

SUPPORTING INFORMATION

Efficient Planar Heterojunction Perovskite Solar Cells Based on Formamidinium Lead Bromide

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The lattice parameters were obtained by X-ray powder diffraction using a *Huber Imaging Plate Guinier Diffractometer G670* (Cu-K $_{\alpha 1}$ -radiation) and the TOPAS package for Rietveld refinements.¹ The refinements are based on a structure published by *Mashiyama et al.*² To describe the rotation of methylammonium in MAPbBr₃, the nitrogen and carbon atoms were displaced around the center of the unit cell. For FAPbBr₃, the carbon atom was placed in the center of the unit cell and the nitrogen atoms were dislocated around it. As a consequence of the fast rotation of the organic cation, the U_{iso} of C and N was restrained in both cases. The refined values can be seen in Table S1 and S2.

Table S1: Results of the Rietveld refinement of MAPbBr₃.

MAPbBr ₃					
space group					
<i>Pm-3m</i> (No.221)					
<i>Z</i>					
1					
lattice parameter [Å]					
5.923 (1)					
volume [Å ³]					
207.8 (1)					
atomic parameters		<i>x</i>	<i>y</i>	<i>z</i>	<i>occ</i>
Pb	1 <i>a</i>	0	0	0	1
Br	12 <i>h</i>	0	0.0724 (2)	0.5	0.25
C	12 <i>j</i>	0.4143 (4)	0.4143 (4)	0.5	0.0833
N	12 <i>j</i>	0.5857 (4)	0.5857 (4)	0.5	0.0833

$U_{\text{iso}} [\text{pm}^2]$	Pb	301 (2)
	Br	241 (4)
	C/N not refined	
$R_{\text{wp}} / R_{\text{p}}$	2.747/2.036	
$\chi^2 / R_{\text{Bragg}}$	1.930/2.916	

Table S2: Results of the Rietveld refinement of FAPbBr₃.

FAPbBr ₃					
space group		<i>Pm-3m</i> (No.221)			
<i>Z</i>		1			
lattice parameter [Å]		5.992 (1)			
volume [Å ³]		215.2 (1)			
atomic parameters		<i>x</i>	<i>y</i>	<i>z</i>	<i>occ</i>
Pb	1 <i>a</i>	0	0	0	1
Br	12 <i>h</i>	0	0.0617 (3)	0.5	0.25
C	1 <i>b</i>	0.5	0.5	0.5	1
N	12 <i>j</i>	0.3633 (5)	0.3633 (5)	0.5	
<i>U</i> _{iso} [pm ²]		Pb	403 (3)		
		Br	286 (6)		
C/N not refined					
<i>R</i> _{wp} / <i>R</i> _p		3.198/2.287			
χ^2 / <i>R</i> _{Bragg}		2.115/2.342			

