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SUPPORTING INFORMATION

Surface stability of ionic-liquid-passivated mixed-cation perovskite probed with in-situ photoelectron spectroscopy

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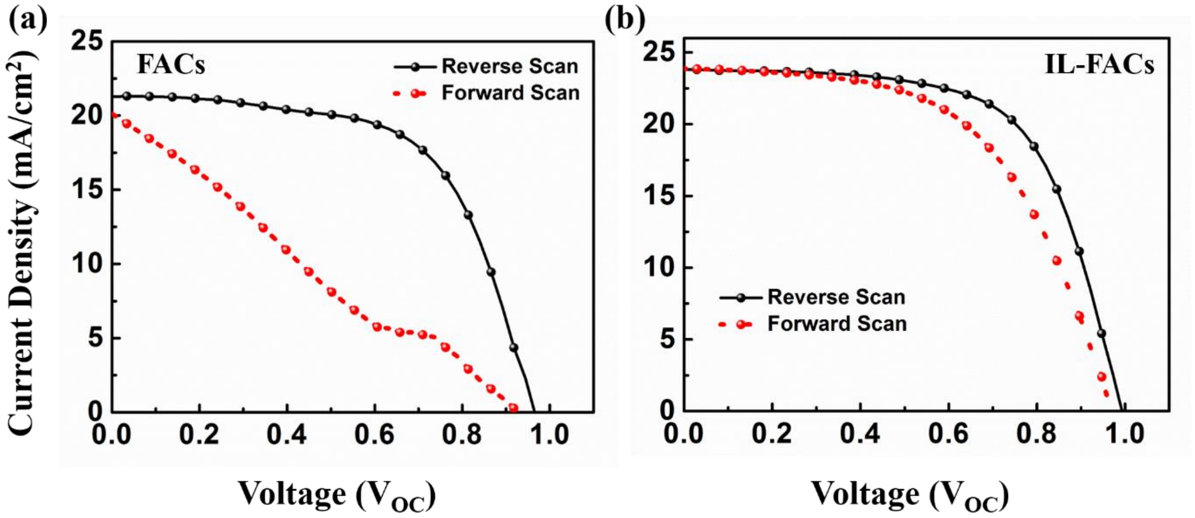

Figure. S1 (a, b) Reverse scan (black) and forward scan (red) *J-V* curves of devices fabricated with FACs and IL-FACs films, respectively.

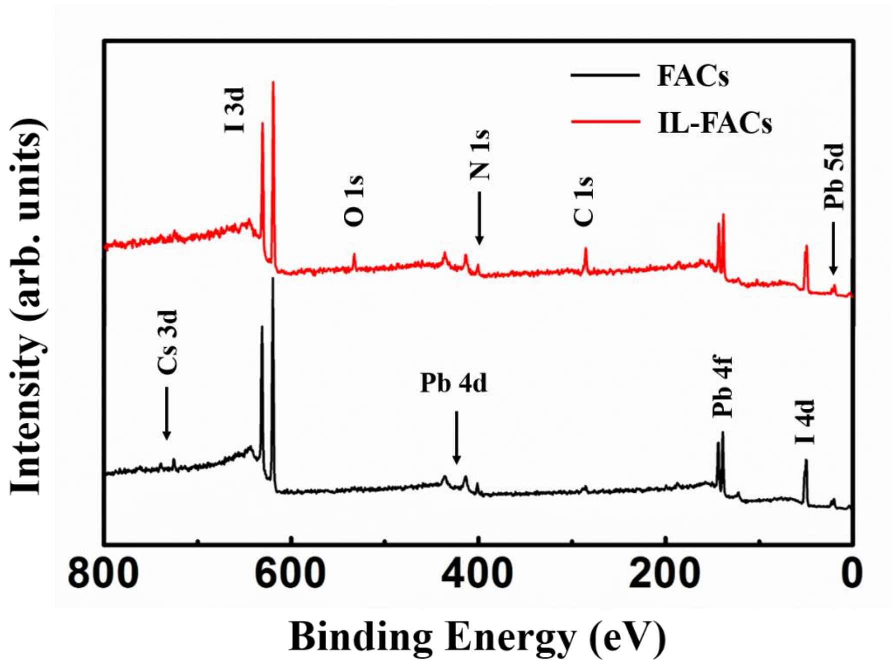

Figure S2. The overview spectra of FACs (black) and IL-FACs (red) measured using XPS at room temperature under UHV conditions.

