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Supplementary Information for *Tailoring Metal Halide Perovskites through Metal Substitution: Influence on Photovoltaic and Material Properties* 

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# **Part I: Methods**

## **Experimental Methods**

Materials. Lead(II) acetate trihydrate (99.999%, Pb(OAc)<sub>2</sub>), iron(II) acetate (>99.99%, Fe(OAc)<sub>2</sub>), hydroiodic acid (57 wt% in water, HI), chlorobenzene (anhydrous 99.8%, CB), N,Ndimethylformamide (anhydrous 99.8%, DMF), and hypophosphourous acid (50 wt. % in H<sub>2</sub>O, HPA) were sourced from Sigma-Aldrich. Cobalt(II) acetate tetrahydrate (99.999%, Co(OAc)<sub>2</sub>), copper(II) acetate (99.999%, Cu(OAc)<sub>2</sub>), magnesium acetate tetrahydrate (99.997% Puratronic, Mg(OAc)<sub>2</sub>), manganese(II) acetate tetrahydrate (99.999% Puratronic, Mn(OAc)<sub>2</sub>), nickel(II) acetate tetrahydrate (99.999% Puratronic, Ni(OAc)<sub>2</sub>), zinc acetate (anhydrous 99.98%, Zn(OAc)<sub>2</sub>), strontium iodide (anhydrous 99.99%, SrI<sub>2</sub>), tin(II) acetate (95%, Sn(OAc)<sub>2</sub>), 1,8-diiodooctane (>97%, DIO), calcium shot (99.5%), bathocuproin (98%, BCP) and aluminum shot (99.999% Puratronic, Al) were sourced from Alfa Aesar. Silver shot (99.99% 1-3 mm granules, Ag) was sourced from Testbourne Ltd. Methylamine solution (40 wt% in methanol, CH<sub>3</sub>NH<sub>2</sub>) was sourced from TCI. Phenyl-C61-butyric acid methyl ester (99.5%, PCBM) for the devices in the screening study was sourced from Nano-C, Inc. PCBM for the optimised MA(Pb:Co)I<sub>3</sub> devices was sourced from Solenne BV. Poly(3,4ethylenedioxythiophene)-poly(styrenesulfonate) (Clevios P VP AI 4083, PEDOT:PSS) was sourced from Heraeus. Methylammonium iodide (MAI) used in the optimised MA(Pb:Co)I<sub>3</sub> devices was sourced from Dyesol.

**Methylammonium Iodide (MAI) Synthesis for Screening Study.** HI solution (30 mL, 57 wt% in water) and  $CH_3NH_2$  solution (27.8 mL, 40 wt% in methanol) were mixed and stirred in an ice bath for 2 hours. MAI was produced by sequentially removing the solvent in a rotary evaporator, recrystallising the solid with ethanol, and washing and filtering the precipitate with diethyl ether to

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achieve the purified product. The material, in the form of white crystals, was then dried in a vacuum oven at 60 °C for 24 hours and stored in a dark, dry environment until further use.

**Mixed-Metal Perovskite Solutions.** Mixed-metal perovskite solutions were freshly prepared before use by fully dissolving the MAI and divalent metal acetate  $(B(OAc)_2)$  precursors in DMF to achieve final solutions containing 2.4 M MAI and 0.8 M total metal acetate content. The metal acetate content in the perovskite solutions was varied from a 1Pb:1B' ratio (*i.e.* 400 mM Pb(OAc)<sub>2</sub> and 400 mM B'(OAc)<sub>2</sub> final solution) to 63Pb:1B' (*i.e.* 787.5 mM Pb(OAc)<sub>2</sub> and 12.5 mM X(OAc)<sub>2</sub> final solution) where B' = {Co, Cu, Fe, Mg, Mn, Ni, Sn, Zn}. Due to the poor solubility of Sr(OAc)<sub>2</sub> in DMF, the iodide precursor (SrI<sub>2</sub>) was used instead and mixed Pb:Sr perovskite solutions were prepared by making separate stocks of (2.4 M MAI):(0.8 M Pb(OAc)<sub>2</sub>) and (0.8 M MAI):(0.8 M SrI<sub>2</sub>), respectively, in DMF. These two stock solutions were mixed immediately before use to achieve the desired ratios of Pb:Sr.

**Solar Cell Fabrication for Screening Study.** Patterned indium tin oxide (ITO) coated glass substrates (Thin Film Devices, Inc.) were cleaned by scrubbing and sonication in a detergent solution (Alconox) followed by thorough rinsing with Milli-Q water (18.2 M $\Omega$ , Millipore). The substrates were then sequentially sonicated for around 10 minutes in Milli-Q water, acetone, and isopropanol solvents, dried under flowing nitrogen, and exposed to air plasma for 10 minutes to remove organic contaminants and render the surface hydrophilic. The as-received PEDOT:PSS solution was initially filtered through a 0.45 µm syringe filter (Pall Corp. Acrodisc Supor membrane) and warmed to room temperature. Several drops of the PEDOT:PSS solution were dispensed through a second syringe filter directly onto the plasma treated substrate and then spun at 3,000 rpm for 50 s with a 1 s ramp. The substrates were immediately transferred to an oven and annealed in air at 125°C for at least 15 minutes, after which they were transferred to a nitrogen glove box for the remainder of the device processing.

The PEDOT:PSS layer (~30 nm thick) was treated by statically dispensing and spin-coating 45  $\mu$ L of a DIO solution (2 vol% in CB) at 2,250 rpm for 40 s with a 1 s ramp. Immediately afterwards, 45  $\mu$ L of a freshly prepared mixed-metal perovskite solution was statically dispensed onto the substrate and spin-coated at 2,250 rpm for 40 s. After spinning, the substrate was immediately removed from the spin-coater chuck and let rest at room temperature for 10 minutes, during which the film colour changed from nearly colourless to a light brown hue. Each device was then annealed on a hot plate at 100°C for 30 minutes and the perovskite film darkened to achieve its final colour within seconds.

A solution of PCBM (35 mg mL<sup>-1</sup> in CB) was prepared the day before use and kept at 80°C overnight to ensure full dissolution. The warm solution was filtered through both a 100 nm and 200 nm PTFE (Whatman) filter an hour before use and kept at 80°C until spin-coating. The perovskite substrates were warmed at 80°C for 10 minutes and 45  $\mu$ L of the warm PCBM solution was statically dispensed and spin-coated at 1,200 rpm for 35 s. Each substrate was immediately transferred to a hotplate and annealed at 90°C for 45 minutes (~100 nm thick). Afterwards, top electrodes consisting of 20 nm Ca and 90 nm of Al were thermally evaporated on top of the fullerene layer to complete the device. Finally, a patterned aluminium film (25 nm thick) was evaporated directly onto the glass backside of each device to act as an aperture mask during photovoltaic performance testing. The final patterned device substrate contained 10 individual solar cells, each with an apertured active area of 0.0113 cm<sup>2</sup>.

The approximate thicknesses of each solution-processed layer in the solar cell, as determined by a profilometer (Veeco Dektak 6M), are: PEDOT:PSS (35 nm), perovskite (290 nm), and  $PC_{60}BM$  (100

nm). Representative thickness measurements of films with each mixed-metal perovskite composition are presented in Table S4.

**Optimised MA(Pb:Co)I<sub>3</sub> Solar Cell Fabrication.** Patterned ITO substrates were cleaned in the same manner as in the screening study and treated with an oxygen plasma for 10 minutes. The PEDOT:PSS was warmed to room temperature, diluted in methanol (1:2 PEDOT:methanol by volume), and filtered with a 0.45  $\mu$ m glass fibre syringe filter immediately prior to use. The PEDOT:PSS solution was dynamically spun on the plasma-treated ITO substrate at 4,000 rpm for 40s with a 1s ramp. The films (~15 nm) were immediately annealed on a hot plate in air at 150°C for at least 10 minutes, after which they were transferred to a nitrogen glove box for the remainder of the solution processing.

MA(Pb:Co)I<sub>3</sub> perovskite solutions were prepared by separately preparing a solution of pure Pb (0.8M Pb(OAc)<sub>2</sub> and 2.4M Dyesol MAI in DMF) and a 7Pb:1Co (0.1M Co(OAc)<sub>2</sub> (anhydrous 99.995% from Sigma-Aldrich), 0.7M Pb(OAc)<sub>2</sub>, and 2.4M Dyesol MAI in DMF). Following a modified version of the procedure developed by Zhang *et al.*,<sup>1</sup> HPA (4.5  $\mu$ L as-received solution per 1 mL of perovskite solution) was added to each of the perovskite stock solutions. The perovskite films were prepared by mixing the pure Pb and 7Pb:1Co stock solutions to the desired ratio and statically dispensing 120  $\mu$ L of the final perovskite solution on the PEDOT:PSS film and spin-coating at 1,900-2,000 rpm for 45 s with a 6 s ramp time. The films were immediately placed on a hot plate at 100°C, annealed for 5-10 minutes, and allowed to cool to room temperature.

Onto the cooled perovskite films, 50  $\mu$ L of a PCBM solution (20 mg mL<sup>-1</sup> in CB, at room temperature) was dynamically dispensed at 1,800 rpm for 30 s. Each substrate was immediately transferred to a hotplate and annealed at 90°C for 10 minutes. After cooling back to room temperature, 70  $\mu$ L of a BCP solution (0.5 mg mL<sup>-1</sup> in isopropanol, at room temperature) was dynamically spin-coated at 4,000 rpm for 20 s. Finally, a 100 nm Ag top electrode was thermally evaporated on top of the fullerene layer to complete the device. The final patterned device substrate contained 8 individual solar cells, each with an apertured active area of 0.0919 cm<sup>2</sup>.

## **Characterisation Methods**

**Device Characterisation for Screening Study.** Current-voltage (JV) characteristics were recorded in a N<sub>2</sub> glovebox using a Keithley 2636A source meter under simulated AM1.5 solar light (1-Sun, 100 mW cm<sup>-2</sup>) generated by a Newport 96000 solar simulator equipped with an AM1.5G filter. After warming the solar simulator, the light intensity was calibrated with a Newport 91150V reference cell prior to testing each batch of devices. Each device was soaked under the AM 1.5G illumination for 5 minutes prior to measurement and the voltage step and time step were 20 mV and 20 ms, respectively (*i.e.* scan rate of 1 V/s). The external quantum efficiency (EQE) measurements were conducted under chopped monochromatic light from an optical fiber in an under-filled geometry without bias. Illumination was provided by coupling the white light from a xenon lamp (Thermo Oriel 66921) through a monochromator (Acton) into the optical fiber and the photocurrent was recorded using a lock-in amplifier (Stanford Research System SR830). Devices were continuously kept in a nitrogen atmosphere after electrode evaporation, including during both JV and EQE measurements. Devices were tested within 12 hours of evaporating the top electrodes.