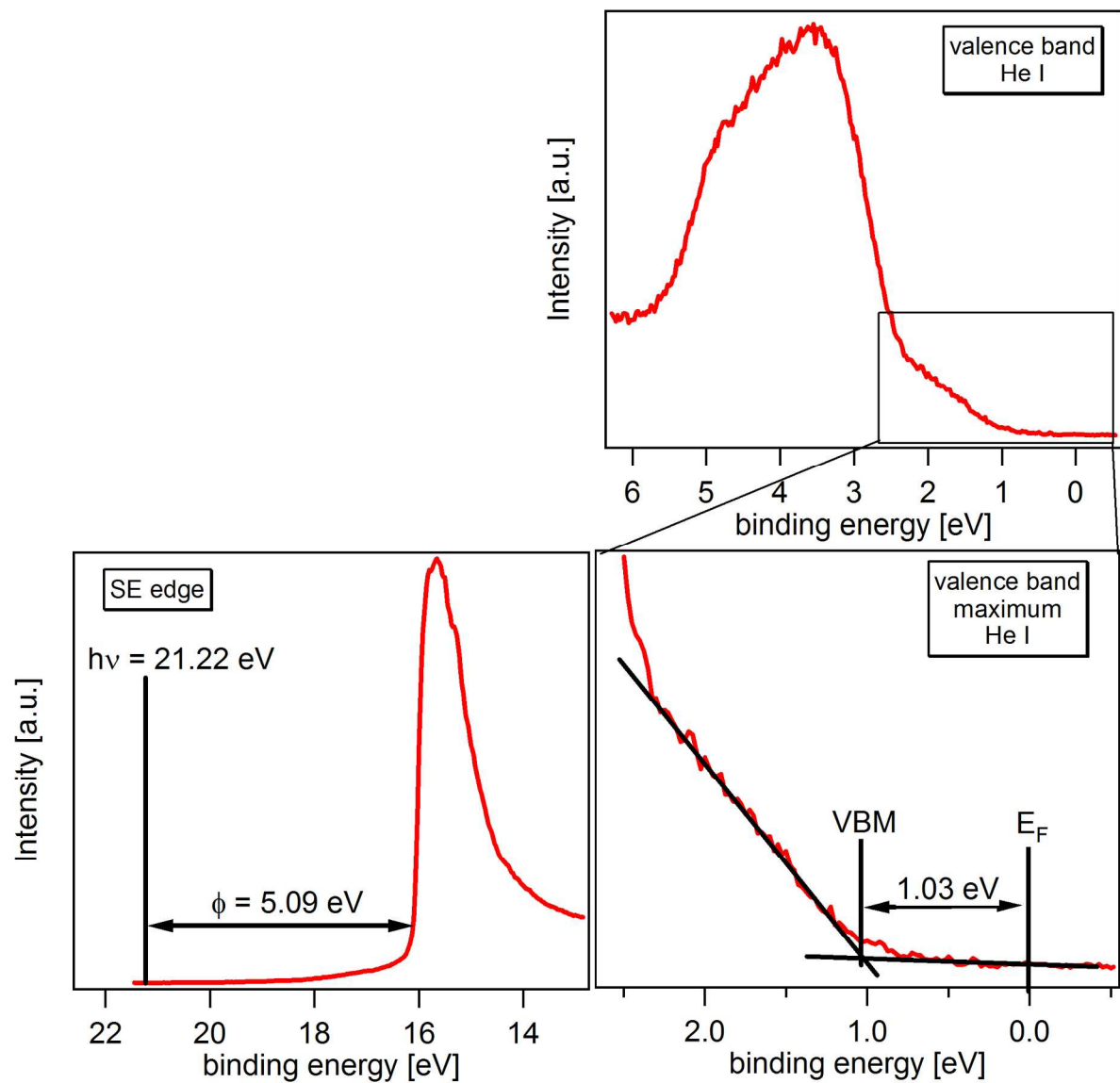


Figure S1: XPS spectra obtained for FAPbBr₃. The graph on the left describes the Fermi level E_F relative to vacuum. The images on the right show the energetic position of the valence band relative to the Fermi level E_F .

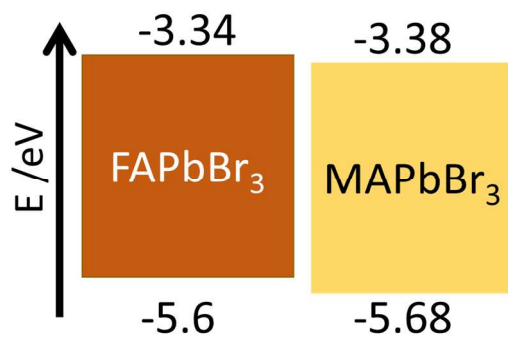


Figure S2: Comparison of the energy levels of FAPbBr₃ and MAPbBr₃. The values for MAPbBr₃ were taken from literature.³