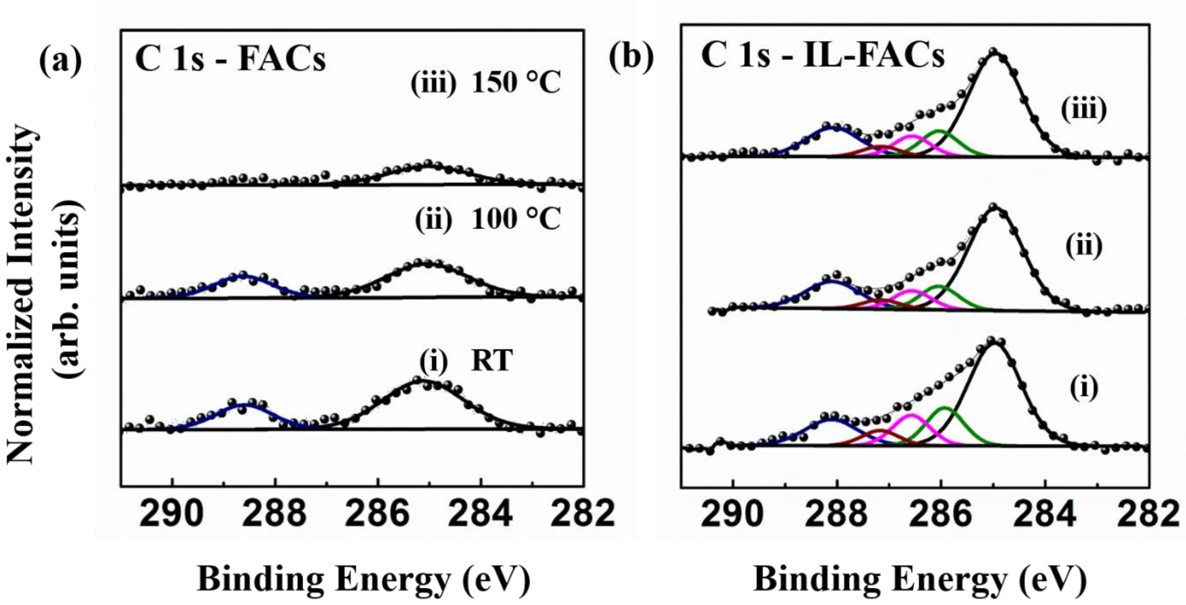

Figure S3. High-resolution C 1s spectra of FACs and IL-FACs measured under UHV conditions during thermal annealing. Spectra labelled as (i), (ii), and (iii) correspond to room temperature, 100 °C and 150 °C, respectively. Spectra have been normalised to the intensity of the Pb $4f_{7/2}$ signal from Pb^{2+} for each condition.

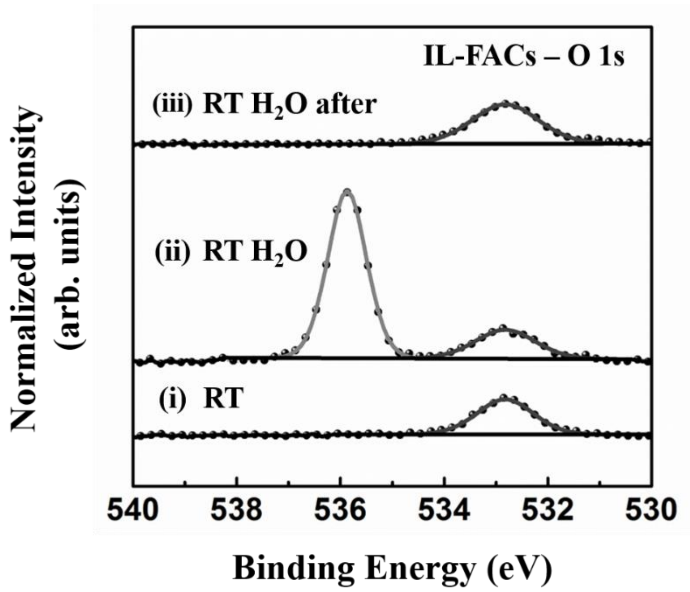

Figure S4. High-resolution O 1s spectra of IL-FACs measured at UHV conditions, during exposure and after exposure to 9 mbar water vapour at room temperature. Spectra labelled (i), (ii), and (iii) correspond to the sample measured before, during, and after exposure, respectively. Spectra are normalized to the intensity of Pb $4f_{7/2}$ core level from Pb^{2+} for each condition.