**Device Characterisation for Optimised MA(Pb:Co)I<sub>3</sub> Devices**. Current-voltage (JV) characteristics of the optimised MA(Pb:Co)I<sub>3</sub> solar cells were recorded in ambient air under simulated AM1.5 solar

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light (1-Sun, 100 mW cm<sup>-2</sup>) generated by an ABET Class AAB sun 2000 simulator calibrated using a National Renewable Energy Laboratories (NREL) calibrated KG5 filtered silicon reference cell. Each device was measured with a 20 mV voltage step and a 20 ms time step (*i.e.* scan rate of 1 V/s) using a Keithley 2400 source meter. All devices were masked with a 0.0919 cm<sup>2</sup> metal aperture to define the active area and eliminate edge effects.

**Materials Characterisation Methods for Screening Study.** Perovskite films for the X-ray diffraction (XRD) and scanning electron microscopy (SEM) were prepared on PEDOT:PSS-coated glass substrates (same size as the device substrates) in the same manner used to fabricate devices. Films for cross-sectioning and energy-dispersive x-ray spectroscopy (EDX) measurements were prepared on PEDOT:PSS-coated silicon substrates (same size as the device substrates) in the same manner used to fabricate devices.

Scanning electron microscopy (SEM) was performed with a Zeiss FESEM Ultra Plus.

XRD patterns were collected using a Bruker D8 x-ray diffractometer with Cu K $\alpha$  radiation in order to verify the crystal structure and material phases of the deposited films.

The film thicknesses reported in Table S4 were measured from each of the SEM samples using a Veeco Dektak 6M profilometer.

Focused ion beam milling with gallium ions was performed using a Zeiss NVision 40 to prepare a cross-sectional sample for transmission electron microscopy (TEM). A thin platinum protective layer was deposited on the sample surface prior to the milling procedure.

Scanning transmission electron microscopy (STEM) imaging and energy-dispersive x-ray spectroscopy (EDS) maps were performed with a Hitachi HD-2700 Cs-corrected CFEG-STEM operating at 200 kV.

X-ray photoelectron spectroscopy (XPS) was conducted using a Thermo Scientific K-Alpha XPS with a monochromatic Al x-ray source (excitation energy 1486.6 eV). Data was collected under a base pressure of  $8 \cdot 10^{-8}$  mbar at a photoelectron take-off angle of 90°. Energy calibration was performed using the position of the primary C 1s peak at 284.80 eV.

Materials Characterisation Methods for Optimised  $MA(Pb:Co)I_3$  Films. Perovskite films for the scanning electron microscopy (SEM) and x-ray diffraction measurements were prepared on PEDOT:PSS-coated ITO substrates (same size as the device substrates) in the same manner used to fabricate the optimised devices.

SEM micrographs were obtained with a Hitachi S-4300 operating at 5 kV.

Powder x-ray diffraction (XRD) patterns were obtained using a Panalytical X'pert powder diffractometer (Cu-K $\alpha$ 1 radiation;  $\lambda = 154.05$  pm) at room temperature with Bragg-Brentano geometry. During measurement, rotation of the sample was enabled to improve the detection statistics. Structural parameters were obtained by Rietveld refinement using General Structural Analysis Software.

The film thicknesses reported in Table S9 were measured from representative samples using a Veeco Dektak profilometer.

**Optical Characterisation Methods for Screening Study.** Perovskite films for the steady-state photoluminescence (PL) and absorbance measurements were prepared by spin-coating the perovskite solution on glass substrates (same size as the device substrates) after plasma treatment with an oxygen plasma for 10 minutes to render the surface hydrophilic. The perovskite samples were prepared with the same procedure used for devices. The final perovskite films were capped with a layer of PMMA

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by statically dispensing 45  $\mu$ L of 10 mg/mL poly(methylmethacrylate) (PMMA) in chlorobenzene on the film and spin-coating at 1,200 rpm for 60 s with a 1 s ramp time. The PMMA capping layer is intended to prevent film degradation during spectroscopy measurements.

Steady-state PL emission spectra were obtained by exciting perovskite films with a 532 nm laser diode and measuring the emission spectra using a visible wavelength detector with a Horiba Jobin Yvon Fluorimeter with an integration time of 1 s and wavelength step of 1 nm.

Optical absorbance measurements were made using a Beckman-Coulter DU800 UV-vis spectrophotometer with a wavelength step size of 0.5 nm.

**Optical Characterisation Methods for Optimised MA(Pb:Co)I<sub>3</sub> Films.** Perovskite films for the steady-state photoluminescence (PL) and absorbance measurements were prepared by spin-coating the perovskite solution on glass substrates (same size as the device substrates) after etching in piranha solution for 90 minutes (followed by rinsing in water, DI water, and EtOH) to render the surface hydrophilic. The perovskite samples were prepared with the same procedure used for devices. The final perovskite films were capped with a layer of PMMA by dynamically dispensing 70  $\mu$ L of 10 mg/mL poly(methylmethacrylate) (PMMA) in chlorobenzene on the film and spin-coating at 1,800 rpm for 60 s with a 2 s ramp time. The PMMA capping layer is intended to prevent film degradation during spectroscopy measurements.

Steady-state PL emission spectra were obtained by exciting perovskite films at 532 nm and measuring the emission spectra using a visible wavelength detector with a Horiba Jobin Yvon Fluorimeter with an integration time of 0.5 s and wavelength step of 1 nm.

Optical absorbance measurements were made using a Varian Cary 300 Bio (Agilent Technologies) UV-vis spectrophotometer with a wavelength step size of 0.5 nm.

**Ultraviolet Photoelectron Spectroscopy Methods**. Ultraviolet photoelectron spectroscopy (UPS) measurements were performed in an Omicron ultrahigh vacuum (UHV) system with a base pressure of  $1 \times 10^{-10}$  mbar. Perovskite samples were deposited onto conducting ITO-coated glass substrates coated with DIO-treated PEDOT:PSS, as described in the main manuscript. Samples were transferred from a nitrogen glovebox (<1ppm O<sub>2</sub>, <10ppm H<sub>2</sub>O) to the UHV system without exposure to air using a custom-built transfer system. During measurement, samples were biased at -5.0 V relative to the electron energy analyser, and illumination at 21.22 eV was provided by the He(I) line of a helium discharge lamp. Electrons were collected at 0° from substrate normal, and spectra were collected in <45 s to minimise the effects of charging and degradation.

# **Part II: Supporting Information for the Screening Study**

# **Compiled Performance Metrics for Mixed-Metal Solar Cells**

For each mixed-metal perovskite composition, at least 36 individual solar cells were tested from two different device batches in order to ensure that observed trends in photovoltaic performance were repeatable. The average values for each photovoltaic performance metric are reported in Figure S1.



**Figure S1**. Compiled average performance metrics of mixed-metal perovskite solar cells produced from mixedmetal films with each secondary metal species at five different molar ratios with Pb: (a) power conversion efficiency, *PCE*; (b) short-circuit current density,  $J_{sc}$ ; (c) open-circuit voltage,  $V_{oc}$ ; and (d) fill factor, *FF*. Average values and standard deviations for the error bars are calculated from at least 36 different solar cells, spanning at least two separate device batches.

The most notable efficiency enhancements arise when  $1/64^{\text{th}}$  of the Pb content, denoted as 63Pb:1B', is replaced with Co, Cu, Sr, or Zn, which improves both the short-circuit current density,  $J_{sc}$ , and open-circuit voltage,  $V_{oc}$ . Modest PCE improvements are also observed for 63Pb:1B' samples of Mg, Mn, and Ni, largely due to increases in  $V_{oc}$ , which clearly demonstrate that the MAPbI<sub>3</sub> perovskite material is not only tolerant of most metal species at relatively low concentrations, but that introducing these atoms can be beneficial to device performance. As more Pb is replaced, the  $J_{sc}$  begins to decrease and the drop becomes quite appreciable between the 15Pb:1B' and 7Pb:1B' molar ratios for Mg, Mn, Ni, and Sr. The perovskite active layer is even more tolerant of Co, Cu, Sn, and Zn whose champion 3Pb:1B' device achieves efficiencies of 4.1%, 8.3%, 9.3%, and 6.0%, respectively (see Figure S2 for corresponding JV characteristics), whereas all other metal species at this replacement level achieve champion efficiencies below 1% (Table S1). Although each secondary metal species has its own tolerance limit, as a general rule the perovskite active layer suffers significant decreases in photocurrent for Pb replacement levels exceeding 15Pb:1B'. The transition metal that appears to be the most highly tolerated by the perovskite material is Zn, whose

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MA(7Pb:1Zn)I<sub>3</sub> composition achieves an average PCE of 8.8%. Even though a champion efficiency of 8.3% was produced by MA(3Pb:1Cu)I<sub>3</sub>, this performance was only obtained for the initial measurement and subsequent scans of the same device were substantially degraded (Figure S22-S23). Copper is unique among the secondary metal species investigated since its ions are more stable in a +1 rather than a +2 oxidation state in the presence of I<sup>-</sup> and the mixed-metal Pb:Cu compositions demonstrated some unusual photovoltaic behaviour, the details of which can be found in the section entitled "Performance of MA(Pb:Cu)I<sub>3</sub> Mixtures". A comprehensive tabulation of the champion and average values for each mixed-metal composition can be found in Tables S1 and S2. In order to ensure that the observed improvement with Pb content substitution was not simply a result of thinner perovskite films or a stoichiometric mismatch between the MAI and Pb(OAc)<sub>2</sub> precursors, two sets of control devices were created and tested in the same manner as the mixed-metal devices (see Figure S4-S5 and Table S5-S6).

Figure S1d shows that the average fill factor, *FF*, varies little between the MAPbI<sub>3</sub> baseline and most of the mixed-metal compositions, however there are a few notable exceptions where the values are noticeably reduced. The champion JV characteristic for each of the Pb:Cu compositions (Figure S2b) displays a decreased shunt resistance, which is likely due to the formation of CuI shunting pathways (see additional peak at  $2\theta$ =25.2° for 3Pb:1Cu and 7Pb:1Cu compositions in Figure S24). Conversely, most of the champion Pb:Sn compositions (Figure S2g) along with the 7Pb:1B' and 3Pb:1B' mixtures of Fe (Figure S2c), Mg (Figure S2d), and Ni (Figure S2f) show increased series resistances. These champion *JV* characteristics also reflect the trend for *V<sub>oc</sub>* presented in Figure S1c, where increases in photovoltage occur in mixed-metal compositions with Co, Cu, Mg, Mn, Ni, Sr, and Zn.

