## Electronic Supplementary Information

## Merged interface construction toward ultra-low $V_{\rm oc}$ loss in inverted two-dimensional Dion-Jacobson perovskite solar cells with efficiency over 18%

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## **Experimental Section**

*Materials*: Ethylene glycol, ethylenediamine, phenylethyl-ammonium iodide (PEAI, 99%), methylammonium thiocyanate (MASCN, 97%) and bathocuproine (BCP, 99%) were purchased from TCI. 3-aminomethylpiperidine dihydroiodide (3AMPI<sub>2</sub>, 99%), methylammonium iodide (MAI) and formamidinium iodide (FAI) were bought from Shanghai Materwin New Materials Co. Ltd. PbI<sub>2</sub> (99.99%) and Poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) (PTAA) was bought from Xi'an Polymer Light Technology Corporation. Nickel(II) nitrate hexahydrate and ethylenediamine were bought from Alfa Aesar. Poly [(9,9-bis(30-(N,N-dimethylamino)propyl)-2,7-uorene)-alt-2,7-(9,9-dioctylfuorene)] (PFN-Br) was purchased from Solarmer Materials Inc. P (6,6)-Phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM, 99%), isopropanol (IPA, 99%), dimethyl sulfoxide (DMSO, Anhydrous) were purchased from Alfa Aesar.

Chlorobenzene (CB) and chloroform (CF) was bought from Sigma Aldrich. All reagents and solvents were used directly if not specified. Other materials are used directly.

Device Fabrication and characterization: ITO glass was cleaned in the order from detergent (2 vol% Hellmanex III), deionized water, acetone, isopropanol, ethanol, and each process is a 15-minute ultrasonic bath, followed by drying process under nitrogen flow. They were also treated with ultraviolet ozone for 20 min before use. Nickel(II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub> $\cdot$ 6H<sub>2</sub>O) was dissolved in ethylene glycol solution containing 1 M nickel(II) nitrate hexahydrate with ethylenediamine (Aldrich). The solution was spin-cast onto the prepared substrate at 4,000 r.p.m. for 40 s to obtained the NiO<sub>x</sub> substrate. Then, the substrate was transferred to the hot plate with the temperature of 300 °C in ambient air for 60 min. Then the cooled substrates were transferred into a glovebox for deposition and further device fabrication. The thin layer of PTAA was obtained by spin coating PTAA solution in toluene (1 mg mL<sup>-1</sup>) at 6000 rpm on NiO<sub>x</sub> substrates, followed by annealing at 100 °C for 10 min. The (3AMP)(MA<sub>0.75</sub>FA<sub>0.25</sub>)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub> precursor solution (0.85 M) was prepared by dissolving 3AMPI<sub>2</sub>, MAI, FAI, PbI<sub>2</sub>, and MASCN in molar ratio of 1:2.25:0.75:4:1 into the mixture of 800 µL DMF and 200 µL DMSO, and the solution was stirred at room temperature overnight in N<sub>2</sub> glove box. Forty microliters of the mixed (3AMP)(MA<sub>0.75</sub>FA<sub>0.25</sub>)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub> precursor solution was spin-coated at 500 rpm for 3 s and then at 4000 rpm for 60s onto the HTL substrate. 0.4 mL of chlorobenzene was dropped on the rotating substrates during high speed spin-coating process. For Route I, PC<sub>61</sub>BM (5 mg/mL in Chloroform) were coated at 2000 rpm for 30 s after the annealing of perovskite film at 100 °C for 10 mins. For Route II, PC<sub>61</sub>BM (5 mg/mL in Chloroform) were coated at 2000 rpm for 30 s after spinning-coating the precursor solution followed by annealing at 100 °C for 10 mins. For Route III, PC<sub>61</sub>BM (5 mg/mL in Chloroform) were coated at 2000 rpm for 30 s after the annealing of perovskite film at 100 °C for 20-25s, and the film was annealed at 100 °C for 10 mins. Then, the BCP (0.5 mg/mL in isopropanol) was coated 3000 rpm for 30 s. At last, 100 nm Ag was deposited in a vacuum chamber with a high vacuum of 2×10<sup>-4</sup> Pa to finish the device fabrication process.

