source (CHESS). All samples were measured in ambient atmosphere while the humidity level was in the range of 10 - 20%. Samples were carefully prepared in a N₂ purged glovebox in which the humidity level was around 0.1ppm. Samples were prepared at KAUST and sent to CHESS under N₂ protective atmosphere. The wavelength of the X-rays was 1.166 Å (10.6 keV). Pilatus 200K detector was used to collect the scattered X-rays with a pixel size of 172 µm x 172 µm. Sample to detector distance was 170.96 mm and it was kept constant for all the samples. Exposure time was set to 1 s and incidence angle was set to 0.5° . For the PbI₂ spin coating experiment, time-resolved

GIWAXS measurements were performed during spin coating using a custom-built and computercontrolled spin coater. For this experiment, the incidence angle was set to 0.25° and an exposure time of 0.2 s was used.

Solar cell performance characterization

The current density-voltage (J-V) characteristics of perovskite solar cells were measured in a N₂ purged glovebox under standard simulated AM1.5 illumination using a solar simulator (Abet Technologies Sun 3000 Solar Simulator) and Keithley 2400 source meter. The scan rate (forward and reverse) was 600 mV/sec. A Newport EQE system was used to perform external quantum efficiency (EQE) measurements in a glovebox.

	DMF	IPA	ME	EE	PE
Chemical formula	HCON(CH ₃) ₂	CH ₃ CHOHCH ₃	CH ₃ OCH ₂ CH ₂ OH	CH ₃ CH ₂ OCH ₂ CH ₂ OH	CH ₃ CH ₂ CH ₂ OCH ₂ CH ₂ OH
Molecular weight (g/mol)	73.095	60.096	76.095	90.122	104.149
Density at 25°C (g/mL)	0.944	0.785	0.965	0.930	0.913
Boiling Point (°C)	153	82	124-125	135	150-153
Vapor pressure at 20°C (mmHg)	2.70	33	6.17	3.80	1.30

 Table S1. Chemical structure and physical properties of solvents used for perovskite processing.



Figure S1. (a) 2D GIWAXS measurements performed during spin-coating of a PbI₂ solution in DMF. The GIWAXS image on the left is consistent with the wet sol-gel complex during the initial \sim 5 s of spin coating at 3500 rpm, characterized by a liquid solvent scattering halo at high q (> 14 nm⁻¹) and a disordered sol-gel precursor scattering halo at low q (< 9 nm⁻¹). The GIWAXS image on the right shows the loss off the liquid solvent scattering halo as well as transformation of the disordered sol-gel scattering halo into diffraction rings associated to the PbI₂·DMF crystalline complex, while the PbI₂ diffraction (9.1 nm⁻¹) is absent. (b) In situ time-resolved UV-vis absorption spectra measured during spin-coating at 3500 rpm of a PbI₂ solution in DMF at different times, showing formation of the wet sol-get phase (1 s) with an absorption onset around 420 nm red-shifting to an absorption onset 450-460 nm associated to the solid-state PbI₂·DMF crystalline complex (15 s and 30 s). Both intermediate phases are significantly blue-shifted with respect to the solid-state PbI₂ phase obtained upon thermal annealing.



Figure S2. Digital pictures of a PbI₂ thin film and of CH₃NH₃PbI₃ absorber layers prepared with different glycol ether additives (scale bar: 1 cm).



Figure S3. SEM micrographs of CH₃NH₃PbI₃ absorber layers prepared with different amounts of glycol ether additives from 10 μ l to 50 μ l (1-5 % v:v) (scale bar: 1 μ m).



Figure S4. AFM images of CH₃NH₃PbI₃ absorber layers prepared with different glycol ether additives: (a) reference sample without additive – average surface roughness 30 nm, with (b) ME – average surface roughness 20 nm, (c) EE – average surface roughness 27 nm, and (d) PE additive – average surface roughness 23 nm (scale bar: 2 μ m).



Figure S5. Absorbance of CH₃NH₃PbI₃ absorber layers prepared with different glycol ether additives: (a) ME, (b) EE, and (c) PE additive, and (d) Tauc plots of CH₃NH₃PbI₃ absorber layers prepared with different glycol ether additives.

Sample	J_{SC}	Voc	FF	η	Rs
	$(mAcm^{-2})$	(V)	(%)	(%)	(Ωcm^2)
ME10	21.4	1.12	64	15.2	5.8
ME20	21.6	1.13	66	16.1	6.2
ME30	21.7	1.13	68	16.7	5.3
ME40	21.8	1.12	62	15.1	8.0
ME50	10.9	0.89	33	3.3	41.0

Table S2. Figures of merit of CH₃NH₃PbI₃ perovskite solar cells prepared with ME additive.

Table S3. Figures of merit of CH₃NH₃PbI₃ perovskite solar cells prepared with EE additive.

Sample	J_{SC}	Voc	FF	η	Rs
	(mAcm ⁻²)	(V)	(%)	(%)	(Ωcm^2)
EE10	21.3	1.07	55	12.7	13.0
EE20	20.8	1.06	46	10.2	18.3
EE30	21.2	1.11	56	13.2	11.7
EE40	13.3	0.64	28	2.4	43.8
EE50	-	-	-	-	-

Table S4. Figures of merit of CH₃NH₃PbI₃ perovskite solar cells prepared with PE additive.

Sample	J_{SC}	Voc	FF	η	Rs
	(mAcm ⁻²)	(V)	(%)	(%)	(Ωcm^2)
PE10	21.2	1.06	66	14.8	5.8
PE20	21.3	1.05	64	14.4	6.1
PE30	22.1	1.03	66	15.0	5.2
PE40	21.7	1.09	63	14.9	8.0
PE50	-	-	-	-	-



Figure S6. Histogram of (a) J_{sc} , (b) V_{oc} , (c) FF and (d) PCE values for the reference, ME, EE, and PE devices based on reverse J-V sweeps. Statistics obtained from a total of 30 devices.



Figure S7. J-V characteristics of planar CH₃NH₃PbI₃ perovskite solar cells measured in reverse and forward sweep mode.



Figure S8. SEM images of reference and ME samples at different annealing times (t= 0, 10, 90, and 300 s) presented together with in situ UV-vis absorption measurements during annealing (scale bar: 1 μ m). Arrows show the grain growth direction and pin holes are marked with circles in the image of the reference sample at t=0 s.



Figure S9. XRD patterns of CH₃NH₃PbI₃ perovskite absorber layers prepared with different glycol ether additives (PE, EE, ME), of the reference sample w/o additives, and a PbI₂ film for comparison.



Figure S10. FT-IR spectra of CH₃NH₃PbI₃ absorber layers prepared with different glycol ether additives, of precursor solutions, and of the additives only. (PbI₂ and MAI precursor solutions are labelled as PbI₂ in DMF and MAI, respectively. Glycol ethers are: 2-methoxyethanol, 2-ethoxyethanol, and 2-propoxyethanol. Perovskite thin films after annealing are labelled as: Reference, ME, EE, and PE, respectively.).