While hysteresis is minimal for MAPbI<sub>3</sub> and mixtures with Cu, Mg, Sr, and Zn, it arises in the other mixed-metal systems and generally becomes more pronounced as more Pb atoms are substituted with the secondary metal species (Figure S2). For many of these embodiments, the scan from short-circuit to forward bias (*i.e.* forward scan) demonstrates a reduced fill factor, but the scan from forward bias to short circuit (*i.e.* reverse scan) often noticeably overshoots the current near the maximum power point for 7Pb:1B' and 15Pb:1B' compositions, as is clearly demonstrated by 7Pb:1Mn in Figure S2e. Hysteresis in perovskite systems has generally been attributed to ion migration primarily affecting interfacial charge transfer and interfacial traps,<sup>2</sup> however understanding the underlying physical mechanisms at work in the mixed-metal systems will require further in-depth study.

With 95% being the highest commercially available purity,  $Sn(OAc)_2$  is the least pure acetate precursor salt used in this study and it is possible an impurity is producing the detrimental effects that cause the Pb:Sn blends to show a contrary trend in performance. Unlike all other compositions, we observed that both the  $V_{oc}$  and *FF* improve in Pb:Sn devices upon additional light-soaking (Figure S18). However, the results reported in Figure S1, Figure S2, and Tables S1-S2 correspond only to the measurements made after five minutes of light-soaking in order to be consistent with the other mixed-metal systems.

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## **Champion Current-Voltage Characteristics for Mixed-Metal Solar Cells**

The current-voltage (JV) characteristics were measured after five minutes of light soaking and both the forward and reverse sweeps of the champion solar cell for each mixed-metal composition are shown in Figure S2.

The champion and average photovoltaic performance metrics for each mixed-metal composition from a set of at least 36 individual solar cells produced from at least two different device batches are reported in Table S1 and S2, respectively.



**Figure S2**. Forward (right-pointing triangles) and reverse (left-pointing triangles) current-voltage characteristic scans measured from the best performing solar cell for each composition in each mixed-metal material set: (a) Pb:Co, (b) Pb:Cu, (c) Pb:Fe, (d) Pb:Mg, (e) Pb:Mn, (f) Pb:Ni, (g) Pb:Sn, (h) Pb:Sr, and (i) Pb:Zn.

# **Champion Performance Metrics for Mixed-Metal Solar Cells**

**Table S1.** The best measured performance metrics for each mixed-metal perovskite composition.  $J_{sc}$ ,  $V_{oc}$ , and *FF* do not necessarily correspond to the device with the champion *PCE*.

	Best Short-Circuit Current Density, <i>J<sub>sc</sub></i> [mA/cm <sup>2</sup> ]					
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'	
Pb Only			18.97			
Pb:Co	19.82	19.06	17.00	14.35	9.57	
Pb:Cu	18.19	16.26	14.57	15.24	19.10	
Pb:Fe	4.94	4.97	4.29	0.04	0.91	
Pb:Mg	15.76	16.39	14.91	4.06	1.86	
Pb:Mn	17.25	17.31	15.01	6.18	1.39	
Pb:Ni	18.40	15.31	13.24	0.33	0.13	
Pb:Sn	11.62	14.14	12.22	15.69	20.40	
Pb:Sr	19.17	17.71	12.89	1.96	0.38	
Pb:Zn	19.71	18.18	16.61	16.99	13.19	
	1	Best Open-C	ircuit Voltag	ge, $V_{oc}$ [V]		
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'	
Pb Only			0.82			
Pb:Co	0.85	0.87	0.89	0.94	0.84	
Pb:Cu	0.93	0.94	0.87	0.80	0.86	
Pb:Fe	0.68	0.73	0.84	0.57	0.77	
Pb:Mg	0.92	0.91	0.73	0.96	0.94	
Pb:Mn	0.91	0.88	0.74	0.96	1.01	
Pb:Ni	0.91	0.85	0.85	0.4	0.52	
Pb:Sn	0.46	0.71	0.50	0.68	0.73	
Pb:Sr	0.88	0.84	0.84	1.02	1.11	
Pb:Zn	0.89	0.88	0.65	0.82	0.70	
		Best Fil	ll Factor, FF	[%]		
Material	63Pb:1B'	Best Fil 31Pb:1B'	ll Factor, <i>FF</i> 15Pb:1B'	' [%] 7Pb:1B'	3Pb:1B'	
Material Pb Only	63Pb:1B'	Best Fil 31Pb:1B'	ll Factor, <i>FF</i> 15Pb:1B' 72.14	' [%] 7Pb:1B'	3Pb:1B'	
Material Pb Only Pb:Co	63Pb:1B'	Best Fil 31Pb:1B' 76.11	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.04	7 [%] 7Pb:1B' 68.82	3Pb:1B' 54.34	
Material Pb Only Pb:Co Pb:Cu	63Pb:1B' 74.10 66.55	Best Fil 31Pb:1B' 76.11 61.29	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.04 61.01	' [%] 7Pb:1B' 68.82 62.88	3Pb:1B' 54.34 66.16	
Material Pb Only Pb:Co Pb:Cu Pb:Fe	63Pb:1B' 74.10 66.55 64.67	Best Fil 31Pb:1B' 76.11 61.29 63.03	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59	7 [%] 7Pb:1B' 68.82 62.88 26.21	3Pb:1B' 54.34 66.16 36.90	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg	63Pb:1B' 74.10 66.55 64.67 75.10	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59 70.36	' [%] 7Pb:1B' 68.82 62.88 26.21 68.95	3Pb:1B' 54.34 66.16 36.90 48.63	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn	63Pb:1B' 74.10 66.55 64.67 75.10 70.65	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19	' [%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58	3Pb:1B' 54.34 66.16 36.90 48.63 59.52	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38	[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Ni Pb:Sn	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14	7 [%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Ni Pb:Sn Pb:Sr	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90	7 [%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Mn Pb:Ni Pb:Sn Pb:Sr Pb:Sr Pb:Zn	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sn Pb:Sr Pb:Zn	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Converting	ll Factor, FF 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, PCE	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03	
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Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sn Pb:Sr Pb:Zn Material Pb Only	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B'	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Conve 31Pb:1B'	ll Factor, <i>FF</i> <u>15Pb:1B'</u> 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici <u>15Pb:1B'</u> 10.27	<sup>7</sup> [%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B'	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B'	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sn Pb:Sr Pb:Zn Material Pb Only Pb:Co	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Conve 31Pb:1B'	ll Factor, <i>FF</i> <u>15Pb:1B'</u> 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici <u>15Pb:1B'</u> <u>10.27</u> 10.21	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B' 8.66	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sr Pb:Sr Pb:Zn Material Pb Only Pb:Co Pb:Cu	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37 10.14	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Conve 31Pb:1B' 11.11 8.37	ll Factor, <i>FF</i> <u>15Pb:1B'</u> 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici <u>15Pb:1B'</u> <u>10.27</u> 10.21 6.57	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B' 8.66 5.46	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14 8.29	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sr Pb:Sr Pb:Zn Material Pb Only Pb:Co Pb:Cu Pb:Cu Pb:Fe	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37 10.14 1.78	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Conve 31Pb:1B' 11.11 8.37 1.75	ll Factor, <i>FF</i> <u>15Pb:1B'</u> 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici <u>15Pb:1B'</u> <u>10.27</u> 10.21 6.57 2.29	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B' 8.66 5.46 0.01	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14 8.29 0.22	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sr Pb:Sr Pb:Zn Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37 10.14 1.78 9.37	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Convo 31Pb:1B' 11.11 8.37 1.75 9.71	ll Factor, <i>FF</i> <u>15Pb:1B'</u> 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici <u>15Pb:1B'</u> <u>10.27</u> 10.21 6.57 2.29 7.11	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, PCE 7Pb:1B' 8.66 5.46 0.01 1.74	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14 8.29 0.22 0.76	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sr Pb:Sr Pb:Zn Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Cu Pb:Fe Pb:Mg Pb:Mg Pb:Mn	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37 10.14 1.78 9.37 10.38	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Convo 31Pb:1B' 11.11 8.37 1.75 9.71 10.02	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici 15Pb:1B' 10.27 10.21 6.57 2.29 7.11 7.17	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B' 8.66 5.46 0.01 1.74 4.30	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14 8.29 0.22 0.76 0.68	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sr Pb:Zn Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37 10.14 1.78 9.37 10.38 9.95	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Conve 31Pb:1B' 11.11 8.37 1.75 9.71 10.02 8.53	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici 15Pb:1B' 10.27 10.21 6.57 2.29 7.11 7.17 6.01	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B' 8.66 5.46 0.01 1.74 4.30 0.06	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14 8.29 0.22 0.76 0.68 0.04	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sr Pb:Sr Pb:Zn Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Ni Pb:Sn	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37 10.14 1.78 9.37 10.38 9.95 2.32	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Conver 31Pb:1B' 11.11 8.37 1.75 9.71 10.02 8.53 5.30	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici 15Pb:1B' 10.27 10.21 6.57 2.29 7.11 7.17 6.01 2.38	7 [%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B' 8.66 5.46 0.01 1.74 4.30 0.06 4.89	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14 8.29 0.22 0.76 0.68 0.04 9.25	
Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Ni Pb:Sn Pb:Sr Pb:Zn Material Pb Only Pb:Co Pb:Cu Pb:Fe Pb:Mg Pb:Mn Pb:Ni Pb:Sn Pb:Sn Pb:Sn	63Pb:1B' 74.10 66.55 64.67 75.10 70.65 76.62 63.25 75.37 73.19 Best 63Pb:1B' 11.37 10.14 1.78 9.37 10.38 9.95 2.32 10.81	Best Fil 31Pb:1B' 76.11 61.29 63.03 72.61 67.50 71.94 57.44 71.69 73.02 Power Conve 31Pb:1B' 11.11 8.37 1.75 9.71 10.02 8.53 5.30 9.29	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.04 61.01 66.59 70.36 70.19 59.38 51.14 70.90 72.98 ersion Effici 15Pb:1B' 10.27 10.21 6.57 2.29 7.11 7.17 6.01 2.38 5.58	7[%] 7Pb:1B' 68.82 62.88 26.21 68.95 73.58 56.51 60.36 66.82 73.78 ency, <i>PCE</i> 7Pb:1B' 8.66 5.46 0.01 1.74 4.30 0.06 4.89 1.16	3Pb:1B' 54.34 66.16 36.90 48.63 59.52 54.77 70.94 65.90 73.03 '[%] 3Pb:1B' 4.14 8.29 0.22 0.76 0.68 0.04 9.25 0.21	

# Mean Performance Metrics for Mixed-Metal Solar Cells

**Table S2.** The compiled average performance metrics of planar mixed-metals for each composition. Error corresponds to the standard deviation.