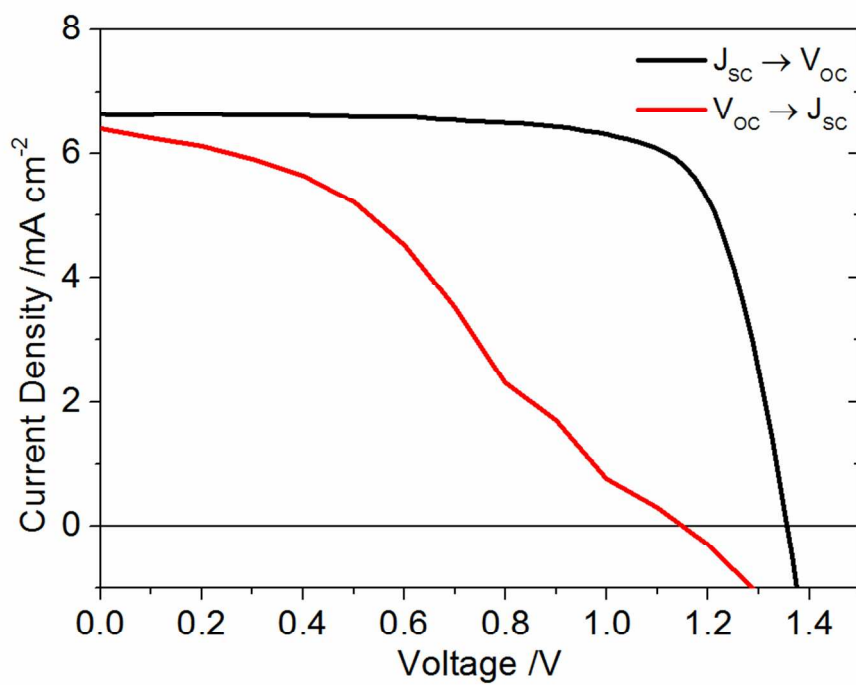


Figure S3: Forward and backward current-voltage sweep for a FAPbBr₃ solar cell.

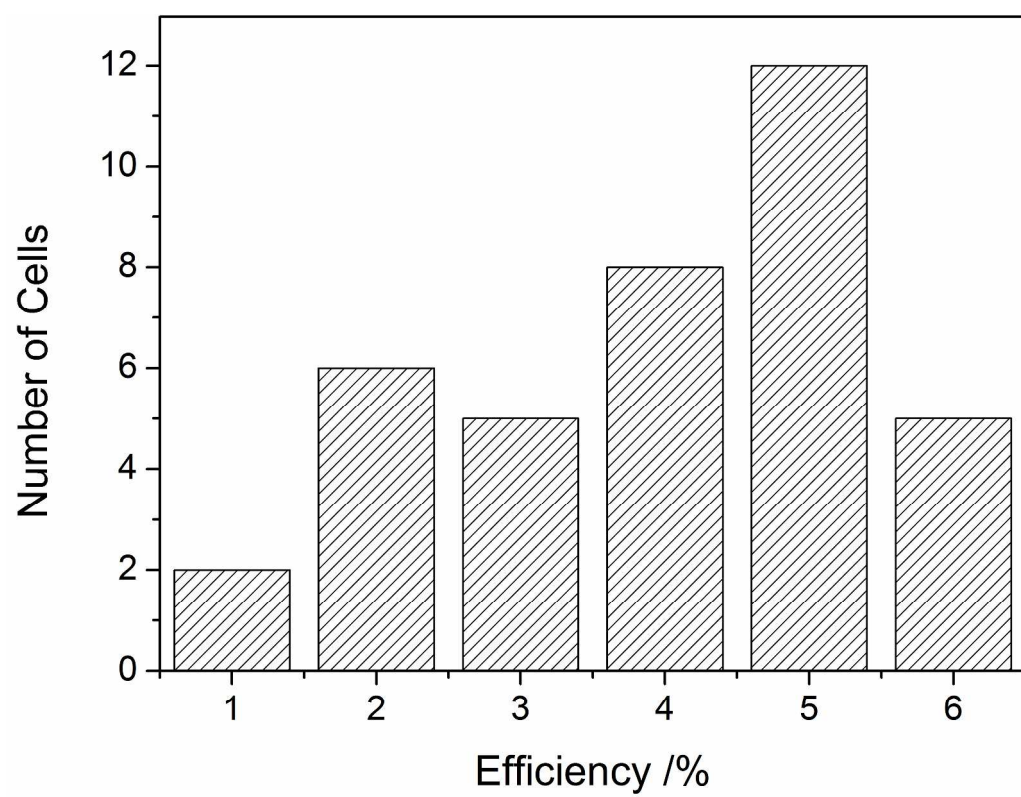


Figure S4: Power conversion efficiency (h) histogram of a batch of 40 devices.