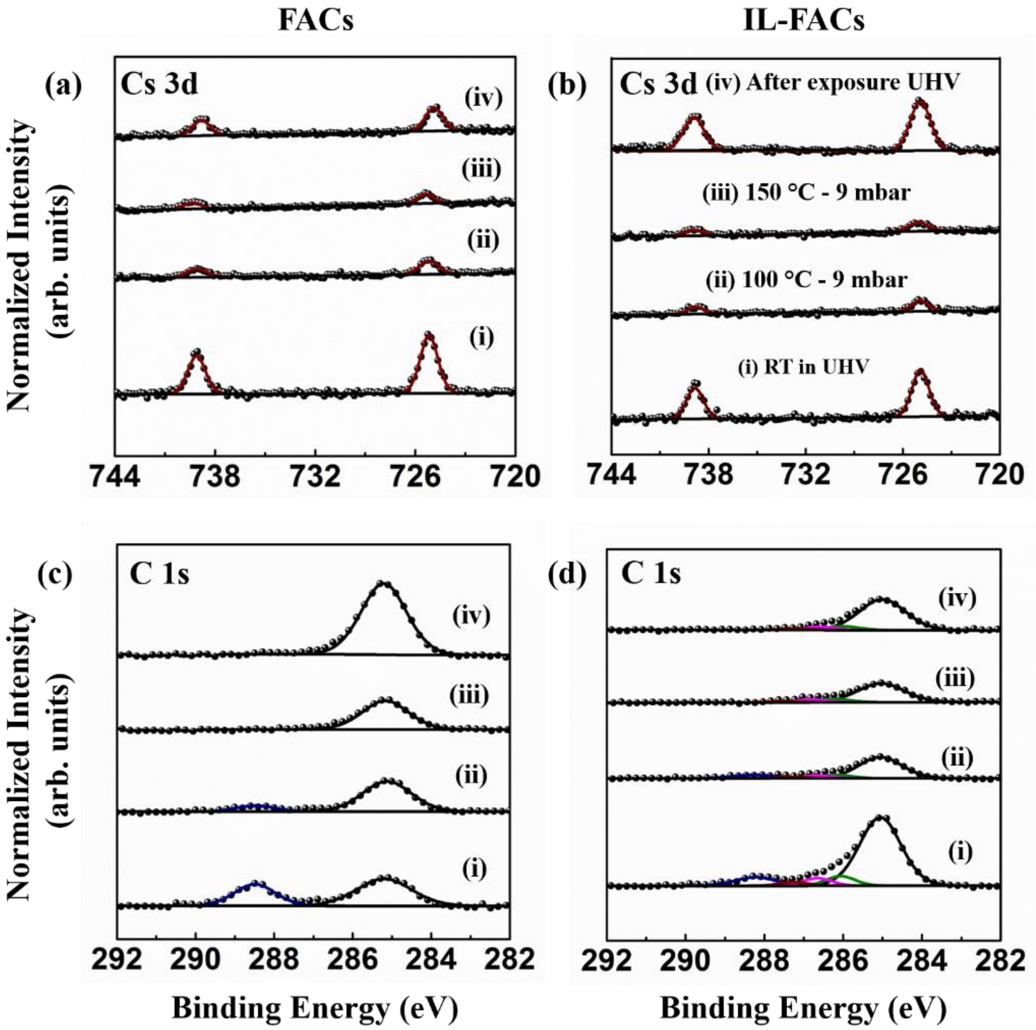

Figure S5. High-resolution core level NAPXPS spectra of (a,b) Cs 3d, (c,d) C 1s obtained from FACs (a,c) and IL-FACs (b,d) measured at different conditions as noted. Spectra labelled (i), (ii), (iii) and (iv) correspond to the sample measured under UHV conditions, at 100 °C in 9 mbar water vapour, 150 °C in 9 mbar water vapour and at room temperature in UHV conditions (after exposure), respectively. For each condition, all spectra are normalized to the intensity of the Pb $4f_{7/2}$ core level from Pb^{2+}.

