





## Effects of 5-Ammonium Valeric Acid Iodide as Additive on Methyl Ammonium Lead Iodide Perovskite Solar Cells

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**Figure S1.** (a) TRPL of *1mp*-MAPI and *1mp*-AVA layers deposited on glass. (b) TRPL of *3mp*-MAPI and *3mp*-AVA layers deposited on mesoporous ZrO<sub>2</sub>/glass.

	Fitting function: $y = A_1 \exp(-x/\tau_1) + A_2 \exp(-x/\tau_2) + A_3 \exp(-x/\tau_3) + y_0$									
	$y_0$	$A_1$	τ <sub>fast</sub> (ns)	RC fast <sup>a</sup>	$A_2$	$ au_{int}$ (ns)	RCint <sup>a</sup>	Аз	$ au_{slow}$ (ns)	RCslow <sup>a</sup>
MAPI on glass	7.6E-4	0.39	3.21	0.03	0.40	25.17	0.25	0.19	153.51	0.72
AVA on glass	1.6E-3	0.452	5.31	0.05	0.39	42.14	0.36	0.12	227.45	0.59
MAPI on ZrO <sub>2</sub> /Glass	3.8E-4	0.31	6.93	0.05	0.58	39.31	0.49	0.24	88.01	0.46
AVA on ZrO <sub>2</sub> /Glass	5.6E-4	0.41	9.85	0.09	0.61	51.47	0.65	0.07	181.4	0.26
AVA on ZrO <sub>2</sub> /Glass	5.6E-4	0.31	9.85	0.05	0.58	51.47	0.49	0.24	181.4	0.46

Table S1. Fitting parameters by a triple exponential function of the TRPL curves of Figure S1.

<sup>a</sup> Relative contribution



**Figure S2.** Pictures of PVK layers: fresh and after 20 h and 120 h aging at  $\geq$ 90% RH/RT. The black/grey aspect of the *3mp* samples is due to the carbon back electrode. (a) *1mp*-MAPI, (b) *1mp*-AVA, (c) *3mp*-MAPI and (d) *3mp*-AVA.



**Figure S3.** Forward and reverse *J-V* curves of (**a**) *1mp*-MAPI, (**b**) *1mp*-AVA, (**c**) *1mp*-MAPI-NoHTM and (**d**) *3mp*-AVA best cells.



Figure S4. External quantum efficiency, EQE, spectra and Jsc integration curves of the various cells.



**Figure S5.** Effect of the light intensity in sun% on the impedance spectra measured at the  $V_{oc.}$  (**a**) *1mp*-MAPI, (**b**) *1mp*-AVA, (**c**) *1mp*-AVA-NoHTM and (**d**) *3mp*-AVA.



**Figure S6**. (**a**,**b**) Equivalent electrical circuits employed to fit impedance spectra of PSCs. See the core text for explanation. R<sub>s</sub>, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are resistances. CPE<sub>1</sub>, CPE<sub>2</sub>, CPE<sub>3</sub> and CPE<sub>4</sub> are constant phase elements.



**Figure S7.** Effect of the applied voltage on the impedance spectra of the investigated cells. (a) *1mp*-MAPI, (b) *1mp*-AVA (c) *1mp*-AVA-NoHTM, (d) *3mp*-AVA low voltage and (e) *3mp*-AVA high voltage.



**Figure S8.** Effect of *V*<sub>appl</sub> on (**a**) *R*<sub>s</sub>, (**b**) R<sub>3</sub> and (**c**) C<sub>3</sub> parameters.

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