Supplementary Information: Composition dependence of X-ray stability and degradation mechanisms at lead halide perovskite single crystal surfaces

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Inelastic mean free path calculations:

The inelastic mean free path (IMFP) was calculated using the TPP-2M method[1], as shown in Table S1. All used parameters are shown in Table S2. The kinetic energies are dependent on the core level and the crystal composition and are included in Table S1.

Table S1: Calculation of the inelastic mean free path (IMFP) for each composition ($MAPbCl_3$, $MAPbI_3$, $MAPbBr_3$, $FAPbBr_3$, $CsPbBr_3$) and in dependence of the kinetic energy of each core level using the TPP-2M method for a photon energy of 600 eV.

			IMFP [nm]				
Core Level		**E_{KIN} [eV]**	**$MAPbCl_3$**	**$MAPbI_3$**	**$MAPbBr_3$**	**$FAPbBr_3$**	**$CsPbBr_3$**
N 1s	**MA^+**	197.78	0.86	0.76	0.71	-	-
	FA^+	199.50	-	-	-	0.74	-
Cs 4d		524.44	1.34	-	-	-	-
Pb 4f		461.46	1.56	1.32	1.21	1.28	1.22
Br 3d		531.58	-	-	1.33	1.42	1.35
I 4d		550.58	-	1.50	-	-	-
Cl 2p		402.03	1.41	-	-	-	-

Table S2: Parameters used for the calculation of the inelastic mean free path for each crystal.

	$MAPbCl_3$	**$MAPbI_3$**	**$MAPbBr_3$**	**$FAPbBr_3$**	**$CsPbBr_3$**
Density [g/cm³]	1.58	4.15	3.80	3.79	4.83
Molecular weight [g/mol]	344.62	618.97	238.26	491.98	340.11
Number of valence electrons	40	40	40	43	26
Energy band gap [eV]	2.90	1.57	2.29	1.57	2.23

Calculation of the fluence:

The number of photons was calculated based on the time required to measure one loop of core levels and the number of photons per loop, considering the corresponding flux for each sample: Low Flux (LF = 1.2 $x10^{11}$ photons/second), High Flux (HF = 3.6 $x10^{11}$ photons/second). The fluence was calculated by multiplying the number of photons with 0.68/0.0023 to receive the number of photons per cm^2 (detailed explanation at experimental section in the manuscript).

Table S3: Number of photons per loop for all crystal compositions and number of photons per square cm.

Sample	**Time per loop (Seconds)**	**Photons per loop**	**Fluence per loop (photons/loop cm^2)**
$MAPbI_3$ HF	684	2.47 $x10^{14}$	7.24 $x10^{16}$
$MAPbBr_3$ LF	675	8.15 $x10^{13}$	2.41 $x10^{16}$
$MAPbCl_3$ LF	684	8.26 $x10^{13}$	2.44 $x10^{16}$
$CsPbBr_3$ HF	606	2.19 $x10^{14}$	6.47 $x10^{16}$
$FAPbBr_3$ HF	675	2.44 $x10^{14}$	7.21 $x10^{16}$
$FAPbBr_3$ LF	675	8.15 $x10^{13}$	2.41 $x10^{16}$

