Electronic Supplementary Information for

Tuning optical/electrical properties of 2D/3D perovskite by the inclusion of aromatic cation

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Table S1. Values of time constants (τ i), normalized (to 100 %) amplitudes (Ai) and offsets of the biexponential functions used to fit the initial TA decays shown in Figure 3b.

$Any_2MA_{n-1}Pb_nI_{3n+1}, \ \lambda_{pump} = 600 \ nm$					
Sample	A_{1} [%]	$\tau_1 \pm 0.1 \ (ps)$	A_{2} (%)	$ au_2 \pm 3 \text{ (ps)}$	Offset (%)
n = 3	87	0.5	13	18	0
n = 5	89	0.5	11	18	0
$3D(n = \infty)$	16	0.6			84

Table S2. Values of time constants (τ i), normalized (to 100 %) amplitudes (Ai) and offsets of the biexponential functions used to fit the TA rise (negative amplitudes) and decays at 735 and 770 nm shown in Figure S4a,b. While the decays were to slow to be analysed within interrogated time interval, the decaying signals were taken only as offset value.

$Any_2MA_{n-1}Pb_nI_{3n+1}, \ \lambda_{pump} = 600 \ nm$					
Sample	$A_{1}[\%]$	$\tau_1 \pm 0.1 \ (ps)$	$A_{2}(\%)$	$\tau_2 \pm 3 \text{ (ps)}$	Offset (%)
n = 3	-88	0.5	-12	40	100
n = 5	-88	0.5	-12	40	100
$3D(n = \infty)$					100

 Table S3. Photovoltaic parameters for champion devices (mean values) at each evaluated temperatures

T [°C]	J _{sc} [mAcm ⁻²]	V _{oc} [mV]	FF [%]	PCE [%]
110	10.39	814.19	70.44	5.96
	(9.72±0.06)	(782.60±4.01)	(66.86 ± 0.66)	(5.10±0.09)
130	11.26	805.80	70.13	6.37
	(10.25±0.09)	(782.03±3.74)	(66.77±0.68)	(5.36±0.09)
150	12.23	821.71	68.31	6.86
	(11.18±0.12)	(791.55±3.40)	(66.92±0.51)	(5.93±0.09)
170	12.51	811.36	68.64	6.97
	(10.96±0.20)	(779.70±4.57)	(62.55±0.89)	(5.39±0.16)
190	13.79	818.59	67.58	7.63
	(9.96±0.33)	(751.94±4.68)	(62.27±0.80)	(4.73±0.20)

1. Chemical structure of cations for 2D materials



Fig. S1 Chemical structure of the main cations used to date. From left to right, butylammonium (BA), ammonium valeric acid (AVA), 2-iodoethylammonium (EA), phenethylammonium (PEA) and anilinium (Any).

2. Determination of surface coating by SEM for films prepared at 130 $^\circ C$ and for n=3 and 5

$Any_2MA_2Pb_3I_{10}$ (n=3)				
Magnification	5000x	10000x		
Surface coating (%)	45	48		
$Any_{2}MA_{4}Pb_{5}I_{16} (n=5)$				
Magnification	5000x	10000x		
Surface coating (%)	67	67		

Fig. S2 The percentage determination of surface covering for $Any_2MA_{n-1}Pb_nI_{3n+1}$ with n=3 and 5, were carried out using the shaded threshold method, using imageJ software.

3. PL & TRPL characterization



Fig. S3 (a) and (b) PL for several selected temperatures in the studied range for n = 5 and 3 aniline samples, respectively; shadow areas around 1.54 eV correspond to some remaining laser pumping the BBO crystal used to double the pulsed Ti:sapphire laser at 808 nm. (c) and (d) TRPL spectra in n= 5 and 3 samples, respectively, detected at the PL peak wavelength for two characteristic temperatures and the corresponding biexponential fitting (orange continuous line).

4. TAS measurements



Fig. S4 Normalized TA (a) rise and (b) decay of 2D/3D Any/MAPbI₃ films (n = 3 and 5) upon fs-excitation at 400 nm and observation at 735 and 770 nm. (c) TA spectra of 2D/3D Any/MAPbI₃ films (n = 5) at 2 ps pump-probe delay upon excitation at 400, 500, 600 and 700 nm. Normalized TA (d) rise and (e) decay of 2D/3D Any/MAPbI₃ films (n = 5) upon fs-excitation at 400, 500, 600 and 700 nm and observation at 770 nm. The solid lines are from the best (a,d) monoexponential and (b,e) multiexponential fits. The used fluence of the absorbed photons was 9×10^{12} ph/cm².