The band gaps of MAPbBr₃ and FAPbBr₃ were determined by plotting $(\alpha h\nu)^2$ against the energy in eV, known as a Tauc plot. The estimated band gap is determined from the extrapolation of the linear region to the energy axis intercept. The absorption coefficient α was determined from absorption spectra collected with an integrating sphere.⁴

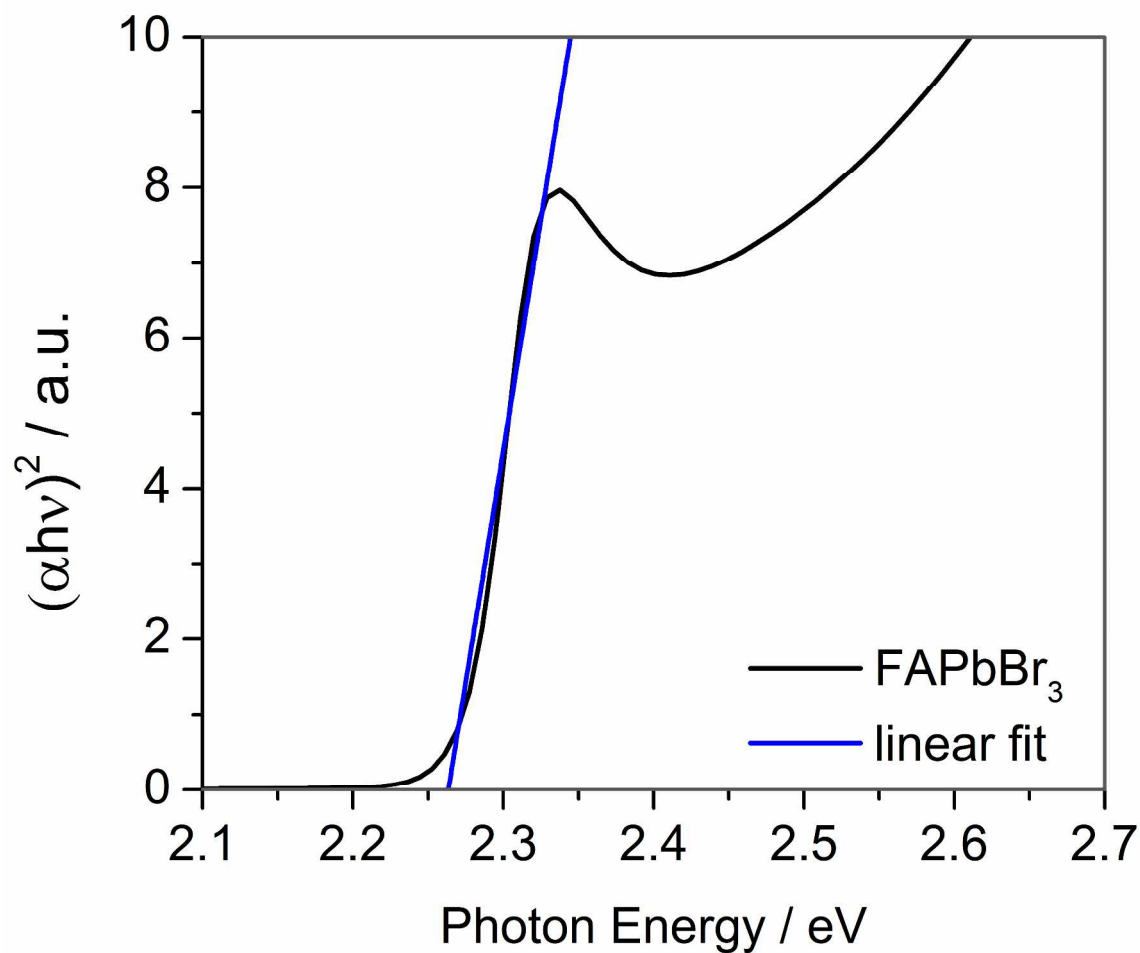


Figure S5: Tauc plot for FAPbBr₃. The estimated band gap is 2.26 eV.