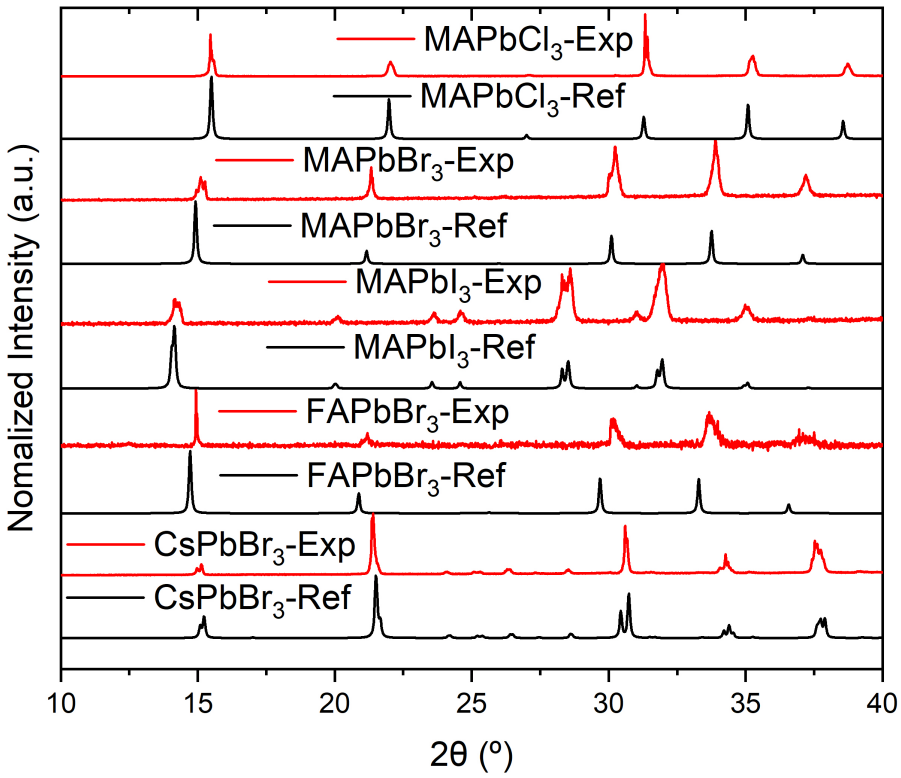


Figure S1: Experimental PXRD pattern of the polycrystalline powder of grounded single crystals (Red) of $CsPbBr_3$, $FAPbBr_3$, $MAPbI_3$, $MAPbBr_3$ and $MAPbCl_3$ compared with the profile obtained from their single crystal structures at room temperature (black).

