Chemical Communications

Supporting Information

Solution triggered facile ion-exchange and phase transformation of ternary cesium-copper halide pseudo-perovskites

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Experimental Methods

Chemicals

Cesium(I) iodide (CsI, VWR, ≥99.9% metals basis), cesium(I) bromide (CsBr, Sigma-Aldrich, 99.999% trace metals basis), copper(I) iodide (CuI, VWR, ≥99.998% metals basis, Puratronic®), copper(I) bromide (CuBr, Sigma-Aldrich, 99.999% trace metals basis), acetonitrile (ACN, VWR, ≥99.9%), methanol (VWR, 100%), MilliQ ultrapure water was used as received. FTO (fluoride doped tin oxide coated glass, Sigma-Aldrich, 7Ω cm^{-2}) and microscopy slides were used as substrates. For the substrate cleaning, we used acetone (VWR, 100%), 2-propanol (VWR, 100%), and deionized (DI) water.

Cs$_3$Cu$_2$Br$_5$ layer preparation

The Cs$_3$Cu$_2$Br$_5$ layers were synthesized by spray coating. We used regular microscopy slides as a substrate. The cleaning procedure consisted of 5-5 minutes of sonication in DI water, acetone, and 2-propanol, respectively. After drying, we performed 10 minutes of oxygen plasma treatment immediately before use. The substrates were preheated on a hotplate at 50 °C. The precursor solution was sprayed on the 1 cm^2 surface with an Alder AD320 airbrush. The precursor solution contained 0.025 M Cs$_3$Cu$_2$Br$_5$ prepared from stoichiometric amounts of CsBr (0.160 g) and CuBr (0.072 g) in a mixture of dry acetonitrile (10 cm^3) and 11 V/V% water (1.2 cm^3). The thickness of the samples was estimated by measuring their mass loading. After preparation the finished layers were placed in a desiccator and stored until further use.

Halide exchange of Cs$_3$Cu$_2$Br$_5$ layers

To perform halide exchange experiments, we prepared CsI solution in methanol with different concentrations (0.03 M, 0.06 M, and 0.11 M). The previously prepared Cs$_3$Cu$_2$Br$_5$ layers were immersed in 5 cm^3 of CsI solution at room temperature, for different soaking times. After removing the layers from the solution, they were dried under atmospheric conditions and subjected to different materials characterization techniques.

Materials characterization

Steady-state and time-resolved photoluminescence (PL) spectra were recorded with a FluoroMax spectrofluorometer with DeltaHub TCSPC controller and NanoLED-295 light source (λ_{max} = 300 nm). For the steady state PL measurements, we used 290 nm excitation wavelength. The photoluminescence quantum yield (PLQY) of the films was measured with a Jasco FP-8500 spectrofluorometer, equipped with an ILFC-847 100 mm diameter integrating sphere unit. The excitation wavelength was 300 nm, and the used aperture was 3 mm. The