		Mean Short-Ci	cuit Current Densit	y, $J_{sc}$ [mA/cm <sup>2</sup> ]	
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$16.02 \pm 1.62$		
Pb:Co	$18.15\pm0.71$	$16.89\pm0.86$	$15.54 \pm 1.12$	$12.25\pm0.96$	$5.00 \pm 1.20$
Pb:Cu	$16.18\pm0.96$	$13.91 \pm 1.46$	$12.81\pm0.99$	$12.28 \pm 1.84$	$13.07\pm2.72$
Pb:Fe	$3.79\pm0.64$	$2.95 \pm 1.61$	$3.88\pm0.19$	$0.02 \pm 0.01$	$0.28\pm0.34$
Pb:Mg	$14.94\pm0.67$	$13.36 \pm 1.73$	$11.64 \pm 2.22$	$1.78 \pm 1.47$	$0.60\pm0.84$
Pb:Mn	$14.68 \pm 1.07$	$14.78 \pm 1.20$	$13.33\pm0.81$	$2.11 \pm 1.87$	$0.75\pm0.48$
Pb:Ni	$14.82 \pm 1.90$	$12.90\pm0.99$	$9.63 \pm 1.90$	$0.14\pm0.10$	$0.06\pm0.04$
Pb:Sn	$8.33 \pm 2.22$	$11.59 \pm 2.29$	$8.80 \pm 2.47$	$13.16 \pm 2.20$	$15.92\pm2.49$
Pb:Sr	$17.16 \pm 1.12$	$15.03\pm2.06$	$10.60 \pm 2.13$	$1.62\pm0.14$	$0.25\pm0.08$
Pb:Zn	$17.66 \pm 1.06$	$16.60\pm0.80$	$15.94\pm0.44$	$15.86\pm0.69$	$5.35\pm3.44$
		Mean O	pen-Circuit Voltage	$, V_{oc}$ [V]	
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$0.67\pm0.07$		
Pb:Co	$0.78\pm0.04$	$0.82\pm0.03$	$0.87\pm0.01$	$0.92\pm0.02$	$0.72\pm0.06$
Pb:Cu	$0.91\pm0.01$	$0.92\pm0.01$	$0.76\pm0.13$	$0.58\pm0.15$	$0.62\pm0.13$
Pb:Fe	$0.67\pm0.01$	$0.68\pm0.03$	$0.82\pm0.01$	$0.47\pm0.08$	$0.65\pm0.19$
Pb:Mg	$0.84 \pm 0.04$	$0.76\pm0.08$	$0.65\pm0.05$	$0.91\pm0.15$	$0.67\pm0.21$
Pb:Mn	$0.79\pm0.07$	$0.79\pm0.05$	$0.70\pm0.02$	$0.91\pm0.07$	$0.91\pm0.09$
Pb:Ni	$0.84 \pm 0.04$	$0.84\pm0.00$	$0.80 \pm 0.03$	$0.32\pm0.04$	$0.32\pm0.12$
Pb:Sn	$0.38 \pm 0.04$	$0.43\pm0.15$	$0.33 \pm 0.06$	$0.49\pm0.06$	$0.69\pm0.02$
Pb:Sr	$0.78 \pm 0.06$	$0.75 \pm 0.05$	$0.65 \pm 0.07$	$0.95 \pm 0.04$	$1.03 \pm 0.04$
Pb:Zn	$0.78\pm0.07$	$0.75\pm0.07$	$0.63\pm0.02$	$0.78 \pm 0.04$	$0.66\pm0.02$
		Me	ean Fill Factor FF [	%]	
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$67.53 \pm 2.54$		
Pb:Co	$63.33 \pm 11.91$	$71.43 \pm 2.04$	$66.99 \pm 2.91$	$64.19 \pm 5.42$	$47.61 \pm 9.65$
Pb:Cu	$62.49 \pm 2.61$	$53.72 \pm 3.17$	$52.03 \pm 5.95$	$55.51 \pm 4.55$	$47.70\pm3.99$
Pb:Fe	$60.25 \pm 3.43$	$53.47 \pm 4.94$	$62.44 \pm 2.70$	$21.39 \pm 1.75$	$23.06 \pm 6.10$
Pb:Mg	$66.41 \pm 5.78$	$69.20 \pm 2.14$	$67.12 \pm 1.43$	$52.63 \pm 10.61$	$40.80 \pm 5.11$
Pb:Mn	$67.24 \pm 2.45$	$64.35 \pm 1.56$	$67.04 \pm 1.59$	$63.32 \pm 8.40$	$47.58 \pm 9.12$
Pb:Ni	$67.83 \pm 6.01$	$64.52\pm6.03$	$55.04 \pm 3.33$	$49.46 \pm 4.97$	$46.45\pm6.01$
Pb:Sn	$53.39 \pm 4.89$	$50.29\pm5.06$	$44.63 \pm 3.81$	$44.81 \pm 5.29$	$57.87 \pm 12.05$
Pb:Sr	$69.60 \pm 2.99$	$69.97 \pm 0.83$	$68.12 \pm 4.27$	$60.05 \pm 4.48$	$53.38 \pm 10.95$
Pb:Zn	$70.73 \pm 1.62$	$71.49\pm0.82$	$69.32 \pm 2.56$	$70.94 \pm 1.93$	$67.95 \pm 5.75$
		Mean Power	Conversion Efficier	ncy, PCE [%]	
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$7.27 \pm 1.18$		
Pb:Co	9.03 ± 1.91	$9.88 \pm 0.69$	$9.06\pm0.61$	$7.23\pm0.82$	$1.73\pm0.61$
Pb:Cu	$9.18\pm0.60$	$6.89\pm0.93$	$5.12 \pm 1.28$	$3.87\pm0.82$	$4.00\pm1.81$
Pb:Fe	$1.51\pm0.17$	$1.08\pm0.60$	$1.98\pm0.17$	$0.00 \pm 0.00$	$0.06\pm0.08$
Pb:Mg	$8.35\pm0.56$	$7.09 \pm 1.45$	$5.15 \pm 1.25$	$0.77\pm0.54$	$0.24\pm0.34$
Pb:Mn	$7.87 \pm 1.19$	$7.57 \pm 1.18$	$6.26\pm0.49$	$1.33 \pm 1.28$	$0.37\pm0.25$
Pb:Ni	$8.40\pm0.78$	$6.98\pm0.84$	$4.28\pm0.97$	$0.02\pm0.02$	$0.01\pm0.01$
Pb:Sn	$1.63 \pm 0.32$	$2.61 \pm 1.34$	$1.38\pm0.58$	$2.99 \pm 0.91$	$6.51\pm2.10$
Pb:Sr	$0.26 \pm 0.74$	$7.91 \pm 1.00$	$4.66 \pm 0.82$	$0.92 \pm 0.10$	$0.13 \pm 0.04$
	$9.20 \pm 0.74$	$7.71 \pm 1.00$	$+.00 \pm 0.02$	$0.72 \pm 0.10$	$0.13 \pm 0.04$

## Energy & Environmental Science

## **Impact of DIO Treatment of PEDOT:PSS on Photovoltaic Performance**

As is shown in the representative JV characteristics of Figure S3 and the average performance metrics of Table S3, treating the PEDOT:PSS with a dilute solution of 1,8-diiodooctane (DIO) in chlorobenzene (CB) prior to spin-coating the perovskite solution improves solar cell performance. These findings are similar to those in previous reports that use DIO as a perovskite additive.<sup>3–5</sup>



**Figure S3.** Solar cells from the same batch of devices show that treating the PEDOT:PSS layer with DIO prior to spin-coating the MAPbI<sub>3</sub> layer improves the short-circuit current and open-circuit voltage of the device compared to devices fabricated without the DIO treatment.

**Table S3.** The average performance metrics for a batches of devices synthesised with or without DIO treatment of the PEDOT:PSS layer prior to perovskite deposition. Average values and standard deviation are calculated from a set of 44 individual solar cells.

Treatment	$J_{sc}  [\mathrm{mA/cm}^2]$	$V_{oc}$ [mV]	FF [%]	PCE [%]
MAPbI <sub>3</sub> on PEDOT:PSS	$13.27\pm0.86$	$0.63\pm0.05$	$63.68 \pm 9.88$	$5.39 \pm 1.13$
MAPbI <sub>3</sub> on PEDOT:PSS w/DIO Treatment	$16.02 \pm 1.62$	$0.67\pm0.07$	$67.53 \pm 2.54$	$7.27 \pm 1.18$

# **Mixed-Metal Perovskite Film Thicknesses**

The thickness of a typical perovskite film for each mixed-metal composition is presented in Table S4. Mixed-metal films with low secondary metal fractions have film thicknesses comparable to that of MAPbI<sub>3</sub>. However, often the film thicknesses and roughness increase substantially for 3Pb:1B' and 1Pb:1B' compositions, which is generally due to the formation of films with large and isolated grains (Figure S6-S14).

Table S4.	Typical film thic	knesses for each mix	ed-metal composition	as measured	with a profilometer
		1	Film Thickness t	[nm]	

	Film Thickness, $t_{film}$ [nm]					
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'	1Pb:1B'
Pb Only			290	).0		
Pb:Co	302.2	309.4	314.8	315.9	403.9	-
Pb:Cu	320.8	314.5	302.7	312.0	337.8	443.0
Pb:Fe	298.9	319.4	302.5	301.2	327.3	-
Pb:Mg	288.0	296.3	319.1	305.2	406.8	-
Pb:Mn	307.0	279.5	323.2	310.4	412.1	-
Pb:Ni	307.5	305.2	311.7	327.1	409.9	-
Pb:Sn	296.1	323.1	328.5	331.9	383.3	369.7
Pb:Sr	302.0	296.5	347.9	320.5	375.8	-
Pb:Zn	292.5	290.9	299.4	313.4	319.8	-
Pb:DMF	287.0	289.0	256.9	242.3	185.1	100.1

# **Perovskite Control Devices**

Two sets of control devices were fabricated to investigate how sensitive the device performance is to two other variables in the fabrication conditions: the concentration of the perovskite solution and the molar ratio of MAI:Pb(OAc)<sub>2</sub>. These conditions are labelled as Pb:DMF and Pb:MAI mixtures in the same manner used for the mixed-metal compositions. These controls are intended to evaluate whether two possible events happen during the fabrication process of the mixed-metal perovskite compositions:

- 1. **Pb:DMF** is intended to evaluate how a device would perform if the  $B'(OAc)_2$  and its corresponding MAI molecules do not become incorporated in the film. Although it is unlikely, one could imagine that the  $B'(OAc)_2$  and any excess MAI might evaporate out of the film, should that compound be sufficiently volatile. Hence, the remaining film would be pure MAPbI<sub>3</sub> but would be thinned since a lower amount of Pb salt was included in the original perovskite solution. This situation is simulated by diluting the initial 0.8 M  $Pb(OAc)_2$  and 2.4 M MAI solution with the appropriate amount of DMF.
- 2. **Pb:MAI** is intended to evaluate how a device would perform in the event that MAI is unsuccessful at detaching the acetate ions from the  $B^{r_{2+}}$  ions. In this situation, the molar ratio between MAI and Pb(OAc)<sub>2</sub> would become higher than 3:1. By intentionally changing this ratio, the impact of a stoichiometric mismatch between MAPbI<sub>3</sub> precursors on device performance was evaluated.