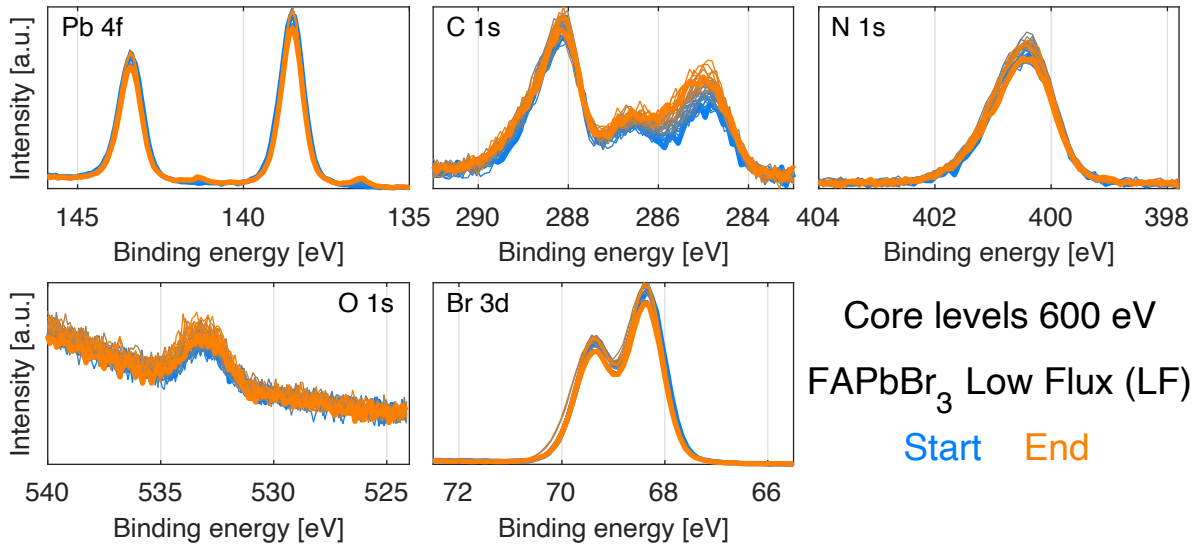
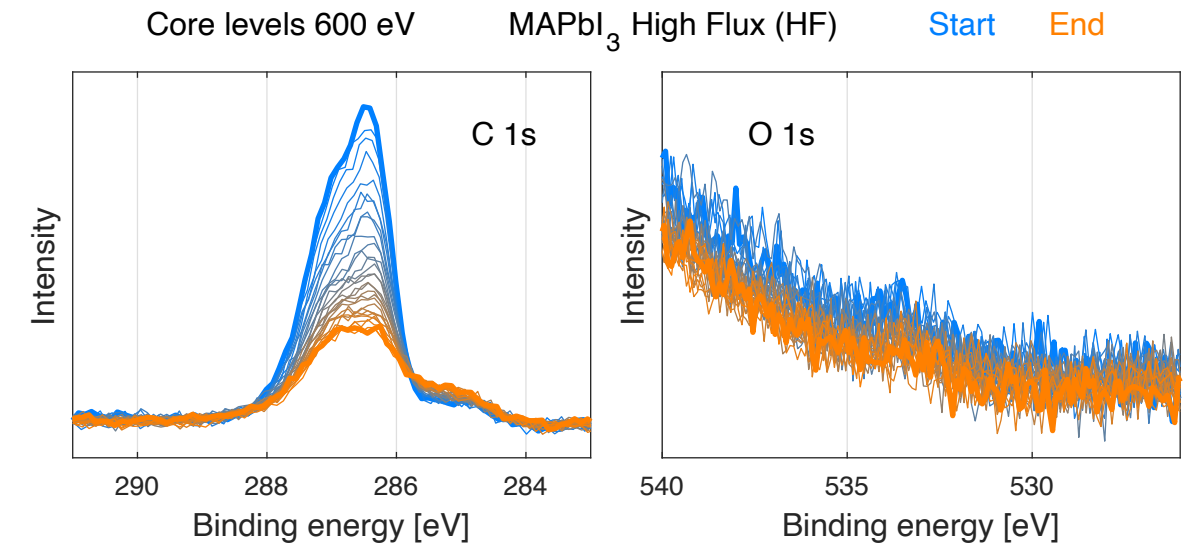