5. XRD patterns and FWHM determination



Fig. S5 (a) The XRD patterns of films fabricated in the range 100-190 °C. (b) As the temperature is gradually increased on going from 100 to 190 °C Full Width at Half Maximum narrows.

T (°C)	Grain size			
	(μm)			
		- Aure - E		
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			0	J Dod Date of the second s
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			300	6
		15	200	102 (particular loss) (b)
			100 0	200 397.4

6. Grain size determination

Fig. S6 Grain size determination.

7. Determination of surface coating by SEM for films prepared at 110, 150 and 190 $^\circ \rm C$

Any ₂ MA ₄ Pb ₅ I ₁₆			
T=110 °C			
Magnification	5000x	10000x	
Surface coating (%)	58	56	
T=150 °C			
Magnification	5000x	10000x	
Surface coating (%)	65	69	
T=190 °C			
Magnification	5000x	10000x	
Surface coating	80	78	
(%)			

Fig. S7 Coating's percentage of the surface. The employed method was based on shaded threshold method using imageJ software.



8. Atomic Force Microscopy imaging of the perovskite films

Fig. S8i (a) Topography and (b) surface potential maps of a typical perovskite film annealed at 110 °C. The scale is $5 \times 5 \mu m$. (c) Line profiles of surface potential variation. The line scan on top of perovskite grain shows a minor variation in the local surface potential whereas a nearly 1 V jump in the surface potential at the grain boundary is due to the TiO₂ layer.



Fig. S8ii Topography (a), resistance and current maps (b & c) of a typical perovskite film annealed at 190 $^{\circ}$ C. Figure (d) demonstrates local current profiles measured at different grain regions marked in (c).

9. Impedance Spectroscopy



Fig. S9 (a) Recombination resistance, R_{rec} , and (b) low frequency capacitance, C_{lf} , obtained from the fitting of the impedance spectra at different applied bias under 1 sun illumination. The fitting has been performed using the equivalent circuits discussed elsewhere.(1-3) R_{rec} has been obtained by addition of the resistances of high frequency and low frequency (lf) semicircles obtained in the Nyquist plot.(3) C_{lf} is related with the accumulation capacitance regulated by moving ions,(2, 4) as it has been obtained from the capacitance of the low frequency arc.





Fig. S10 Statistical distribution for each photovoltaic parameter and fabrication's temperature.

11. Stability response to environmental conditions



Fig. S11 Stability curves. The devices fabricated between 110 °C to 150 °C show a higher PCE than 3D perovskite based devices after 288 h under an ambient humidity over 40%. The totalities of the samples were stored in dark conditions.

REFERENCES

1. Guerrero A, Garcia-Belmonte G, Mora-Sero I, Bisquert J, Kang YS, Jacobsson TJ, et al. Properties of Contact and Bulk Impedances in Hybrid Lead Halide Perovskite Solar Cells Including Inductive Loop Elements. The Journal of Physical Chemistry C. 2016 2016/04/21;120(15):8023-32.

2. Zarazua I, Han G, Boix PP, Mhaisalkar S, Fabregat-Santiago F, Mora-Seró I, et al. Surface Recombination and Collection Efficiency in Perovskite Solar Cells from Impedance Analysis. The Journal of Physical Chemistry Letters. 2016 2016/12/15;7(24):5105-13.

3. Zarazúa I, Sidhik S, Lopéz-Luke T, Esparza D, De la Rosa E, Reyes-Gomez J, et al. Operating Mechanisms of Mesoscopic Perovskite Solar Cells through Impedance Spectroscopy and J–V Modeling. The Journal of Physical Chemistry Letters. 2017 2017/12/21;8(24):6073-9.

4. Zarazua I, Bisquert J, Garcia-Belmonte G. Light-Induced Space-Charge Accumulation Zone as Photovoltaic Mechanism in Perovskite Solar Cells. The Journal of Physical Chemistry Letters. 2016 2016/02/04;7(3):525-8.