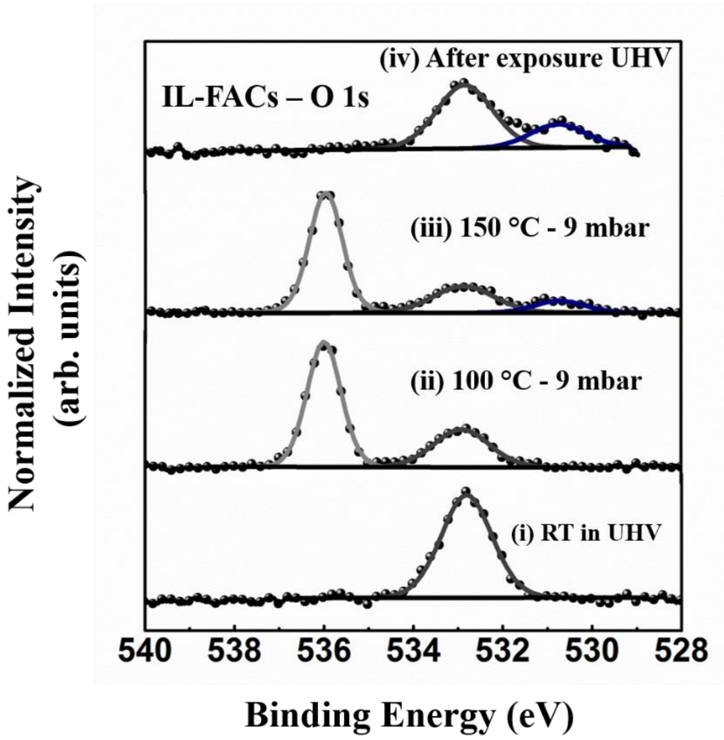

Figure S6. High-resolution O 1s spectra of IL-FACs measured at different conditions as noted. Spectra labelled (i), (ii), (iii) and (iv) correspond to the sample measured under UHV conditions, at 100 °C in 9 mbar water vapour, 150 °C in 9 mbar water vapour and at room temperature in UHV conditions (after exposure), respectively. Spectra are normalized to the intensity of Pb $4f_{7/2}$ core level from Pb^{2+} for each condition.

Table S1. Elemental stoichiometry calculated from XPS (and normalised to $[Pb^{2+}]=1.0$, *i.e.* I/Pb^{2+}, N/Pb^{2+}, C/Pb^{2+}, Cs/Pb^{2+}, and Pb^{0}/Pb^{2+}) of the FACs[1] and IL-FACs sample as a function of temperature.

Sample conditions	**Pb^{2+}**	**I**	**N (FA)**	**N (IL)**	**C-N(FA)**	**C-N (IL)**	**C-H**	**Cs**	**Metallic Pb^{0}**
Nominal	1.0	3.0	1.8		0.9			0.1	0
FACs pristine	1.0 ± 0.1	2.7 ± 0.2	1.2 ± 0.2	-	0.7 ± 0.2	-	1.9 ± 0.2	0.07 ± 0.02	0.07 ± 0.02
FACs 100 °C	1.0 ± 0.1	2.6 ± 0.2	1.0 ± 0.2	-	0.6 ± 0.2	-	1.3 ± 0.2	0.05 ± 0.02	0.11 ± 0.02
FACs 150 °C	1.0 ± 0.1	2.1 ± 0.2	0.4 ± 0.2	-	0.2 ± 0.2	-	0.7 ± 0.2	0.04 ± 0.02	0.17 ± 0.02
IL-FACs pristine	1.0 ± 0.1	3.2 ± 0.2	1.4 ± 0.2	0.5 ± 0.1	0.8 ± 0.2	1.6 ± 0.2	3.2 ± 0.2	0.12 ± 0.02	-
IL-FACs 100 °C	1.0 ± 0.1	3.5 ± 0.2	1.6 ± 0.2	0.5 ± 0.1	0.9 ± 0.2	1.4 ± 0.2	3.9 ± 0.2	0.08 ± 0.02	-
IL-FACs 100 °C	1.0 ± 0.1	3.5 ± 0.2	1.6 ± 0.2	0.5 ± 0.1	0.9 ± 0.2	1.4 ± 0.2	3.8 ± 0.2	0.05 ± 0.02	0.02

Table S2. Elemental stoichiometry calculated from XPS (and normalised to $[Pb^{2+}]=1.0$, *i.e.* I/Pb^{2+}, N/Pb^{2+}, C/Pb^{2+}, Cs/Pb^{2+}, and Pb^0/Pb^{2+}) of the FACs[1] and IL-FACs samples calculated from XPS before and after exposure to 9 mbar water vapour.