For each of these conditions several devices were fabricated and tested in the same manner as the devices with mixed-metal compositions. However, instead of using a solution of 2.4 M MAI and 0.8M B'(OAc)<sub>2</sub> in DMF to replace part of the lead content, neat DMF was used for the Pb:DMF cases and 2.4 M MAI in DMF was used for the Pb:MAI cases. The photovoltaic performance statistics, champion JV curves, and the EQE spectra for both of these control sets are shown in Figure S4. Likewise, the average and champion performance metrics for both of these controls are tabulated in Table S5 and S6, respectively.

For each set of controls, the usual MAPbI<sub>3</sub> device performed better on average than any of the control conditions. This demonstrates that both the  $3:1 \text{ MAI:Pb}(OAc)_2$  molar ratio and the concentration of the perovskite solution have been properly optimised to maximise photovoltaic power conversion efficiency for the pure Pb baseline devices. As expected, the Pb:DMF devices supply lower currents as the perovskite solution becomes increasingly dilute since thinner perovskite films, as shown in Table S4, are formed on the substrate. Thinner films also produce slightly higher fill factors since charge carriers generated in the bulk of the film have a shorter distance to travel to the electrodes and have less grain boundaries to pass through, which results in lower series resistances.

The Pb:MAI cases are more interesting because they display similar trends to those observed in the mixed-metal compositions: the voltage generally increases with higher levels of replacement until the 3Pb:1MAI condition, while the current sees a precipitous drop after 7Pb:1MAI. The main difference between this set and the mixed-metal compositions is that the average performance does not improve above the baseline efficiency. However, the 15Pb:1MAI case did once produce an 11% efficient solar cell, which outperforms the champion baseline MAPbI<sub>3</sub> device. This finding does suggest that the performance of the solar cell is very sensitive to the stoichiometric ratio of the MAI to acetate precursor materials, which is often difficult to precisely control since both the acetate salts and MAI materials are hygroscopic and the actual water content in the salts when massed is not known. Subsequent attempts failed to reproduce this 11% performance in four separate device batches.



**Figure S4.** The photovoltaic performance of control device where the MAPbI<sub>3</sub> material is diluted with DMF (Pb:DMF) or has a stoichiometric mismatch between the MAI and Pb(OAc)<sub>2</sub> precursor materials (Pb:MAI). (a) The compiled average performance metrics of the control devices. Error bars correspond to the standard deviation. (b-c) Forward and reverse current-voltage characteristic scans measured from the best performing solar cell for each control set. (d-e) Typical external quantum efficiency measurements for each solar cell control.



**Figure S5**. The colour of the pure Pb perovskite film changes when a significant excess of MAI is added to the precursor solution used to synthesise the active layers of the solar cell.

The other interesting feature of the Pb:MAI control batches is that the colour of the film changed from the usual dark brown colour to red for 3Pb:1MAI and yellow for 1Pb:1MAI samples as is seen in Figure S5. This result is consistent with the EQE trends shown in Figure S4e where the  $MA(1Pb:1MAI)I_3$  and  $MA(3Pb:1MAI)I_3$  compositions produce substantially less current with low energy photons. Although absorbance is not significant between 650 and 800 nm, there is a long absorbance tail in this region, which suggests that it might still be the MAPbI<sub>3</sub> material but have a number of trap states in the band gap that are detrimental to performance. Alternatively, the excess of

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MAI might also induce an increased amount of disorder that prevents the material from fully crystallising. In contrast, Figure S4d shows that the Pb:DMF control series maintained the same EQE edge near 800 nm but the efficiency at low photon energies was reduced for thinner samples. This can be explained simply by the fact that thinner films are not able to fully capture these photons and some red and infrared light passes through the films without being absorbed.

 Mean Short-Circuit Current Density,  $J_{sc}$  [mA/cm<sup>2</sup>]

 21Ph:1P/
 2Ph:1P/

Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$16.02 \pm 1.62$		
Pb:DMF	$15.31 \pm 1.64$	$15.50\pm1.04$	$15.10\pm0.98$	$13.37 \pm 1.38$	$11.95 \pm 1.87$
Pb:MAI	$14.06\pm2.69$	$13.72\pm2.31$	$14.92 \pm 1.56$	$10.53\pm3.80$	$3.24 \pm 1.11$
		Mean O	pen-Circuit Voltage	e, V <sub>oc</sub> [V]	
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$0.67\pm0.07$		
Pb:DMF	$0.63\pm0.08$	$0.65\pm0.04$	$0.62\pm0.04$	$0.62\pm0.05$	$0.54\pm0.03$
Pb:MAI	$0.62\pm0.08$	$0.65\pm0.04$	$0.71\pm0.10$	$0.84\pm0.15$	$0.55\pm0.26$
		Me	an Fill Factor, FF	[%]	
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$67.53 \pm 2.54$		
Pb:DMF	$63.17 \pm 7.32$	$67.02 \pm 2.99$	$69.11 \pm 1.42$	$69.31 \pm 1.48$	$68.76 \pm 1.41$
Pb:MAI	$67.72 \pm 1.62$	$67.51 \pm 3.68$	$70.68 \pm 2.79$	$70.35\pm2.17$	$51.87 \pm 7.90$
		Mean Power	Conversion Efficien	ncy, <i>PCE</i> [%]	
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'
Pb Only			$7.27 \pm 1.18$		
Pb:DMF	$6.33 \pm 1.90$	$6.82 \pm 0.81$	$\overline{6.45\pm0.84}$	$5.74 \pm 1.01$	$4.46\pm0.67$
Pb:MAI	$5.93 \pm 1.35$	$6.14 \pm 1.43$	$7.63 \pm 2.07$	$5.87 \pm 1.27$	$1.05\pm0.80$

Table S6. The best measu	red performance me	etrics for each solar	cell control	composition.	J <sub>sc</sub> ,	V <sub>oc</sub> ,	and	FF	do
not necessarily correspond	to the device with the	the champion PCE.							

	Best Short-Circuit Current Density, <i>J<sub>sc</sub></i> [mA/cm <sup>2</sup> ]						
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'		
Pb Only			18.97				
Pb:DMF	18.24	17.45	17.21	16.03	14.49		
Pb:MAI	18.58	16.77	17.53	17.17	4.93		
	1	Best Open-C	ircuit Voltag	ge, <i>V<sub>oc</sub></i> [V]			
Material	63Pb:1B'	31Pb:1B'	15Pb:1B'	7Pb:1B'	3Pb:1B'		
Pb Only			0.82				
Pb:DMF	0.72	0.72	0.69	0.67	0.59		
Pb:MAI	0.81	0.70	0.85	0.96	0.97		
	Best Fill Factor, FF [%]						
		Best Fil	ll Factor, FF	[%]			
Material	63Pb:1B'	Best Fil 31Pb:1B'	ll Factor, <i>FF</i> 15Pb:1B'	' [%] 7Pb:1B'	3Pb:1B'		
Material Pb Only	63Pb:1B'	Best Fil 31Pb:1B'	ll Factor, <i>FF</i> 15Pb:1B' 72.14	' [%] 7Pb:1B'	3Pb:1B'		
Material Pb Only Pb:DMF	63Pb:1B' 71.45	Best Fil 31Pb:1B' 72.41	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.85	' [%] 7Pb:1B' 71.59	3Pb:1B' 70.94		
Material Pb Only Pb:DMF Pb:MAI	63Pb:1B' 71.45 70.3	Best Fil 31Pb:1B' 72.41 71.58	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.85 75.17	'[%] 7Pb:1B' 71.59 73.47	3Pb:1B' 70.94 62.75		
Material Pb Only Pb:DMF Pb:MAI	63Pb:1B' 71.45 70.3 Best	Best Fil 31Pb:1B' 72.41 71.58 Power Conve	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.85 75.17 ersion Effici	' [%] 7Pb:1B' 71.59 73.47 ency, <i>PCE</i>	3Pb:1B' 70.94 62.75 [%]		
Material Pb Only Pb:DMF Pb:MAI Material	63Pb:1B' 71.45 70.3 Best 63Pb:1B'	Best Fil 31Pb:1B' 72.41 71.58 Power Conve 31Pb:1B'	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.85 75.17 ersion Effici 15Pb:1B'	' [%] 7Pb:1B' 71.59 73.47 ency, <i>PCE</i> 7Pb:1B'	3Pb:1B' 70.94 62.75 [%] 3Pb:1B'		
Material Pb Only Pb:DMF Pb:MAI Material Pb Only	63Pb:1B' 71.45 70.3 Best 63Pb:1B'	Best Fil 31Pb:1B' 72.41 71.58 Power Conve 31Pb:1B'	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.85 75.17 ersion Effici 15Pb:1B' 10.27	<ul> <li>[%]</li> <li>7Pb:1B'</li> <li>71.59</li> <li>73.47</li> <li>ency, <i>PCE</i></li> <li>7Pb:1B'</li> </ul>	3Pb:1B' 70.94 62.75 [%] 3Pb:1B'		
Material Pb Only Pb:DMF Pb:MAI Material Pb Only Pb:DMF	63Pb:1B' 71.45 70.3 Best 63Pb:1B' 8.62	Best Fil 31Pb:1B' 72.41 71.58 Power Conve 31Pb:1B' 8.12	ll Factor, <i>FF</i> 15Pb:1B' 72.14 71.85 75.17 ersion Effici 15Pb:1B' 10.27 8.20	<pre>'[%] 7Pb:1B' 71.59 73.47 ency, PCE 7Pb:1B' 7.62</pre>	3Pb:1B' 70.94 62.75 [%] 3Pb:1B' 5.61		

# **Scanning Electron Micrographs of Film Morphologies**

The film morphology for each composition was investigated by imaging the top surface of a representative sample with scanning electron microscopy (SEM). Images with a 50,000X magnification are shown for the mixed-metal material sets in Figures S6-S14.

The morphology of the baseline  $MAPbI_3$  perovskite sample, labeled as the 1Pb:0Co sample in the bottom-right panel of Figure S6, reveals that the perovskite films on PEDOT:PSS consists of randomly oriented plate-like grains that are roughly 100 nm in size.

The general trend across all compositions is that the morphology remains similarly small-grained with increasing B' content until a molar ratio of 7Pb:1B'. At this point the films transition to often dramatically different morphologies as more Pb content is further replaced. The cases of 3Pb:1Co, 3Pb:1Cu, 3Pb:Sn, and 7Pb:1Zn (Figures S6, S7, S12, and S14) are instances where the grains are substantially larger than samples with lower B' content. The films for both 1Pb:1Cu and 3Pb:1Mg (Figures S7 and S9) clearly show two different material phases, one consisting of large grains with a finer material filling in the space between them.