calibration of the integrating sphere was performed using an ESC-142 calibrated white light source. The crystal structure of the prepared layers was studied by X-ray diffraction (XRD) with a Rigaku Mini Flex II desktop diffractometer equipped with a Cu Kα (λ=1.5418 Å) X-ray source. The diffraction patterns were recorded in the 10 – 80 ° 2theta range with 2.0 °/min scanning speed. The divergence slit, receiving slit, and anti-scattering slit were 1.25°, 0.3 mm and 1.25°, respectively. The individual lattice parameters and the lattice volume was derived from Le Bail fitting with GSAS-II software.[1] A chebyschev-1 function was used to model the amorphous background of the raw data. Based on the halide content of the samples the starting unit cell dimensions for the refinement was $Cs_3Cu_2Br_5$ (COD #7246299). If spurious peaks were remaining additional phases were added to better the fit (e.g., $CsCu_2I_3$ (COD #1536279) $Cs_3Cu_2I_5$ (COD #7246300). Top-down scanning electron microscopy (SEM) images were recorded with a Thermo Scientific Apreo 2 instrument using Everhart–Thornley detector (ETD). For the determination of the elemental composition of the layers Energy-dispersive X-ray spectroscopy (EDX) was performed with a Bruker XFlash 6-30 detector. An Agilent 7900 inductively coupled plasma torch connected to a mass spectrometer (ICP-MS) was used to determine the Cs, Cu, Br and I content of each sample. The samples were diluted with DI water and contained 1 vol% HNO_3 (made from ICP-MS grade cc. acid, NORMATOM® by VWR) as well as 0.1 ppm Y and Lu used as internal standards (made from 10 ppm standard solution, ARISTAR® by VWR). For calibration, a 11-point sample series was prepared in the concentration range of 0–1 ppm for Cu, Br, I, and Cs. Cu and Cs were added using a 10 ppm multielement standard solution (ARISTAR® by VWR). As for Br and I, a 1000 ppm stock solution was prepared directly before the measurements. Here, a.r. grade KBr (Merck) and KI (Honeywell/Fluka) salts were used after a 3-hour long drying period at 100°C to remove water from the salts. All calibration samples contained the same amount of internal standard and HNO_3. For quantitation, the ^{63}Cu, ^{65}Cu, ^{79}Br, ^{81}Br, ^{127}I, and ^{133}Cs isotopes were used. The counts of ^{89}Y was used for Cu and Br, and those of ^{175}Lu was used for Br determination, whereas no internal standard was needed for I quantification. At the end of each measurement, two calibration points were remeasured to check the signal stability. Accordingly, the recovery of the concentrations was within 2% in most cases, except for I (6%), which may partially be due to the known decomposition of potassium iodide in aqueous solution when exposed to air and light for extended periods of time.
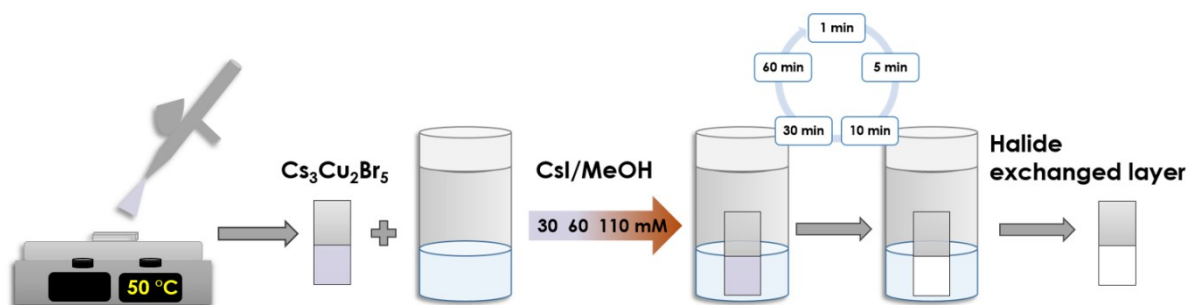
Figure S1. Schematic illustration of the workflow of performing the halide exchange experiments. First step is the $Cs_3Cu_2Br_5$ layer preparation by spray-coating. This is followed by the soaking of the layers in CsI solutions of three different concentrations in MeOH for different periods of time.
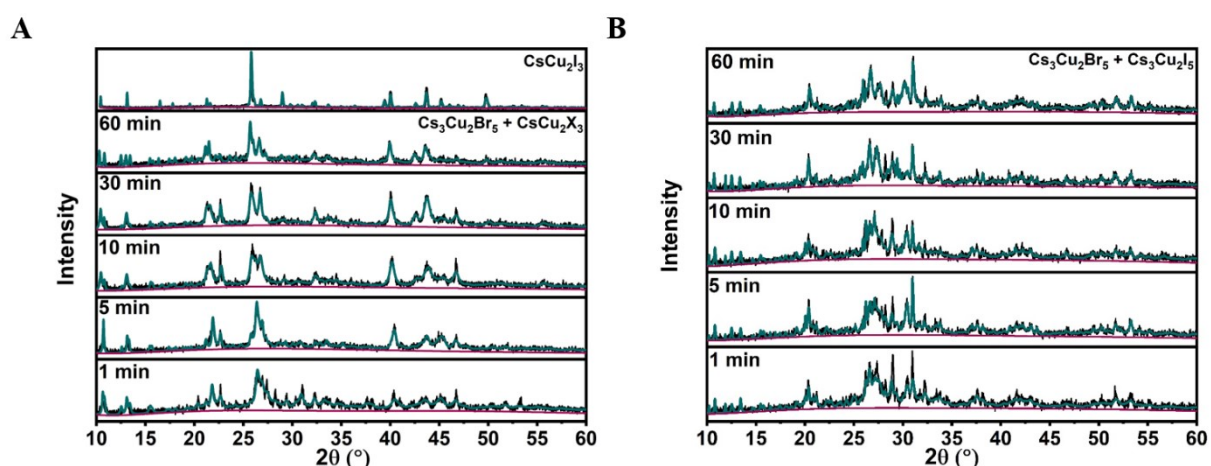