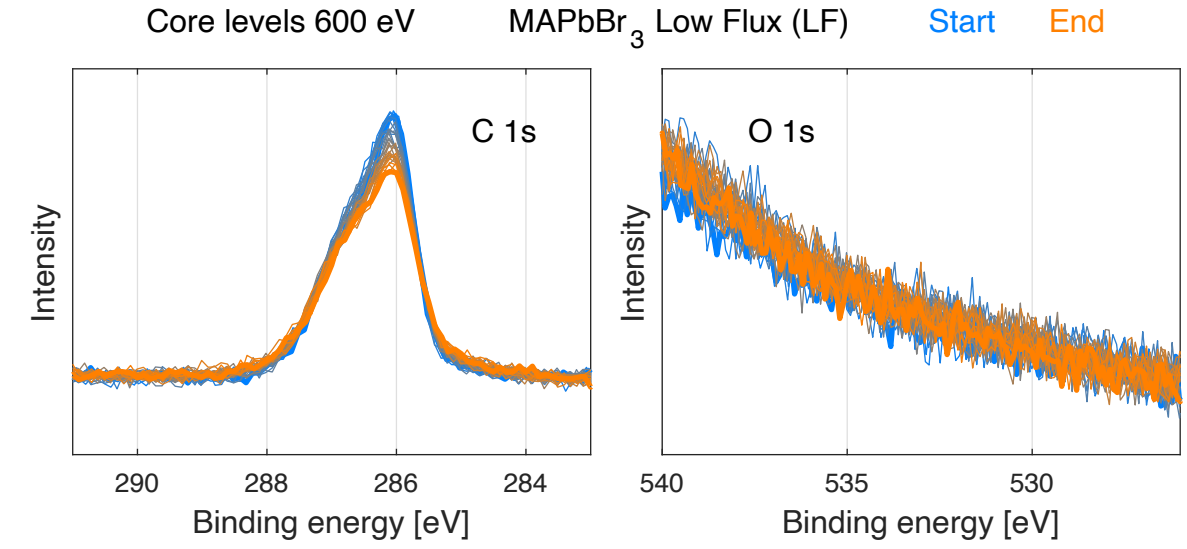
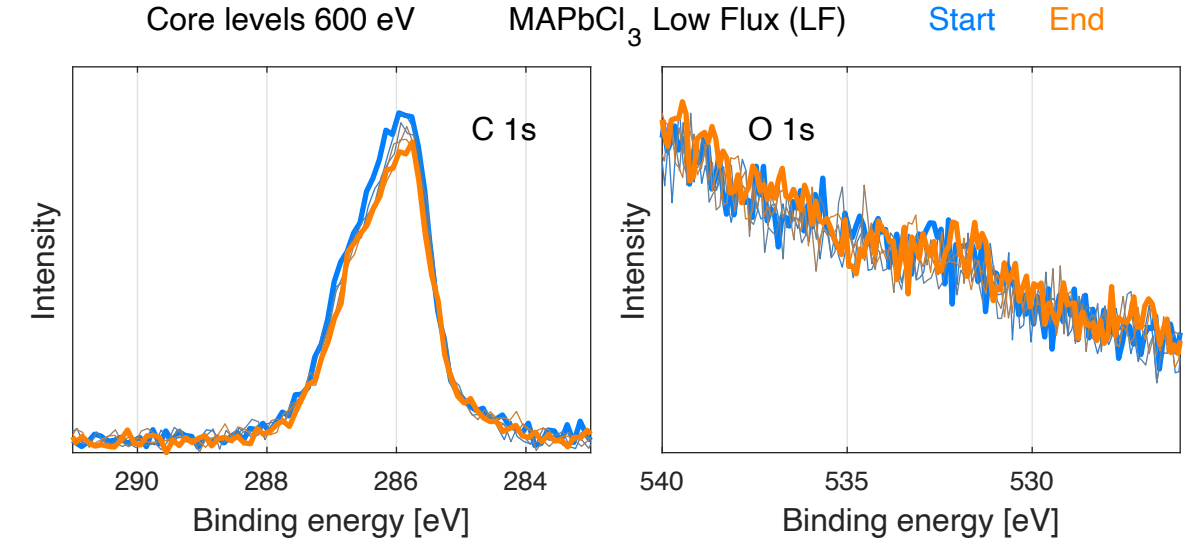