The second noticeable trend is that grain sizes are slightly smaller than MAPbI<sub>3</sub> and the pinhole density is similar at low levels of Pb replacement, which is particular evident in blends with Co (Figure S6), Fe (Figure S8), Mg (Figure S9), Mn (Figure S10), and Sr (Figure S13). The exceptions to this trend are Cu (Figure S7) and Zn (Figure S14), whose morphologies show that the grain size of the MAPbI<sub>3</sub> film is preserved at low replacement levels and that the film seems to have less pinholes with more tightly packed grains comprising the film. Furthermore, the frequency of platelet-like grains seems to reduce with increasing Cu content until the 7Pb:1Cu and 7Pb:1Zn films, where they disappear altogether. In the case of Pb:Zn, at 7Pb:1Zn a second population of dark grains arise that more frequently appear in the 3Pb:1Zn samples (Figure S14).



Figure S6. Scanning electron micrographs of  $MA(Pb:Co)I_3$  perovskite films with different metal replacement fractions.



Figure S7. Scanning electron micrographs of  $MA(Pb:Cu)I_3$  perovskite films with different metal replacement fractions.



Figure S8. Scanning electron micrographs of  $MA(Pb:Fe)I_3$  perovskite films with different metal replacement fractions.



Figure S9. Scanning electron micrographs of  $MA(Pb:Mg)I_3$  perovskite films with different metal replacement fractions.



Figure S10. Scanning electron micrographs of  $MA(Pb:Mn)I_3$  perovskite films with different metal replacement fractions.



Figure S11. Scanning electron micrographs of  $MA(Pb:Ni)I_3$  perovskite films with different metal replacement fractions.



Figure S12. Scanning electron micrographs of  $MA(Pb:Sn)I_3$  perovskite films with different metal replacement fractions.



Figure S13. Scanning electron micrographs of  $MA(Pb:Sr)I_3$  perovskite films with different metal replacement fractions.



Figure S14. Scanning electron micrographs of  $MA(Pb:Zn)I_3$  perovskite films with different metal replacement fractions.

## Normalised Absorbance and Photoluminescence Spectra

In order to investigate the optical properties of each mixed-metal perovskite material, films were built directly on plasma-treated glass substrates without PEDOT:PSS in order to avoid photoluminescence quenching from occurring at the interface between the perovskite and PEDOT:PSS. In order to protect the films from ambient conditions during measurement, they were coated with a layer of poly(methyl methacrylate) (PMMA), which is hydrophobic and prevents moisture from accessing the perovskite.

The band gap of each material was determined from the position of the photoluminescence emission peak measured with a fluorimeter. The trends in PL peak shifts can be confirmed by corresponding shifts in the absorbance edge of the material. Hence, the normalised absorbance and PL emission spectra for each mixed-metal composition are presented together in Figures S16 and S17. In each case, the PL emission peak was locally fit to a parabola in order to compensate for any noise in the spectrum and identify the position of the emission peak. The PL emission peak positions and the shift from the MAPbI<sub>3</sub> control films synthesised for each material set are tabulated in Table S7. Only the absorbance spectra are reported for Pb:Sn blends in Figure S15 because several of the films in this composition set were not emissive enough to generate clean PL spectra.



Figure S15. The normalised absorbance spectra of mixed-metal Pb:Sn perovskite films compositions.



**Figure S16**. The normalised absorbance (solid lines) and photoluminescence emission (dotted lines) spectra of perovskite films from the following composition sets: (a) Pb:Co, (b) Pb:Cu, (c) Pb:Fe, and (d) Pb:Mg. The wavelength and photon energy of each PL peak position is determined by fitting the region around each peak to a parabola.



**Figure S17**. The normalised absorbance (solid lines) and photoluminescence emission (dotted lines) spectra of mixed-metal perovskite films compositions sets: (a) Pb:Mn, (b) Pb:Ni, (c) Pb:Sr, and (d) Pb:Zn. The wavelength and photon energy of each PL peak position is determined by fitting the region around each peak to a parabola.

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**Table S7.** Optical band gap as determined from the location of the photoluminescence emission peak of mixedmetal perovskite films and the shift from peak position of pure  $MAPbI_3$  control sample taken with each material set

	PL Peak	Position	Peak Shift fr	rom MAPbI <sub>3</sub>
Material	$\lambda_{PL}$ [nm]	$E_{PL}$ [eV]	$\Delta\lambda_{PL}$ [nm]	$\Delta E_{PL}$ [eV]
MAPbI <sub>3</sub>	774	1.602	-	-
MA(63Pb:1Co)I <sub>3</sub>	773	1.604	-1	0.002
$MA(31Pb:1Co)I_3$	771	1.608	-3	0.006
$MA(15Pb:1Co)I_3$	770	1.610	-4	0.008
$MA(7Pb:1Co)I_3$	758	1.636	-16	0.034
$MA(3Pb:1Co)I_3$	765	1.620	-9	0.018
MAPbI <sub>3</sub>	770	1.610	-	-
$MA(63Pb:1Cu)I_3$	765	1.621	-5	0.011
$MA(31Pb:1Cu)I_3$	765	1.620	-5	0.010
$MA(15Pb:1Cu)I_3$	771	1.608	1	-0.002
$MA(7Pb:1Cu)I_3$	766	1.618	-4	0.008
$MA(3Pb:1Cu)I_3$	769	1.612	-1	0.002
MAPbI <sub>3</sub>	769	1.612	-	-
MA(63Pb:1Fe)I <sub>3</sub>	770	1.610	1	-0.002
$MA(31Pb:1Fe)I_3$	761	1.629	-8	0.017
$MA(15Pb:1Fe)I_3$	750	1.654	-19	0.042
$MA(7Pb:1Fe)I_3$	753	1.646	-16	0.034
$MA(3Pb:1Fe)I_3$	740	1.675	-29	0.063
MAPbI <sub>3</sub>	764	1.622	-	-
$MA(63Pb:1Mg)I_3$	771	1.609	7	-0.013
$MA(31Pb:1Mg)I_3$	767	1.617	3	-0.005
$MA(15Pb:1Mg)I_3$	760	1.630	-4	0.008
MA(7Pb:1Mg)I <sub>3</sub>	739	1.678	-25	0.056
MA(3Pb:1Mg)I <sub>3</sub>	731	1.696	-33	0.074
MAPbI <sub>3</sub>	764	1.622	-	-
$MA(63Pb:1Mn)I_3$	771	1.609	7	-0.013
$MA(31Pb:1Mn)I_3$	771	1.607	7	-0.015
$MA(15Pb:1Mn)I_3$	765	1.621	1	-0.001
$MA(7Pb:1Mn)I_3$	761	1.629	-3	0.007
$MA(3Pb:1Mn)I_3$	755	1.642	-9	0.020
MAPbI <sub>3</sub>	772	1.605	-	-
MA(63Pb:1Ni)I <sub>3</sub>	772	1.606	0	0.001
MA(31Pb:1Ni)I <sub>3</sub>	770	1.611	-2	0.006
$MA(15Pb:1Ni)I_3$	765	1.620	-7	0.015
$MA(7Pb:1Ni)I_3$	744	1.666	-28	0.061
$MA(3Pb:1Ni)I_3$	746	1.662	-26	0.057
MAPbI <sub>3</sub>	773	1.604	-	-
$MA(63Pb:1Sr)I_3$	766	1.619	-7	0.015
$MA(31Pb:1Sr)I_3$	769	1.612	-4	0.008
$MA(15Pb:1Sr)I_3$	750	1.652	-23	0.048
$MA(7Pb:1Sr)I_3$	739	1.677	-34	0.073
$MA(3Pb:1Sr)I_3$	714	1.736	-59	0.132
MAPbI <sub>3</sub>	769	1.612	-	-
$MA(63Pb:1Zn)I_3$	767	1.617	-2	0.005
$MA(31Pb:1Zn)I_3$	767	1.616	-2	0.004
$MA(15Pb:1Zn)I_3$	773	1.603	4	-0.009
$MA(7Pb:1Zn)I_3$	769	1.613	0	0.001
$MA(3Pb:1Zn)I_3$	773	1.604	4	-0.008

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# Impact of Light-Soaking on Performance of MA(Pb:Sn)I<sub>3</sub> Blends

Out of all the mixed-metal material sets, only Pb:Sn demonstrated significant changes in the currentvoltage characteristics beyond the standard five minutes of light soaking prior to measurement. The compositions with low Sn content exhibited this behaviour, whereas 3Pb:1Sn films did not. An example is shown in Figure S18 for a MA(15Pb:1Sn)I<sub>3</sub> device that initially displayed both hysteresis and low open-circuit voltages, which were improved upon measurement after an additional five minutes of light-soaking.



**Figure S18.** Light-soaking the same solar cell with the  $MA(15Pb:1Sn)I_3$  mixed-metal composition for an additional 5 minutes improves device performance by increasing the open-circuit voltage.

# **External Quantum Efficiency**

External quantum efficiency (EQE) measurements were performed on multiple solar cells of each mixed-metal composition. The EQE spectra reported for each mixed-metal set in Figure S19 were selected from the same device batch to ensure that changes between devices in a given series is a result of changing the metal Pb:B' ratio rather than batch-to-batch variation. Hence, the measurements for the MAPbI<sub>3</sub> control devices will vary slightly between each set of blends.

The EQE spectra can also provide the band gap of the material by plotting it against photon energy and fitting a line to the absorption edge. The band gap,  $E_g$  is taken as the *x*-intercept of the linear fit. The EQE spectra as a function of photon energy and the linear fit at the edges are shown in Figure S20 and the corresponding band gaps are reported in Table S8.

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**Figure S19.** Typical external quantum efficiency measurements for the compositions in each set of mixed-metal perovskite devices: (a) Pb:Co, (b) Pb:Cu, (c) Pb:Fe, (d) Pb:Mg, (e) Pb:Mn, (f) Pb:Ni, (g) Pb:Sn, (h) Pb:Sr, and (i) Pb:Zn. Note that the MAPbI<sub>3</sub> curve in each plot corresponds to the control device that was fabricated in the same device set as the presented mixed-metal devices.



**Figure S20**. The optical band gap,  $E_g$ , is estimated by fitting a line to the edge of the EQE and extracting the intercept at the *x*-axis for each set of mixed-metal devices: (a) Pb:Co, (b) Pb:Cu, (c) Pb:Fe, (d) Pb:Mg, (e) Pb:Mn, (f) Pb:Ni, (g) Pb:Sn, (h) Pb:Sr, and (i) Pb:Zn. Note that the MAPbI<sub>3</sub> curve in each plot corresponds to the control device that was fabricated in the same device set as the presented mixed-metal devices.

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**Table S8.** The band gap,  $E_g$ , determined from the EQE spectra as a function of photon energy (Figure S19) for the mixed-metal compositions. Note that the MAPbI<sub>3</sub> value listed was fabricated in the same device set as the mixed-metal values presented.