The UV-Visible absorption spectra were obtained via UV-2450 UV-Vis Shimadzu Spectrophotometer. X-ray diffraction (XRD) patterns were measured by using a Rigaku D/max-2550PC X-ray diffractometer with Cu  $K_{\alpha}$  radiation (1.5406 nm). Film

morphologies and cross-sectional images of films were characterized using SEM (Quanta 400). X-ray photoelectron spectrometer (XPS) measurements was conducted on an ESCALAB 250Xi (Thermo) system. The steady-state PL and time-resolved photoluminescence (TRPL) spectra were both obtained with an FLSP920 Spectro fluorometer at an excitation wavelength of 470 nm and 405 nm, respectively. The *J-V* measurement was performed via the solar simulator (SS-F5-3A, Enlitech) along with AM 1.5G spectra whose intensity was calibrated by the certified standard silicon solar cell (SRC-2020, Enlitech) at 100mW/cm<sup>2</sup>. The external quantum efficiency (EQE) data were obtained by using the solar-cell spectral-response measurement system (QE-R, Enlitech). For humidity-stability measurement, the PSCs were kept in a humidity-controlled cabinet (Hr =  $45 \pm 5\%$  or  $25 \pm 5\%$ ; Bossmen, PR1852(A)-SH).

Transient absorption spectroscopy (TAS). For femtosecond transient absorption spectroscopy, the fundamental output from a Yb:KGW laser (1030 nm, 220 fs Gaussian fit, 100 kHz, Light Conversion Ltd) was separated into two light beams. One was introduced to NOPA (ORPHEUS-N, Light Conversion Ltd) to produce a certain wavelength for the pump beam (we used 750 nm), and the other was focused onto a YAG plate to generate a white light continuum as the probe beam. The pump and probe overlapped on the sample at a small angle of less than 10°. The transmitted probe light from the sample was collected using a linear CCD array. We obtained the transient differential transmission signals using the equation below:

 $\Delta T/T = (T_{pump-on} - T_{pump-off})/T_{pump-off}$ 

We followed the study by Jin and Sargent (J. Phys. Chem. Lett. 2019, 10, 419, J. Am. Chem. Soc. 2017, 139, 1432) to quantify the charge transfer time. More specifically, we consider the ascending part of the TA kinetics (Fig. 3c, f) as a charge transfer process, and a single exponential fitting model is used to extract the charge transfer time.

The time-of-fight secondary-ion mass spectrometry (TOF-SIMS) spectra were recorded on a TOF-SIMS V instrument (ION-TOF GmbH, Münster, Germany) to track the depth distributions of  $C_8^-$  and PbI<sup>-</sup> from the top of the perovskite film down to the ITO substrate. Dual beam depth probing used a pulsed 60 keV Bi3<sup>++</sup> liquid metal ion gun as a primary ion source with the beam current being adjusted to 0.24 pA at a pulse repeating frequency of 10 kHZ and a 10 keV argon gas cluster ion beam (Ar<sub>1700</sub><sup>+</sup>) with the beam current being lowered to 1 nA as a sputtering ion source in an interlaced mode. The analysis area was  $100 \times 100 \ \mu\text{m}^2$  at the center of a crater of  $300 \times 300 \ \mu\text{m}^2$ . A low energy flood gun was used for charge compensation during analysis.

Transient photocurrent (TPC) and transient photovoltage (TPV) measurements: For the TPV measurements, the device was held at open circuit under steady-state conditions controlled by a continuous white light bias and a small pulsed perturbation of excess charge carriers produced by a laser beam (470 nm). The TPC measurements were taken using the same setup as that for the TPV measurements but without the continuous white light, which was under a short circuit. The device was connected to an oscilloscope (1 M $\Omega$  and 50  $\Omega$  input impedance for TPV and TPC, respectively). The lifetime ( $\tau$ ) was calculated by fitting a single exponential function to the TPC or TPC decay curves.