Figure S2: Pb 4f, C 1s, N 1s, O 1s and Br 3d core level spectra of $FAPbBr_3$ single crystal, recorded using the FlexPES beamline (MAX IV) with a photon energy of 600 eV under Low Flux (LF) of photons. The spectra are intensity normalized to the total amount of Pb 4f and energy calibrated against Pb $4f_{7/2}$ (Pb^{2+}) = 138.54 eV binding energy.


Core levels 600 eV
MAPbI3 High Flux (HF)
Start
End
C 1s
O 1s
Intensity
290
288
286
284
540
535
530
Binding energy [eV]


Core levels 600 eV
MAPbBr3 Low Flux (LF)
Start
End
C 1s
O 1s
Intensity
290
288
286
284
540
535
530
Binding energy [eV]


Core levels 600 eV
MAPbCl3 Low Flux (LF)
Start
End
C 1s
O 1s
Intensity
290
288
286
284
540
535
530
Binding energy [eV]

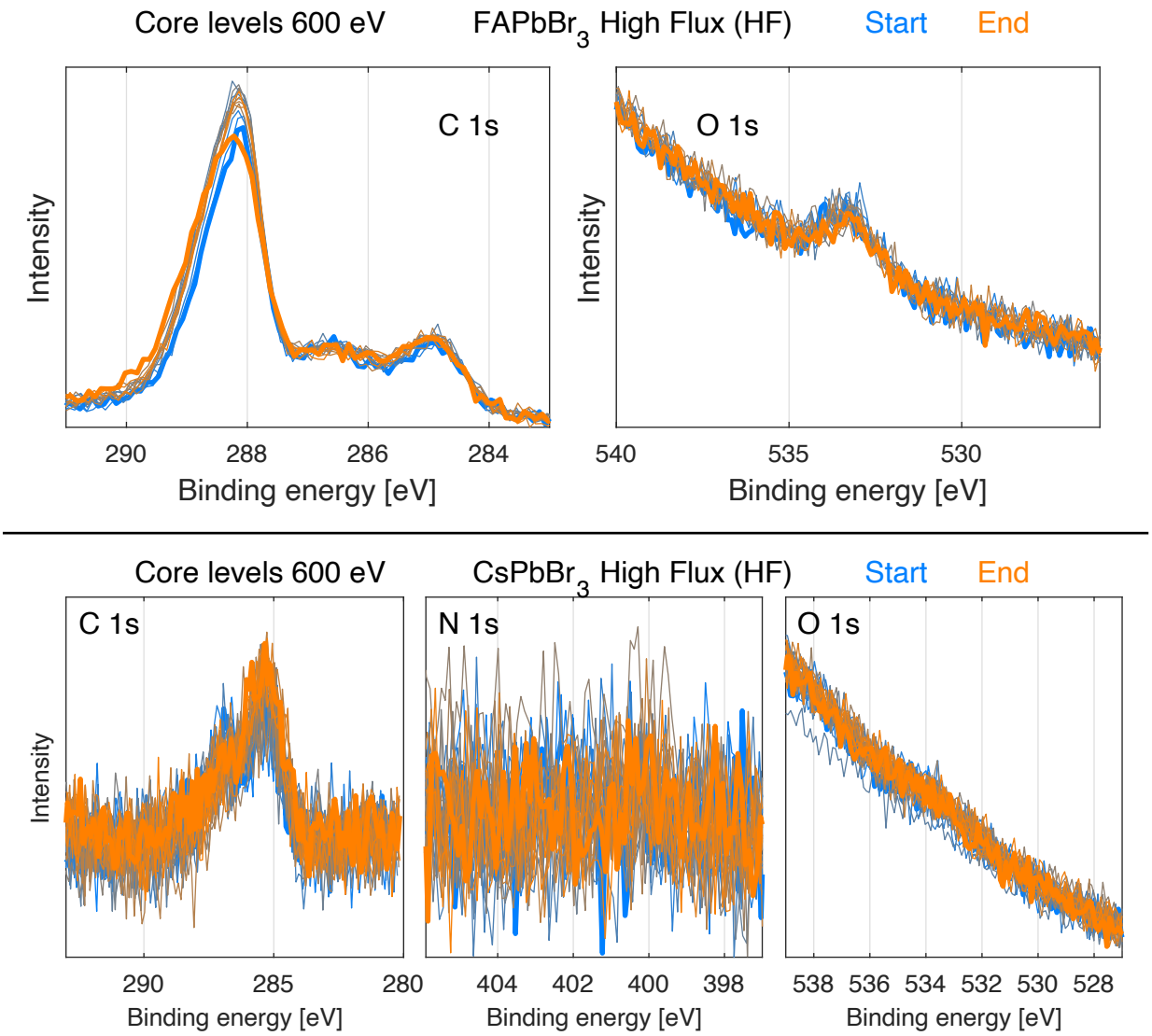


Figure S3 Core level spectra of Pb 4f, N 1s, Cs 4d, C 1s, O 1, I4d/ Br 3d/ Cl 2p of $MAPbI_3$, $MAPbBr_3$, $MAPbCl_3$, $FAPbBr_3$ and $CsPbBr_3$, recorded using the FlexPES beamline (MAX IV) with a photon energy of 600 eV. The spectra are intensity normalized to the total amount of Pb 4f and energy calibrated against Pb $4f_{7/2}$ (Pb^{2+}) = 138.54 eV binding energy. Low flux (LF = 1.2 $x10^{11}$ photons/second), high flux (HF = 3.6 $x10^{11}$ photons/second).