	Band Gap,		Band Gap,
Material	$E_g[eV]$	Material	$E_g[eV]$
MAPbI <sub>3</sub>	1.559	MAPbI <sub>3</sub>	1.559
$MA(63Pb:1Co)I_3$	1.559	MA(63Pb:1Ni)I <sub>3</sub>	1.564
$MA(31Pb:1Co)I_3$	1.559	MA(31Pb:1Ni)I <sub>3</sub>	1.564
$MA(15Pb:1Co)I_3$	1.559	$MA(15Pb:1Ni)I_3$	1.564
$MA(7Pb:1Co)I_3$	1.564	MA(7Pb:1Ni)I <sub>3</sub>	1.596
$MA(3Pb:1Co)I_3$	1.559	MA(3Pb:1Ni)I <sub>3</sub>	1.591
MAPbI <sub>3</sub>	1.559	MAPbI <sub>3</sub>	1.563
$MA(63Pb:1Cu)I_3$	1.559	MA(63Pb:1Sn)I <sub>3</sub>	1.560
$MA(31Pb:1Cu)I_3$	1.559	$MA(31Pb:1Sn)I_3$	1.563
$MA(15Pb:1Cu)I_3$	1.559	MA(15Pb:1Sn)I <sub>3</sub>	1.560
$MA(7Pb:1Cu)I_3$	1.559	$MA(7Pb:1Sn)I_3$	1.406
$MA(3Pb:1Cu)I_3$	1.559	MA(3Pb:1Sn)I <sub>3</sub>	1.312
$MA(1Pb:1Cu)I_3$	1.559	MA(1Pb:1Sn)I <sub>3</sub>	1.240
MAPbI <sub>3</sub>	1.565	MAPbI <sub>3</sub>	1.564
MA(63Pb:1Fe)I <sub>3</sub>	1.565	$MA(63Pb:1Sr)I_3$	1.563
MA(31Pb:1Fe)I <sub>3</sub>	1.562	$MA(31Pb:1Sr)I_3$	1.563
MA(15Pb:1Fe)I <sub>3</sub>	1.565	$MA(15Pb:1Sr)I_3$	1.563
MA(7Pb:1Fe)I <sub>3</sub>	1.578	$MA(7Pb:1Sr)I_3$	1.572
MA(3Pb:1Fe)I <sub>3</sub>	1.569	$MA(3Pb:1Sr)I_3$	1.653
MAPbI <sub>3</sub>	1.564	MAPbI <sub>3</sub>	1.564
$MA(63Pb:1Mg)I_3$	1.564	$MA(63Pb:1Zn)I_3$	1.564
$MA(31Pb:1Mg)I_3$	1.564	$MA(31Pb:1Zn)I_3$	1.564
$MA(15Pb:1Mg)I_3$	1.564	$MA(15Pb:1Zn)I_3$	1.564
$MA(7Pb:1Mg)I_3$	1.569	$MA(7Pb:1Zn)I_3$	1.559
$MA(3Pb:1Mg)I_3$	1.574	$MA(3Pb:1Zn)I_3$	1.564
MAPbI <sub>3</sub>	1.565	MAPbI <sub>3</sub>	1.562
$MA(63Pb:1Mn)I_3$	1.562	MA(63Pb:1MAI)I <sub>3</sub>	1.562
$MA(31Pb:1Mn)I_3$	1.562	MA(31Pb:1MAI)I <sub>3</sub>	1.562
$MA(15Pb:1Mn)I_3$	1.562	$MA(15Pb:1MAI)I_3$	1.567
$MA(7Pb:1Mn)I_3$	1.562	MA(7Pb:1MAI)I <sub>3</sub>	1.571
$MA(3Pb:1Mn)I_3$	1.556	MA(3Pb:1MAI)I <sub>3</sub>	1.835

# **Photoluminescence Spectra of Pb:Fe Mixtures**



**Figure S21**. The photoluminescence emission spectra for  $MA(Pb:Fe)I_3$  perovskite films show substantial emission quenching as illustrated by (a) linear and (b) logarithmic plots of emission intensity.

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## Performance of MA(Pb:Cu)I<sub>3</sub> Compositions

The identification of Cu as a possible candidate for blending with Pb merits some special attention. Although a champion value of 8.3% was obtained for  $MA(3Pb:1Cu)I_3$  devices, only one batch of devices was able to attain this level of performance and these devices only achieved high performance during the first current-voltage characteristic measurement. As is shown in Figure S22, when a second measurement was performed after another five minutes of light soaking, the JV curve became unstable as the measured photocurrent was often discontinuous during the bias voltage sweep.



**Figure S22**. The initial JV sweep (black lines) of  $MA(3Pb:1Cu)I_3$  yield high currents with little hysteresis. However, the same solar cell after light-soaking for another 5 minutes (blue lines) produces a destabilised JV characteristic.

To explore the possible origins of this strange behaviour, the same solar cell presented in Figure S22 was allowed to rest for several hours. Then a set of JV sweeps was performed after device was held at forward bias (1.4 V) in the open-circuit configuration for various periods of time. Doing so was intended to allow any mobile ions and charges to migrate to a new configuration that might either promote performance or damage it. These tests revealed several interesting observations:

- 1. The 8.3% solar cell was able to recover from its erratic encore performance after several hours of resting and operate with well-behaved JV curves. However, the PCE was reduced from 8.3% to 4.3%.
- 2. As the devices are held at forward bias for longer periods of time, the hysteresis between the forward and reverse sweeps grows until the reverse sweep becomes erratic.

It is unclear exactly why substituting Pb with Cu produces this behaviour, however we speculate it is related to the fact that copper is the only metal species out of those investigated that is more stable with a +1 rather than a +2 oxidation state in the presence of iodide anions. It is possible that sometimes the initial mixed-metal perovskite contains  $Cu^{2+}$  ions in the perovskite, however during device operation, photogenerated electrons or mobile iodide ions might reduce the  $Cu^{2+}$  species to  $Cu^+$ , which would locally disrupt the perovskite crystal and create a set of newly formed mobile ions that might account for the erratic JV behaviour. The  $Cu^+$  ions would then be unable to replace the B-site cation in the perovskite lattice and would form a second phase of CuI in the perovskite film, allowing the device to operate again. It has been reported that CuI is an efficient hole transport material for perovskite devices,<sup>6</sup> and it is possible that it might initially benefit device performance by providing a pathway for hole-transport from the bulk of the lattice. However, CuI can also act as a shunt if it directly contacts the fullerene and PEDOT:PSS layers, which would explain why the shunt resistance is noticeably lower for the JV curves of the Pb:Cu blends in Figure S2b. Furthermore, the

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XRD spectra for 3Pb:1Cu and 7Pb:1Cu films (Figure S24) display an additional peak at  $2\theta = 25.2^{\circ}$ , which is consistent with the (111) planes of CuI. The JV curves for the Pb:Cu devices are also the only ones to demonstrate deviation from diode behaviour near reverse bias conditions.



**Figure S23**. The effect of holding each composition of mixed-metal MA(Pb:Cu)I<sub>3</sub> solar cells at forward bias (1.4 V) between 0 and 60 seconds prior to JV curve measurement.

Figure S23 presents the results of the pre-biasing study where the MA(Pb:Cu)I<sub>3</sub> devices, including the exact device that achieved the 8.3% performance, were first held at forward bias ( $V_{bias} = 1.4$  V) for 0 to 60 seconds prior to measuring the JV curves. For short hold times, the MA(3Pb:1Cu)I<sub>3</sub> had minimal hysteresis. However, as the hold times lengthen, the hysteresis between forward and reverse scans increases until eventually the reverse scan completely destabilises and the JV curve becomes erratic. The 15Pb:1Cu device demonstrate an increase in hysteresis with increasing hold times, but this instability is not observed (Figure 23b). For devices with even lower Cu content, such as 63Pb:1Cu in Figure 23c, the JV curves become well-behaved and very little hysteresis or anomalous behaviour is observed regardless of bias time.

When the behaviour of a device changes substantially with initial biased hold times, it is likely some

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charge carriers or ions are responding to the applied electric field through the device and are migrating into a new configuration. Since this behaviour is exacerbated with increasing Cu content, it is reasonable to conclude that the Cu content is indeed responsible for the behaviour. It is possible that films with higher Cu content contain more mobile ions or charge carriers that are able to migrate in response to the electric field and create substantial hysteresis that generate unfavourable conditions for device performance.



Figure S24. The x-ray diffraction spectra of Pb:Cu mixed-metal perovskite films compositions

# X-ray Photoelectron Spectroscopy

Survey scans with x-ray photoelectron spectroscopy (XPS) of MAPbI<sub>3</sub> and MA(31Pb:1Co)I<sub>3</sub> films are shown in Figure S25a. Figure S25b presents a high-resolution scan of the Co 2p peaks along with peak fittings obtained using the K-alpha (Thermo Scientific) software package. A peak in the range of 777.8-778.5 eV corresponding to  $Co^0$  is absent<sup>7,8</sup> from Figure S25b, which suggests that cobalt is incorporated in the film as a cation. The observation of a satellite feature for the Co  $2p_{3/2}$  peak near 787 eV is evidence that the species exists in the Co(II) oxidation state.<sup>9</sup>



**Figure S25.** a) XPS survey scan for MAPbI<sub>3</sub> and MA(31Pb:1Co)I<sub>3</sub> films. b) High-resolution XPS spectrum with peak fittings of Co 2p region for MA(31Pb:1Co)I<sub>3</sub>.

## **Ultraviolet Photoelectron Spectroscopy**

**Data Processing of UPS Measurement.** Vacuum energies were determined from the intersection of a linear extrapolation of the secondary electron cut-off to zero, subtracted from the 21.22 eV photon energy. Valence band binding energies were determined from the intersection of a linear extrapolation of the primary electron cut-off to a linear extrapolation of the baseline. The absolute energy resolution is estimated to be ~0.15 eV. The ultraviolet photoelectron spectra for PEDOT:PSS, MAPbI<sub>3</sub>, and the MA(Pb:Co)I<sub>3</sub> materials are shown in Figure S26.



**Figure S26**. Secondary electron edge (left panel) and primary electron edge (right panel) of a representative ultraviolet photoelectron spectrum (middle panel) for PEDOT:PSS and MA(Pb:Co)I<sub>3</sub> mixed-metal perovskite films built on a DIO-treated PEDOT:PSS film on ITO.

**Energetics at Perovskite/PEDOT:PSS Interface.** As is evident from the left-hand panel of Figure S26, the work function of MAPbI<sub>3</sub> is greater than the work function of PEDOT:PSS. As the Co content in the perovskite is increased, the work function becomes progressively shallower, eventually becoming shallower than the PEDOT:PSS for the 15Pb:1Co material. The position of the perovskite Fermi level relative to that of PEDOT:PSS determines the vacuum energy shift and built-in electric field in the region of the perovskite/PEDOT:PSS interface under equilibrium. Based on the energy levels determined from the UPS measurements, a band diagram was constructed for the perovskite/PEDOT:PSS junction for each Pb:Co composition (Figure S27) in order to better understand how the mismatches in Fermi energy might influence device behaviour.