V <sub>oc</sub>	$V_{\rm oc}$ loss	Eg*	Jsc	FF	PCE	Structure	Ref	
_(V)	(eV)	(eV)	$(mA/cm^2)$	(%)	(%)	Structure		
						FTO/cp-TiO <sub>2</sub> /mp-		
0.84	0.75	1.59	11.49	72.00	7.11	TiO <sub>2</sub> /Perovskite/Spiro-	1	
						OMeTAD/Au		
						ITO/ nano-		
1.21	0.47	1.68	17.97	76.00	16.53	TiO <sub>2</sub> /Perovskite/Spiro-	2	
						OMeTAD/Au		
1.06	0.59	164	21.02	67 10	15.01	ITO/ SnO <sub>2</sub> /Perovskite/Spiro-	2	
1.00	0.38	1.04	21.03	07.10	13.01	OMeTAD/Au	3	
						FTO/cp-TiO <sub>2</sub> /mp-		
1.07	0.56	1.63	22.07	65.00	15.16	TiO <sub>2</sub> /Perovskite/Spiro-	4	
						OMeTAD/Au		
1 1 2	0.46	6 1.59	9 21.20	76.00	18.20	FTO/ TiO <sub>2</sub> /Perovskite/Spiro-	~	
1.13	0.46					OMeTAD/Au	5	
1 10	0.51	1 (1	17.20	72 50	12.00	ITO/ SnO <sub>2</sub> /Perovskite/Spiro-	(	
1.10	0.51	1.61	17.30	/2.50	13.80	OMeTAD/Ag	6	
0.00	0.65	1.62	10.00	72 10	12.00	ITO/PEDOT:PSS/Perovskite/	7	
0.98	0.65	1.63	18.00	/3.10	12.90	C <sub>60</sub> /BCP/Ag	/	
1.07	0.70	1.0.4	10.17		7.00	FTO/PEDOT:PSS/Perovskite/	0	
1.06	0.78	1.84	10.17	67.60	7.32	C <sub>60</sub> /BCP/Ag	8	
1 00		1 (1	12 (2)	01.04	10 04	FTO/PEDOT:PSS/Perovskite/	0	
1.09	0.52	1.61	13.69	81.04	12.04	C <sub>60</sub> /BCP/Ag	9	
1 00		105	14.24			FTO/PEDOT:PSS/Perovskite/	10	
1.08	0.77	1.85	14.34	59.58	9.20	C <sub>60</sub> /BCP/Ag	10	
1.0.4	o <b>F</b> O	1.60	• • • • •	<b>-</b> 0.00	16.00	ITO/PEDOT:PSS/Perovskite/		
1.04	0.59	1.63	20.01	79.00	16.38	PC <sub>61</sub> BM/LiF/Al	11	
	0.40	1 50	1605	01.45	1 4 50	ITO/PTAA/Perovskite/	10	
1.11	0.48	1.59	16.07	81.45	14.53	PC <sub>61</sub> BM/BCP/Ag	12	
						ITO/ PEDOT:PSS/		
1.07	0.54	1.61	19.55	75.46	15.75	Perovskite/PC <sub>41</sub> BM/BCP/Ag	13	
	0.56	0.56 1.63	53 19.93		15.60	ITO/ PEDOT PSS	14	
1.07				73.25		/Perovskite/PC <sub>61</sub> BM/BCP/Ag		
						ITO/(NiO_/PTAA)/nerovskite		
1.24	0.35	1.59	19.51	77.27	18.67	$/PC_{c1}BM/BCP/Ag$	This	

Table S1. Reported quasi-2D DJ PVSCs.

\*) The bandgap is calculated according to the PL spectra.  $/PC_{61}BM/BCP/Ag$ 



Fig. S1 Enlarged top-view SEM images for different regions of the MA-based perovskite film shown in Fig. 1c: (a) the region inside the gaps/holes, (b) the region covered by the nanorod-like structure.



Fig. S2 Steady-state PL spectra of the (3-AMP)(MA<sub>0.75</sub>FA<sub>0.25</sub>)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub> film fabricated by PMA process excited from back (glass side) and front (perovskite side) sides.