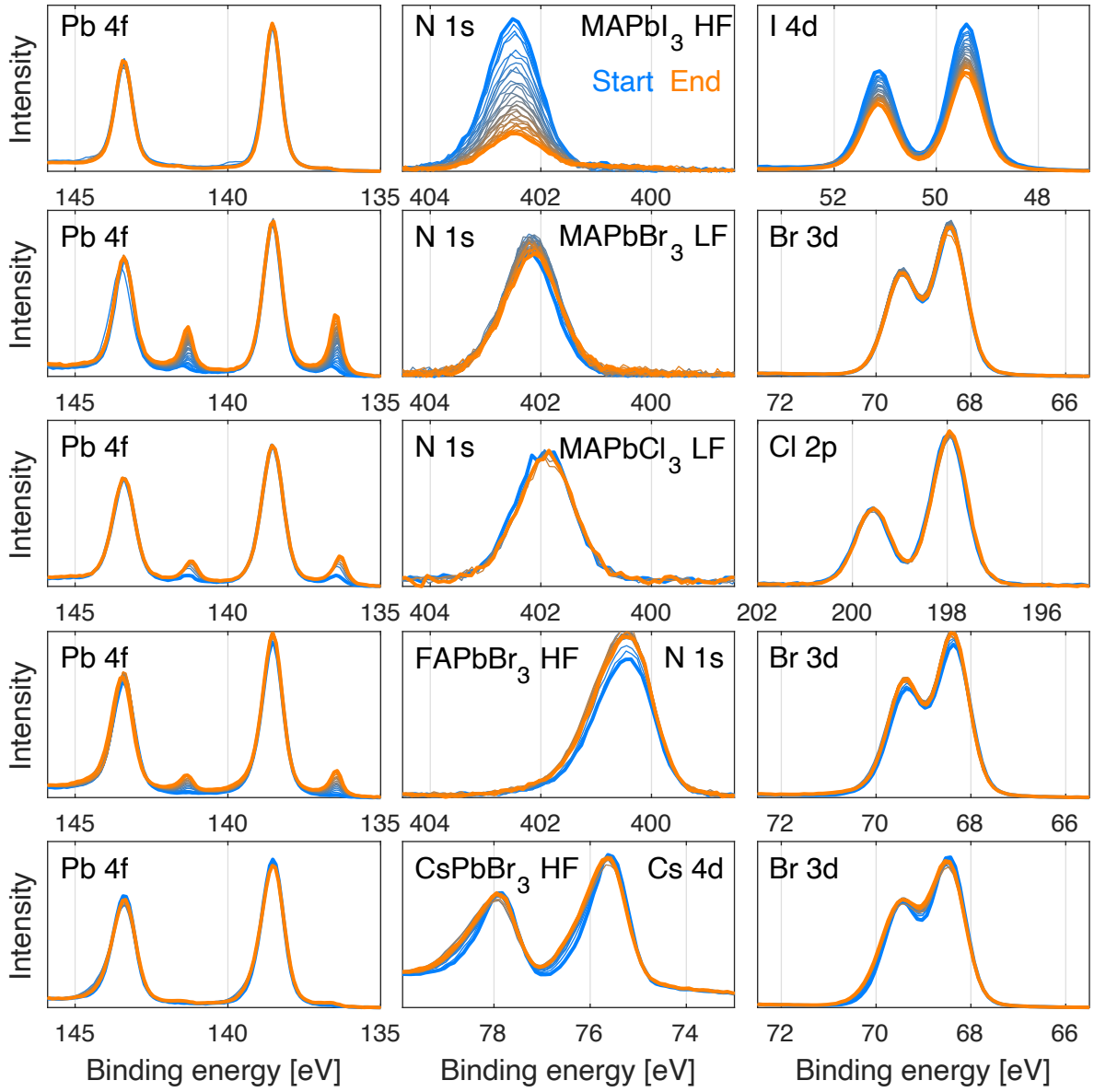


Figure S4: Core level spectra of Pb 4f, N 1s/ Cs 4d and I4d/ Br 3d/ Cl 2p of $MAPbI_3$, $MAPbBr_3$, $MAPbCl_3$, $FAPbBr_3$ and $CsPbBr_3$ single crystals, recorded using the FlexPES beamline (MAX IV) with a photon energy of 600 eV. The spectra are intensity normalized to Pb^{2+} and energy calibrated against Pb $4f_{7/2}$ (Pb^{2+}) = 138.54 eV binding energy. Low flux (LF = 1.2 $x10^{11}$ photons/second), High Flux (HF = 3.6 $x10^{11}$ photons/second).