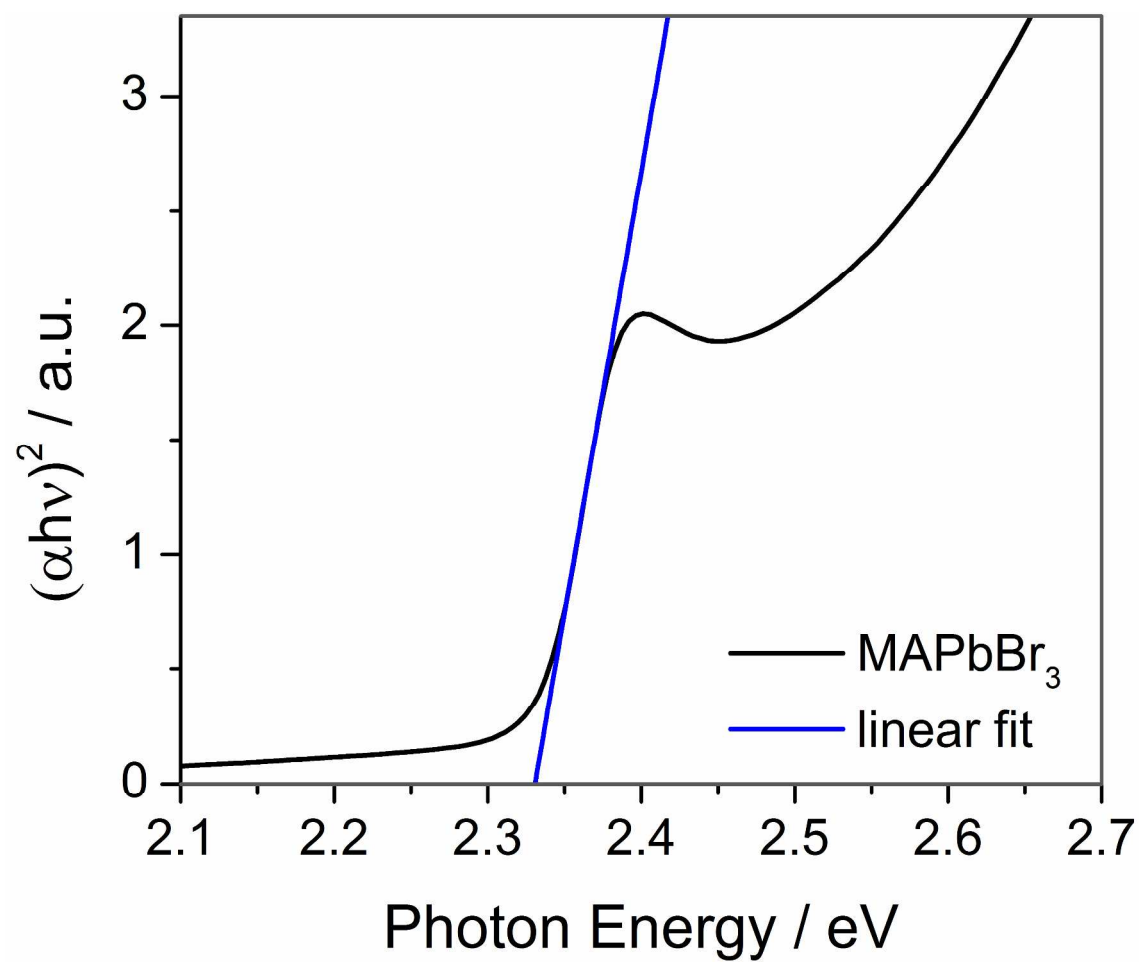


Figure S6: Tauc plot for MAPbBr₃. The estimated band gap is 2.34 eV.

