## SUPPORTING INFORMATION

## Effect of storage cycle on improvement in photovoltaic parameters of planar triple cation perovskite solar cells

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**Fig. S1** schematic diagram of the two different fabrication procedures of PSCs: fabrication process I and II. After  $SnO_2$  deposition in humid air onto glass/ITO, substrates were inserted in N<sub>2</sub>-filled glove box, with RH<1ppm and perovskite and HTM are deposited by spinning onto glass/ITO/SnO<sub>2</sub>. The former batch (a) was inserted into another N2-filled glove box, with a thermal evaporator for Au electrical contact deposition (*devices completed inside the GB*). The latter (b) was transferred outside the glove box using an evaporator in another laboratory (*devices completed outside the GB*). The time in air, between the time from transferring and loading in another evaporator, is about 1h. All the devices were stored in humid air, RH = (30 ± 10) %, and finally placed in low vacuum chamber.



**Fig. S2**: (a) architecture of single-junction perovskite solar cell; (b) photograph of typical perovskite solar cell, 2 x 2 cm<sup>2</sup> with gold contacts before silver deposition on ITO. Active area is 0.11 cm<sup>2</sup>



**Fig. S3**: Ion image of FIB cross section of a typical device with values of layer thickness measured by software of Quanta 200 3D

 Table S1 Summary of efficiency of PSCs respect to ambient fabrication or storage conditions in function of perovskite chemical composition, thickness and architecture (\*capping layer)

Perovskite	Thickness	Architecture	Fabrication or	PCE (%)	Ref.	
	(nm)		condition			
ΜΑΡΙ	~ 400	ITO/Planar SnO <sub>2</sub> /C60- SAM/perovskite/Spiro- OMeTAD/Au	under atmospheric conditions (RH=50%)	18.7	Ugur et al. 2020 [11]	
(FAPbl <sub>3</sub> ) <sub>0.85</sub> (MAPbBr <sub>3</sub> ) <sub>0.15</sub>	~ 400*	FTO/compact TiO <sub>2</sub> /mesoTiO <sub>2</sub> /perovskite/Spiro- OMeTAD/Au	Ambient RH=(20± 10)%	20.4	Cho et al 2021 [46]	
$Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_{3}$	not reported	FTO/compact TiO <sub>2</sub> /meso TiO <sub>2</sub> /perovskite/Spiro- OMeTAD/Au	Ambient moderate humidity (RH=40%)	14.8	Mesquita et al. 2020 [9]	
(FAPbI <sub>3</sub> ) <sub>0.97</sub> (MAPbBr <sub>3</sub> ) <sub>0.03</sub>	760 650	ITO/SnO₂ / perovskite/Spiro- OMeTAD/Au	Ambient air (RH=30/40%)	19.9 20.9	Jiang et al 2017 [69, 75]	
C <sub>2</sub> H <sub>5</sub> PbI <sub>3</sub>	~170	FTO/SnO <sub>2</sub> /perovskite/Spiro- OMeTAD/Au	Ambient air (RH =20/30%)	17.38	Zhang et al 2020 [16]	
Cs <sub>0.05</sub> FA <sub>0.8</sub> MA <sub>0.15</sub> PbI <sub>2.5</sub> Br <sub>0.5</sub>	320	ITO/SnO₂ / perovskite/Spiro- OMeTAD/Au	Ambient air (RH=30± 10)% and low vacuum	20.9	This work	

 Table S2: Average and best parameters of devices completed outside the GB over storage time in humid air/low vacuum environment cycle

Time (h)		V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm²)	FF (%)	PCE (%)
0	Average	916 ± 5	23.6 ± 0.1	55.3 ± 0.9	12.0 ± 0.3
	Champion	922	23.70	56.3	12.2
72	Average	1013 ± 12	22.9 ± 0.2	72.8 ± 2.9	$17.0 \pm 1.0$
(humid air storage)	Champion	1017	22.86	74.8	17.4
312	Average	1064 ± 16	21.4 ± 0.1	72.5 ± 2.6	16.5 ± 0.9
(humid air storage)	Champion	1083	21.76	74.1	17.5
720	Average	1068 ± 12	23.4 ± 0.6	74.8 ± 5.6	18.7 ± 2.1
(vacuum storage)	Champion	1083	24.72	73.6	19.7

Table S3: Average and	best parameters c	of completed	inside th	ne GB	devices of	over	storage	time in	humid	air/low	vacuum
environment cycle											

Time (h)		V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
0	Average	977 ± 30	21.5 ± 0.9	61.4 ± 3.8	12.7 ± 1.6
	Champion	975	22.1	61.4	13.2
72	Average	1104 ± 16	23.4 ± 0.8	77.3 ± 3.6	19.9 ± 1.9
(humid air storage)	Champion	1080	23.58	81.6	20.8
312	Average	1086 ± 25	21.1 ± 0.8	76.1 ± 4.8	17.4 ± 2.2
(humid air storage)	Champion	1074	21.40	81.6	18 .8
720	Average	1110±30	23.6 ± 0.4	76.0 ± 3.4	19.9 ± 1.8
(vacuum storage)	Champion	1121	24.07	77.3	20.9



Fig. S4: distribution of grain area of devices completed inside (blue) and outside (orange) the GB . PSCs completed outside show a larger grain population of small area respect to area size of grains of devices completed inside the GB



Fig. S5: dark J-V of different stored devices after 720 h from fabrication day

Table S4:  $N_t$  calculated from equation (1)

	N <sub>t</sub> (cm⁻³)
Devices completed inside the GB	0,9 x 10 <sup>16</sup>
	0,4 x 10 <sup>16</sup>
Devices completed outside the GB	1,9 x 10 <sup>16</sup>
	1,6 x 10 <sup>16</sup>



Fig. S6: Intensity-dependent  $J_{sc}$  for device (a) completed outside and (b) inside G