Fig. S3 AFM images of the  $(3AMP)(MA_{0.75}FA_{0.25})_3Pb_4I_{13}$  films fabricated by CA (a) and PMA (b) process.



Fig. S4 UV-vis absorption spectra of (3-AMP)(MA0.75FA0.25)3Pb4I13 films fabricated by CA and PMA process.



Fig. S5 Distribution of  $V_{oc}$  (a),  $J_{sc}$  (b) and FF (c) based on 30 devices prepared by CA and PMA processes. (d) stabilized PCE measurements of the PMA-based device.



福建省计量科学研究院 FUJIAN METROLOGY INSTITUTE (国家光伏产业计量测试中心) National PV Industry Measurement and Testing Center

报告编号: 21Q3-00025

检测结果/说明: Results of Test and additional explan

1 Standard Test Condition (STC): Total Irradiance: 1000 W/m<sup>2</sup>

Temperature: 25.0 ℃

Spectral Distribution: AM1.5G

2 Measurement Data under STC

Test Times	Isc (mA)	V <sub>oc</sub> (V)	I <sub>MPP</sub> (mA)	V <sub>MPP</sub> (V)	P <sub>MPP</sub> (mW)	FF (%)	η (%)
1	1.082	1.225	1.001	1.029	1.030	77.71	17.22
2	1.095	1.231	1.044	1.023	1.068	79.23	17.86
3	1.081	1.231	1.042	1.024	1.067	80.18	17.84
Average Value	1.086	1.229	1.029	1.025	1.055	79.04	17.64

Mismatch factor: 1.006

3 I-V & P-V Characteristic Curves under STC



检测报告续页专用 Continued page of test report	
	第3页/共7页 Page of Pages

Fig. S6 Summary of the certificate from National PV Industry Measurement and Testing Center, China.



Fig. S7 Reverse-forward J-V curves of devices fabricated by CA and PMA.

Table S2 The charge transfer time of small-n to large-n of CA- and PMA- based perovskite films, calculated by fitting the carrier dynamics via a double exponential equation.

	$n = 2 \rightarrow n = 3$	$n = 3 \rightarrow n = 4$	$n = 4 \rightarrow n = \infty$
CA	0.33±0.04 ps	4.62±0.26 ps	21.38±1.4 ps
PMA	0.21±0.01 ps	0.96±0.11 ps	13.21±0.86 ps



Fig. S8 Steady-state PL spectra (a) and time-resolved PL decay (b) of the  $PC_{61}BM$  coated perovskite films deposited by CA and PMA process on quartz substrates.

	$\tau_1$ (ns)	frac. τ <sub>1</sub> (%)	$\tau_2$ (ns)	frac. τ <sub>2</sub> (%)	$ au_{ m avg}( m ns)$
СА	4.33	44.2%	17.49	55.8%	11.67
PMA	1.87	59.9%	9.92	40.1%	5.09

Table S3 Time-resolved PL data of the CA- and PMA- based perovskite films on quartz with  $PC_{61}BM$  on the perovskite.



Fig. S9 Steady-state PL spectra of the CA- and PMA- based perovskite films rinsed away the  $PC_{61}BM$  layer, with quartz as substrate.



Fig. S10 TOF-SIMS depth profiles showing  $C_8^-$  and PbI<sup>-</sup> signals of the (3AMP)(MA<sub>0.75</sub>FA<sub>0.25</sub>)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub> film with PC<sub>61</sub>BM fabricated by CA(a) and PMA(b) process.



Fig. S11 Dark state J-V curves of the PVSCs fabricated by CA and PMA processes.



Fig. S12 (a) TPC decay curves of the devices fabricated by CA and PMA process. (b) Charge collection probability (or) normalized photocurrent with saturated photocurrent as a function of internal voltage for cells fabricated by CA and PMA process.



40 min 45 min 50 min Fig. S13 Color change of the CA- and PMA- based films exposed to the air atmosphere with humidity of about 70%.



**4min 4.5min 5min 5.5min 6min 6.5min 7min 7.5min** Fig. S14 Color change of the CA- and PMA- based films annealed at 200 °C in the glovebox.

## Notes and references

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