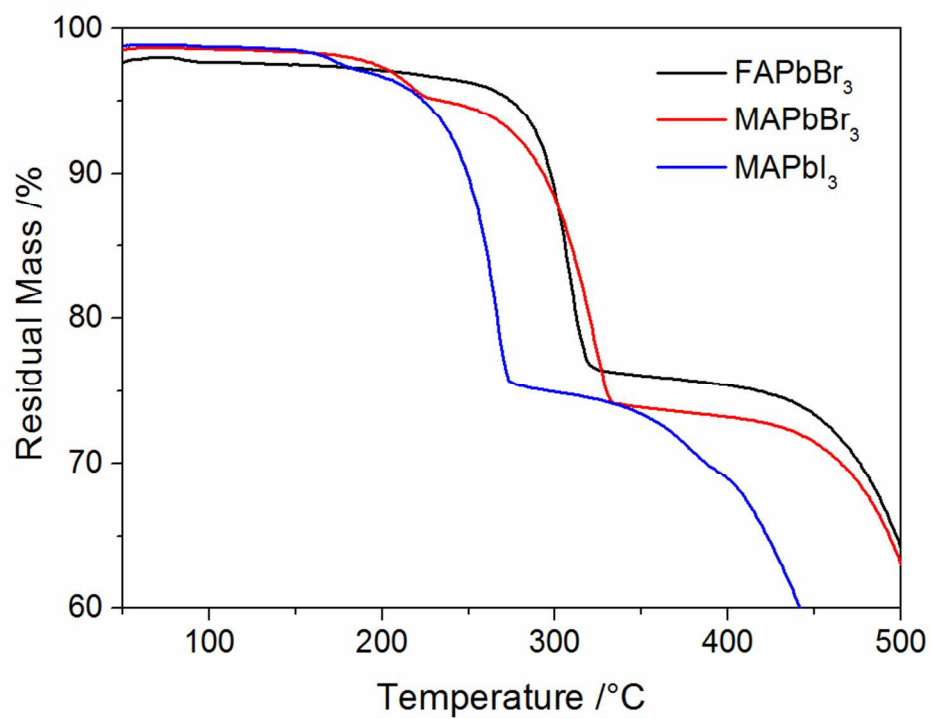


Figure S7: Thermogravimetric analysis (TGA) of MA and FAPbBr₃. For comparison we include the TGA for the literature known methylammonium lead iodide perovskite.

Preparation of the precursors: Methylammonium bromide was prepared by adapting a recipe published earlier.⁵ In short, 24 mL of methylamine solution (33 % in ethanol) was diluted with 100 mL of absolute ethanol in a 250 mL roundbottom flask. To this solution, 8 mL of an aqueous solution of hydrobromic acid (48 wt%) was added under constant stirring. After a reaction time of one hour at room temperature, the solvents were removed by rotary evaporation. The obtained white solid was washed with dry diethyl ether and finally recrystallized from ethanol.

Formamidinium bromide was synthesized following a known procedure.⁶ Formamidinium acetate was dissolved in a double molar excess of aqueous HBr (48 wt%), and stirred at 50 °C for 60 minutes. The solvent and remaining HBr was removed by rotary evaporation to obtain a slightly yellow powder. Washing with dry diethyl ether and recrystallization from ethanol led to the white, crystalline product.

Solar cell preparation: Fluorine doped tin oxide (FTO) coated glass sheets (15 Ω /sq, Dyesol Italy) were patterned by etching with zinc powder and 3 M HCl. They were subsequently cleaned with a 2 % Hellmanex solution and rinsed with de-ionized water, acetone and ethanol. Directly before applying the blocking layer, last organic residues were removed by an oxygen plasma treatment for 5 minutes. The dense TiO₂ layer was prepared from a sol-gel precursor solution by spin-coating onto the substrates and calcining at 500 °C in air.⁷ For the sol-gel solution a 27.2 mM solution of HCl in 2-propanol was added dropwise to a vigorously stirred 0.43 mM solution of titanium isopropoxide in 2-propanol. The solution stayed clear during the addition and was discarded otherwise.