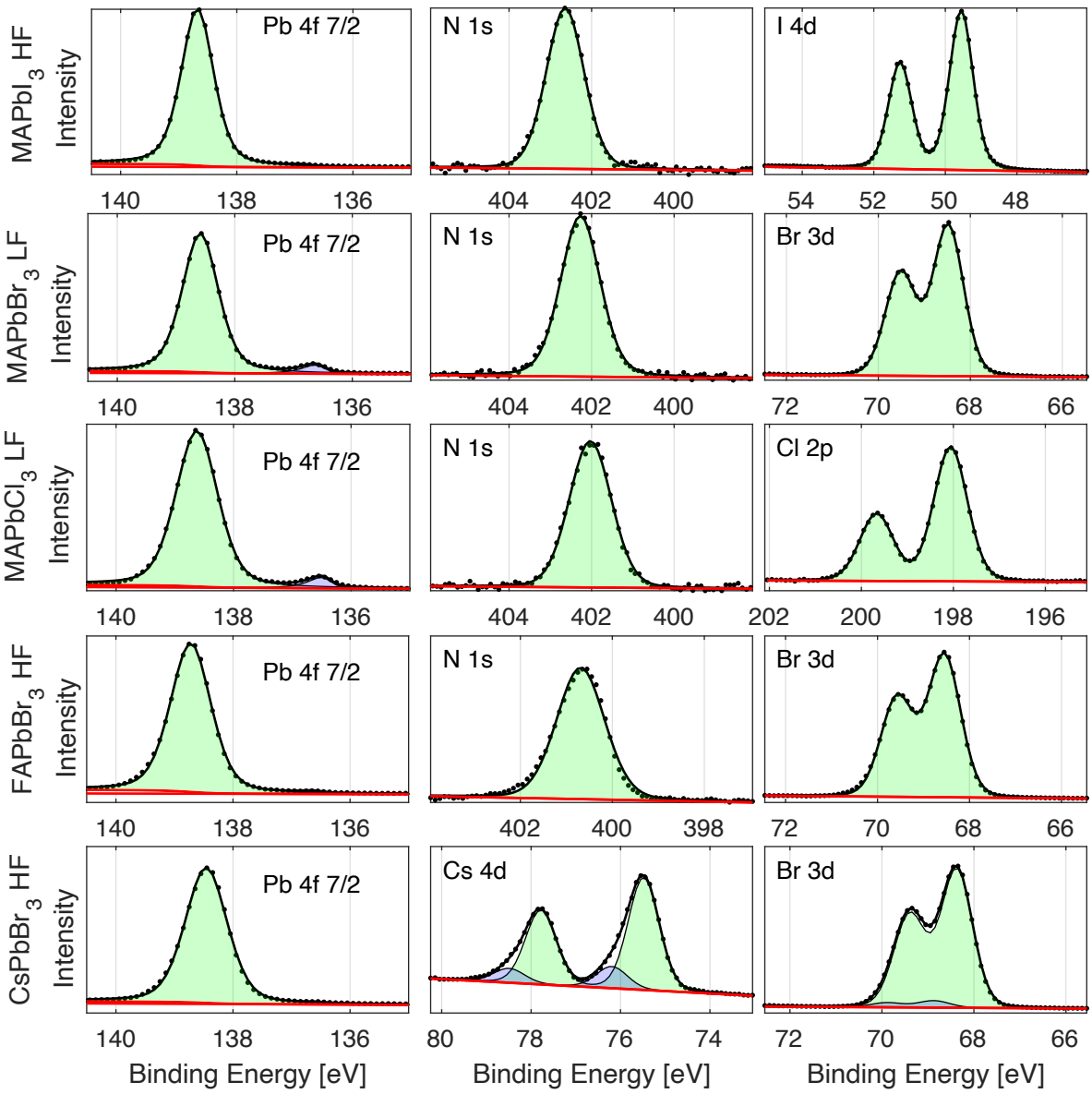


Figure S5: Exemplary curve fitting using Voigt functions for the first loop of measurements of the core levels Pb 4f, N 1s/ Cs 4d and I4d/ Br 3d/ Cl 2p of $MAPbI_3$, $MAPbBr_3$, $MAPbCl_3$, $FAPbBr_3$ and $CsPbBr_3$.