As is shown in Figure S27, there is an unfavourable vacuum energy offset (*i.e.*  $\Delta E > 0$ ) at the interface between PEDOT:PSS and MAPbI<sub>3</sub>, which is manifested either as a surface dipole or as band-bending. This vacuum energy offset indicates the presence of a built-in electric field across the interface that opposes the transfer of holes from the valence band edge of MAPbI<sub>3</sub> into PEDOT:PSS. As the Co content in the perovskite film is increased, the mixed-metal perovskite work function decreases and – for Co loadings greater than 15Pb:1Co – becomes shallower than the PEDOT:PSS work function, indicating a reversal in the polarity of the built-in electric field for these samples. This change in polarity is illustrated by the upward band-bending of the perovskite energy levels at the PEDOT:PSS/perovskite interface for the 15Pb:1Co and 7Pb:1Co compositions. Hence, introducing Co into the perovskite material shifts the work function into a more favourable alignment that is expected to improve hole extraction at the PEDOT:PSS interface, and thereby improve the

photovoltaic performance of the device.



**Figure S27**. The expected band-bending behaviour of the perovskite/PEDOT:PSS junction for MAPbI<sub>3</sub> and each mixed-metal MA(Pb:Co)I<sub>3</sub> perovskite. The bending of the perovskite band edges at the interface results from the mismatch in Fermi energies between the perovskite and PEDOT:PSS.

**Open-Circuit Voltage Improvement.** In addition to producing an unfavourable electric field that opposes hole injection into PEDOT:PSS, the downward band-bending illustrated in Figure S27 for the MAPbI<sub>3</sub>/PEDOT:PSS interface could drive electrons in MAPbI<sub>3</sub> toward the PEDOT:PSS, which presents a possible leakage pathway through the device. In contrast, the upward band-bending of the mixed-metal perovskites with higher Co content could provide a beneficial interfacial barrier that reduces electron leakage into the PEDOT:PSS. This reduction in election leakage into the PEDOT:PSS should correspond to a decrease in forward-bias dark current. Although PEDOT:PSS is generally considered to be an electron-blocking material, the EDX maps of Figure 2d-f (main text) suggest that I, Pb, and Co atoms are all present in the PEDOT:PSS layer. It is possible that the electron-blocking property of PEDOT:PSS has been compromised by defect states resulting from the leaching of these elements from the perovskite into the PEDOT:PSS layer. Indeed, the UPS spectrum of PEDOT:PSS near the valence band edge (right-panel of Figure S26) is quite broad without a sharp cut-off, suggesting that such states could extend into the band.

According to the standard diode model of the solar cell, the open-circuit voltage,  $V_{OC}$ , is logarithmically-inversely related to the diode saturation current density,  $J_S$ :

$$V_{OC} = \frac{nk_BT}{q} \ln\left(\frac{J_{SC}}{J_S} + 1\right),\tag{S1}$$

where *n* is the diode ideality factor,  $k_B$  is Boltzmann's constant, *T* is temperature, *q* is the charge of the electron, and  $J_{SC}$  is the short-circuit current density when under illumination.





**Figure S28**. (a) Linear and (b) semi-logarithmic current-voltage characteristics for representative MA(Pb:Co)I<sub>3</sub> mixed-metal perovskite solar cells under 1-sun illumination (solid lines) and in the dark (dotted lines).

Equation S1 shows that the open-circuit voltage will increase if the diode saturation current is reduced (*i.e.* if there is less recombination current or leakage current through the solar cell, corresponding to a lower dark current). Figure S28 shows that the forward-bias dark current decreases with increasing Co content, matching the trend of increasing  $V_{OC}$  for these materials. This trend in dark current and  $V_{OC}$  could be explained by the band-bending effects noted above: as the Co content is increased, the barrier to electron leakage into the PEDOT:PSS is strengthened, thus reducing the dark current and increasing the  $V_{OC}$ . It is possible that the decrease in  $V_{OC}$  that occurs when too much Co content is introduced (*i.e.* the 3Pb:1Co composition) might result from the Co atoms producing a significant amount of trap states within the band gap of the perovskite bandstructure. The increasing conduction-band offset between the mixed-metal Pb:Co perovskites and PCBM as the Co content is increased could also decrease the forward-bias leakage current by making electron transfer from PCBM to the perovskite less favourable.

This relationship between Co content, Fermi level shift, leakage current, and open-circuit voltage offers an explanation why the reductions of the mixed-metal perovskite work function with Co content produces a more beneficial energetic configuration, which is consistent with the observed enhancement trends in open-circuit voltage produced by Pb:Co perovskite devices.

# Part III: Supporting Information for the Optimised MA(Pb:Co)I<sub>3</sub> Solar Cells

# Thicknesses for Optimised MA(Pb:Co)I<sub>3</sub> Solar Cells

The thickness of a typical perovskite film for each optimised  $MA(Pb:Co)I_3$  composition is presented in Table S9.

Table S9. Typical film thicknesses for optimised MA(Pb:Co)I<sub>3</sub> perovskite films

	Film Thickness, <i>t<sub>film</sub></i> [nm]						
Material	127Pb:1B'	63Pb:1B'	31Pb:1B'	15Pb:1B'			
Pb Only		334	.3				
Pb:Co	322.4	328.0	334.5	339.3			

# Mean Performance Metrics for Optimised MA(Pb:Co)I<sub>3</sub> Solar Cells

**Table S10.** The compiled average performance metrics from a set of at least 20 devices for each of the optimised  $MA(Pb:Co)I_3$  compositions. Error corresponds to the standard deviation.

	PCE	J <sub>sc</sub>	$V_{oc}$	FF
Device Designation	[%]	[mA/cm <sup>2</sup> ]	[V]	[%]
MAPbI <sub>3</sub>	$14.39 \pm 1.39$	$19.80 \pm 1.55$	$0.96\pm0.02$	$75.60\pm2.69$
MA(127Pb:1Co)I <sub>3</sub>	$14.92\pm0.85$	$19.60\pm0~.84$	$1.00\pm0.03$	$76.47 \pm 3.22$
MA(63Pb:1Co)I <sub>3</sub>	$15.00\pm0.92$	$19.17\pm0.93$	$1.03\pm0.02$	$76.18\pm3.16$
MA(31Pb:1Co)I <sub>3</sub>	$12.38\pm0.99$	$16.54 \pm 1.43$	$1.05\pm0.03$	$71.73 \pm 4.61$
MA(15Pb:1Co)I <sub>3</sub>	$5.65\pm0.86$	$8.96 \pm 1.30$	$0.99\pm0.03$	$64.21 \pm 6.19$

# Champion Performance Metrics for Optimised MA(Pb:Co)I<sub>3</sub> Solar Cells

**Table S11.** The best measured performance metrics for each of the optimised MA(Pb:Co)I<sub>3</sub> compositions.  $J_{sc}$ ,  $V_{oc}$ , and *FF* do not necessarily correspond to the device with the champion *PCE*.

Device Designation	<i>PCE</i> [%]	$J_{sc}$ [mA/cm <sup>2</sup> ]	$V_{oc}$	FF [%]
MAPbI <sub>3</sub>	16.58	21.68	1.00	79.25
MA(127Pb:1Co)I <sub>3</sub>	16.69	21.20	1.06	80.49
MA(63Pb:1Co)I <sub>3</sub>	17.15	21.10	1.06	82.55
MA(31Pb:1Co)I <sub>3</sub>	14.21	19.42	1.08	80.48
MA(15Pb:1Co)I <sub>3</sub>	8.31	13.06	1.02	74.98

# Stabilised Power Output for Optimised MA(Pb:Co)I<sub>3</sub> Solar Cells

In order to ensure that the photocurrent and power output of the optimised solar cells stabilised under illumination, the champion devices were biased at the voltage of the maximum power point (as determined by the JV characteristic) and the photocurrent was measured as a function of time. Figure S29 presents both the photocurrent and power conversion efficiency as a function of time for the baseline MAPbI<sub>3</sub> material and each of the optimised MA(Pb:Co)I<sub>3</sub> films.



**Figure S29.** Champion stabilised power output measurement for the optimised  $MA(Pb:Co)I_3$  solar cells measured by monitoring the current while biasing the device at the voltage of the maximum power point.

# Dark J-V Characteristics for Optimised MA(Pb:Co)I<sub>3</sub> Solar Cells

In the sub-section entitled "Open-Circuit Voltage Improvement" discussed in the section "Ultraviolet Photoelectron Spectroscopy" of Part II, it was discussed in detail how the open-circuit voltage will increase if the diode saturation current is reduced (*i.e.* if there is less recombination current or leakage current through the solar cell, corresponding to a lower dark current). This explanation is still supported for the optimised baseline MAPbI<sub>3</sub> and MA(Pb:Co)I<sub>3</sub> perovskite films as is evidenced by typical dark current curves shown in Figure S30 also reproducing the same behaviour witnessed in the corresponding devices of the screening study. That is, as the cobalt content is increased in the devices, the  $V_{oc}$  in the light curves increase and the saturation current,  $J_s$ , in the dark curves decrease.

This evidence supports the explanation given above for voltage improvement: the Co content improves the energetic alignment of the PEDOT:PSS with the perovskite film, which increasingly mitigates leakage through the device, thereby enhancing the  $V_{oc}$  in accordance with Equation S1.





**Figure S30.** (a) Linear and (b) semi-logarithmic current-voltage characteristics for a representative solar cell with optimised film morphologies for each MA(Pb:Co)I<sub>3</sub> composition under 1-sun illumination (solid lines) and in the dark (dotted lines).

## Absorbance Spectra of Optimised MA(Pb:Co)I<sub>3</sub> Perovskite Films

As was observed for the  $MA(Pb:Co)I_3$  perovskite films produced in the screening study (Figure S15a), the absorbance edges plotted in Figure S31 do not change from the baseline  $MAPbI_3$  material as a function of Co content for films with an optimised morphology.



**Figure S31.** The normalised absorbance for  $MA(Pb:Co)I_3$  films with an optimised morphology. The band gap taken from extrapolating the absorbance edge to the *x*-axis is printed in the colour indicated in the legend for each composition.

# Photoluminescence of Optimised MA(Pb:Co)I<sub>3</sub> Perovskite Films

As was observed for the  $MA(Pb:Co)I_3$  perovskite films produced in the screening study (Figure S16a), the position of the steady-state photoluminescence emission spectra (Figure S31) do not

significantly vary from the baseline  $MAPbI_3$  materials as a function of Co for films with an optimised morphology.



**Figure S32.** Normalised absorbance (solid lines) and steady-state photoluminescence (PL) emission spectra (dashed lines) for each of the optimised MA(Pb:Co)I<sub>3</sub> films with optimised film. The circle indicates the PL peak position and the corresponding wavelength and photon energy are denoted.



Figure S33. A representative steady-state photoluminescence emission spectrum for each of the optimised  $MA(Pb:Co)I_3$  films.

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