An approximately 250 nm thick layer of PbBr₂ was prepared by spin-coating 75 μ L of a 1 M PbBr₂ solution in dry *N,N*-Dimethylformamide (DMF) onto the TiO₂ covered substrates at 2000 RPM for 15 seconds. To obtain smooth, homogeneous layers it was important to heat both,

the PbBr₂ solution and the substrate, to 60 °C before spin-coating and to perform the deposition dynamically with hot solution onto the hot substrate.

The lead bromide layer was transformed into either the MAPbBr₃ or FAPbBr₃ perovskite by immersing it into a 20 mM solution of either MABr or FABr in isopropanol respectively. For the MAPbBr₃ perovskite, the PbBr₂ coated substrates were immersed into 40 mL of the solution, which was heated to 60 °C for 5 minutes. For FAPbBr₃ the solution had to be heated to 70 °C and the immersion was performed for 30 minutes. After taking the films out of the solution, they were rinsed in an isopropanol bath and carefully dried in a nitrogen stream.

Afterwards, the films were covered with a 400 nm layer of Spiro-OMeTAD (Borun Chemicals, 99.1 % purity) “spiro”. 75 mg of spiro were dissolved in 1 mL of chlorobenzene and mixed with 10 mL 4-*tert*-Butylpyridine (*t*BP) and 30 µL of a 170 mg mL⁻¹ bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) solution in acetonitrile. This solution was spin-coated dynamically at 800 RPM for 45 seconds. In a second step the sample rotation was accelerated to 2000 RPM for 5 seconds to allow the solvent to dry completely. Before evaporating the gold electrodes, Spiro-OMeTAD was left to oxidize in air over night at room temperature and 15 – 20 % rel. humidity.

PL sample preparation: Perovskite samples for steady state and time resolved PL measurements were prepared as described for the solar cell preparation. In this case non-conductive glass substrates were used and the perovskite was covered with a poly(methyl methacrylate) (PMMA) layer to prevent degradation by ambient moisture. The layer was deposited by spin coating 75 µL of a 10 mg mL⁻¹ solution of PMMA in chlorobenzene at 1000 RPM for 45 seconds.

Characterization details: *J-V* curves were recorded with a Keithley 2400 sourcemeter under simulated AM 1.5 sunlight, calibrated to 100 mW cm⁻² with a Fraunhofer ISE certified silicon

cell. The active area of the solar cells was defined with a square metal aperture mask of 0.0831 cm^2 .

Steady-state absorption spectra were acquired with a Lambda 1050 UV/Vis spectrophotometer (Perkin Elmer) using an integrating sphere.

Steady state and time resolved PL measurements were performed with a Fluotime 300 Spectrofluorometer (Picoquant GmbH). The excitation wavelength was fixed at 510 nm. The emission for time resolved measurements was monitored at the maximum intensity of the steady state photo emission.

Scanning electron microscopy (SEM) images were obtained using a Jeol JSM-6500F microscope equipped with a secondary electron detector.

Samples for powder XRD measurements were obtained by preparing perovskite films on glass substrates following the procedure described for solar cells and removing them from the glass. The measurements were performed on a Huber Imaging Plate Guinier Diffractometer G670 (Cu- $K_{\alpha 1}$ -radiation). Rietveld refinement was performed using the Bruker TOPAS package.¹

The photoelectron spectroscopy experiments were performed using an Escalab 250 spectrometer equipped with a monochromatized Al anode X-ray source ($h\nu = 1486.6 \text{ eV}$), and a helium discharge lamp ($h\nu = 21.2 \text{ eV}$) as excitation sources for X-ray photoelectron spectroscopy (XPS) and UV photoelectron spectroscopy (UPS), respectively. The energetic resolution determined by the 2σ Gaussian broadening used to fit the Fermi edge of a freshly sputter-cleaned silver sample measured at room temperature is 0.35 eV for XPS and 0.13 eV for UPS. All spectra are

referenced in binding energy to the Fermi level. The core level lines of in-situ cleaned Au, Ag and Cu metal foils were used to calibrate the XPS binding energy scale.

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