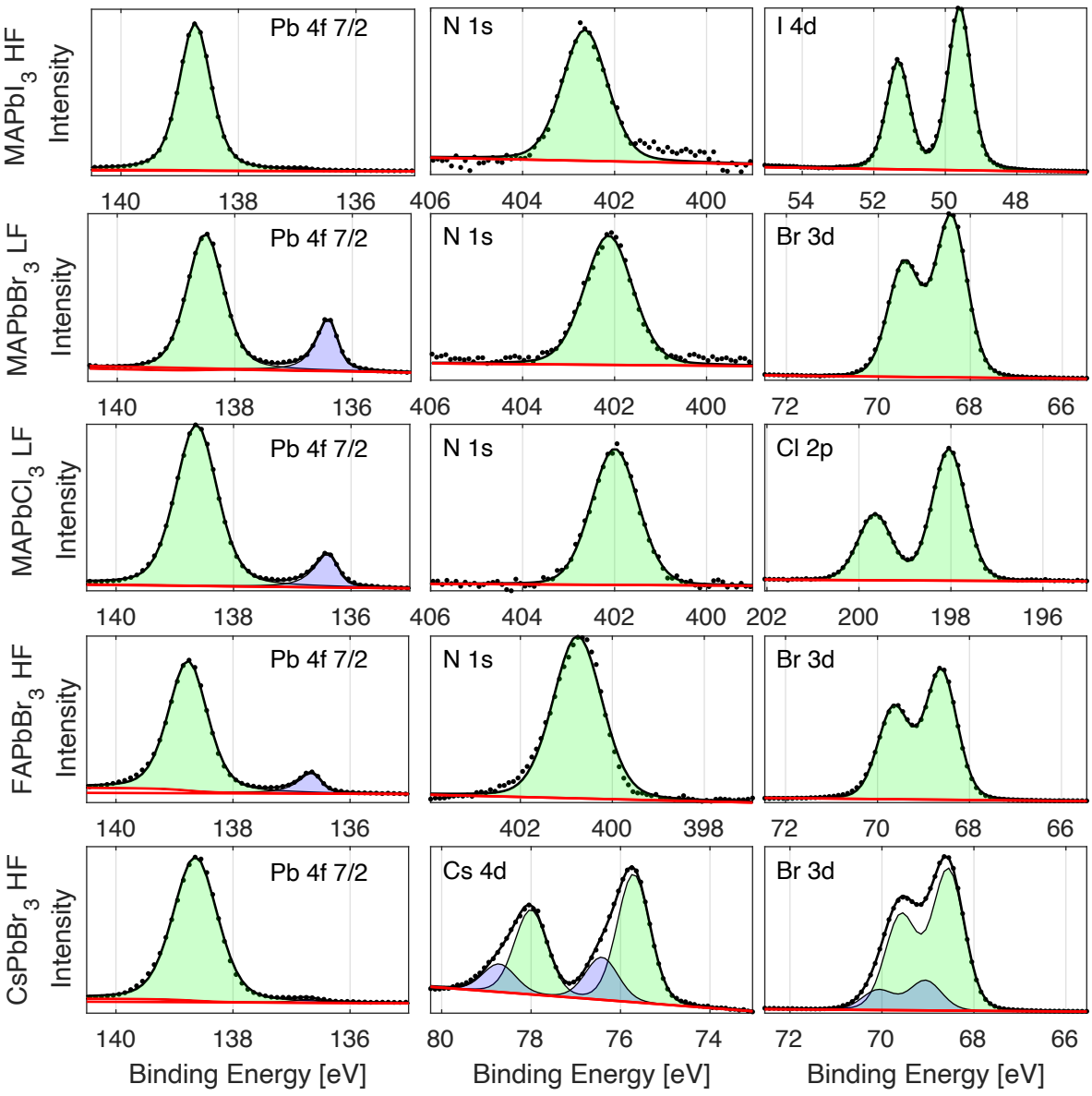


Figure S6: Curve fitting of the last loop of measurements using Voigt functions of the core levels Pb 4f, N 1s/ Cs 4d and I4d/ Br 3d/ Cl 2p of $MAPbI_3$, $MAPbBr_3$, $MAPbCl_3$, $FAPbBr_3$ and $CsPbBr_3$.

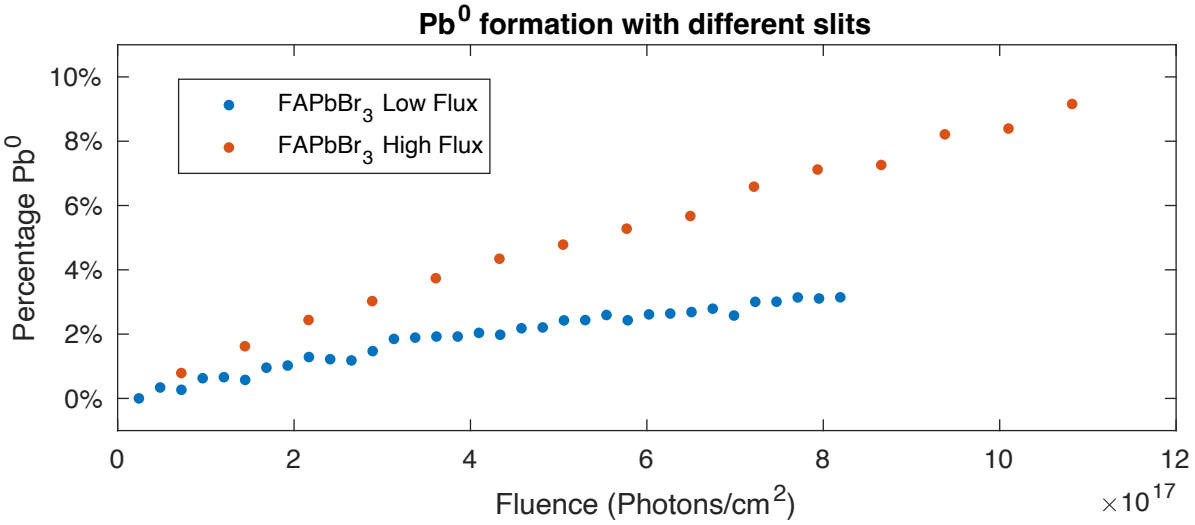


Figure S7: Impact of different photon flux on metallic lead formation of the $FAPbBr_3$ single crystal. The data represented with the blue dots was recorded using the low flux conditions (LF = 1.2 $x10^{11}$ photons/second), the data for the red dots was obtained using the higher flux (HF = 3.6 $x10^{11}$ photons/second). The Pb 4f spectra were recorded at a photon energy of 600 eV and the amount of metallic lead was determined using curve fitting and the Pb^0 intensity/ total Pb intensity relation.

References

1 C. J. Powell, *Journal of Vacuum Science & Technology A*, 2020, **38**, 023209.