Sample conditions	Pb^{2+}	**I**	**O 1s**	**N (FA)**	**N (IL)**	**C-N(FA)**	**C-N (IL)**	**C-H**	**Cs**	**Metallic** Pb^0
Nominal	1.0	3.0		1.8		0.9			0.1	0
FACs before exposure	1.0 ± 0.1	2.6 ± 0.2	0.6 ± 0.1	1.2 ± 0.2	-	0.8 ± 0.2	-	2.3 ± 0.2	0.04 ± 0.03	0.06 ± 0.02
FACs after exposure	1.0 ± 0.1	2.4 ± 0.2	0.6 ± 0.1	1.0 ± 0.2	-	0.7 ± 0.2	-	3.6 ± 0.2	0.01 ± 0.03	0.06 ± 0.02
IL-FACs before exposure	1.0 ± 0.1	2.7 ± 0.2	1.5 ± 0.1	1.5 ± 0.2	0.5 ± 0.1	0.9 ± 0.2	1.0 ± 0.2	5.9 ± 0.2	0.1 ± 0.02	0.02 ± 0.02
IL-FACs after exposure	1.0 ± 0.1	2.6 ± 0.2	2.1 ± 0.1	1.5 ± 0.2	0.4 ± 0.1	0.9 ± 0.2	1.0 ± 0.2	5.8 ± 0.2	0.03 ± 0.02	0.02 ± 0.02

Table S3. Elemental stoichiometry calculated from XPS (and normalised to $[Pb^{2+}]=1.0$, *i.e.* I/Pb^{2+}, N/Pb^{2+}, C/Pb^{2+}, Cs/Pb^{2+}, and Pb^{0}/Pb^{2+}) of the FACs and IL-FACs samples calculated from NAPXPS before and after annealing to 100 and 150 °C in 9 mbar water vapour.

Sample conditions	**Pb^{2+}**	**I**	**N (FA)**	**N (IL)**	**C-N(FA)**	**C-N (IL)**	**C-H**	**Cs**	**Metallic Pb^{0}**
Nominal	1.0	3.0	1.8		0.9			0.1	0
FACs before exposure	1.0 ± 0.1	2.8 ± 0.2	1.8 ± 0.2	-	0.9 ± 0.2	-	1.7 ± 0.2	0.08 ± 0.02	0.1 ± 0.02
FACs after exposure and annealing	1.0 ± 0.1	1.7 ± 0.2	0.1 ± 0.2	-	0 ± 0.2	-	3.2 ± 0.2	0.03 ± 0.02	0.1 ± 0.02
IL-FACs before exposure	1.0 ± 0.1	2.7 ± 0.2	1.4 ± 0.2	0.4 ± 0.1	0.9 ± 0.2	1.1 ± 0.2	7.0 ± 0.2	0.09 ± 0.02	0.1 ± 0.02
IL-FACs after exposure and annealing	1.0 ± 0.1	2.0 ± 0.2	0.2 ± 0.2	0.2 ± 0.1	0.0 ± 0.2	0.8 ± 0.2	4.2 ± 0.2	0.12 ± 0.02	0.2 ± 0.02

Table S4. Stoichiometry ratio of O 1s calculated from XPS (and normalised to $[Pb^{2+}]$=1.0, *i.e.* O/Pb^{2+}) of the FACs and IL-FACs samples calculated from XPS before and after annealing to 100 and 150 °C in 9 mbar water

Sample Conditions	O_{ads}	$O_{lattice}$
FACs before exposure	0.4 ± 0.1	
FACs after exposure and annealing	0.4 ± 0.1	0.2 ± 0.1
IL-FACs before exposure	1.8 ± 0.1	
IL-FACs after exposure and annealing	1.4 ± 0.1	0.5 ± 0.1

Reference

1 S. Maniyarasu, J. C. R. Ke, B. F. Spencer, A. S. Walton, A. G. Thomas and W. R. Flavell, *ACS Appl. Mater. Interfaces*, 2021, **13(36)**, 43573-43586.