Figure S2. X-ray diffraction of the layers soaked in **A:** 30mM and **B:** 110 mM CsI/MeOH solution including $CsCu_2I_3$ reference. The results of the Le Bail fitting is shown in green and the measured curve is with black.
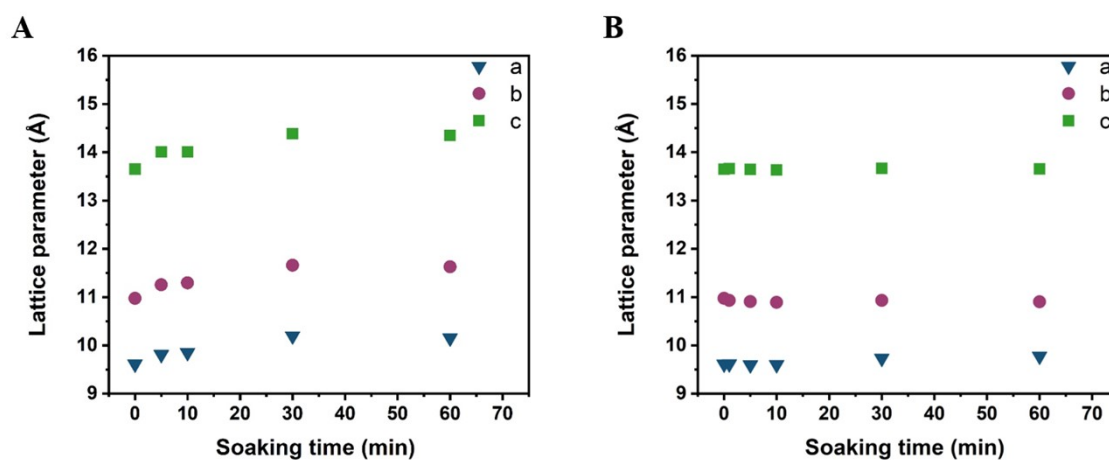

Figure S3. Material characterization: Individual (a, b, c) cell parameters, from the X-ray diffraction data. **A:** 60 mM and **B:** 110 mM CsI/MeOH soaking solution.
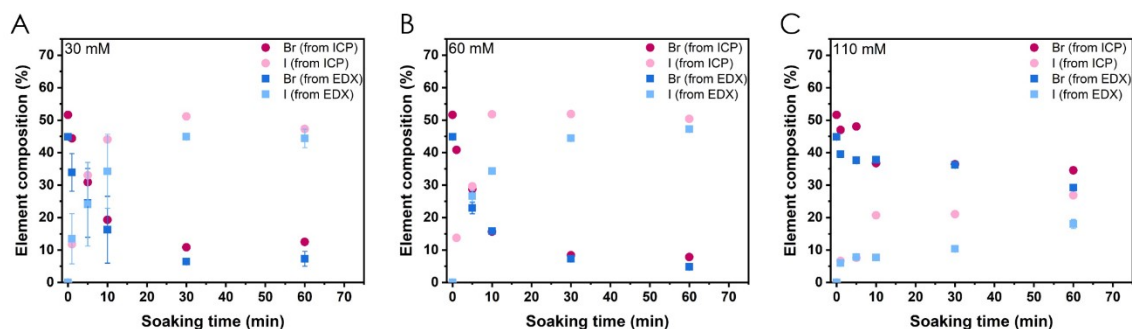
Figure S4. The elemental composition of the layers, determined with EDX and ICP-MS measurements. **A:** 30 mM, **B:** 60 mM and **C:** 110mM CsI/MeOH soaking solution.

By performing the soaking of the $Cs_3Cu_2Br_5$ layers in CsI both halide exchange and compositional changes occur, that alter the stoichiometry of the films. The determined composition from ICP-MS measurements **(Table S1-S3)** highlight the differences caused by the soaking solution (CsI/MeOH) concentrations. In the case of the most dilute soaking solution (30 mM CsI/MeOH) the original $Cs_3Cu_2Br_5$ film is gradually converted to the rod-like $CsCu_2X_3$ composition. This transition results in the change of the original Cs:Cu ratio to decrease from its original 1.41 (theoretical 1.50) to 0.46 (theoretical 0.5) as can be deduced from the ICP-MS results summarized in **Table S1**. As cesium-halides (e.g., CsBr, CsI) have better solubility than copper-halides in methanol, this process is realized through the loss of cesium from the films. As this process is also accompanied by the halide exchange the gradual incorporation of halide can also be observed in tandem with this process.

If the soaking solution concentration is increased to 60 mM, the mechanism of the exchange is changed. The rod like ($CsCu_2X_3$) morphology will appear as an intermediate phase and the original stoichiometry ($Cs_3Cu_2X_5$) will dominate after 10 min. This process can be also followed by the change of the Cs:Cu ratio of the films (ICP-MS results in **Table S2**). After a minimum at 10 minutes a recovery of the cesium content can be observed. This still falls short of the expected stoichiometry ($Cs_3Cu_2X_5$), however this signals that this later conversion is confined to the surface of the films. This process is accompanied by the halide exchange as well, signalled by the gradual exchange of the halides in the film.

At the most concentrated soaking solution with 110 mM CsI (saturated solution), no rod like morphology can be observed. Thus, the formation of $CsCu_2X_3$ intermediate phase will not alter the Cs:Cu ratio of the films (as corroborated by the ICP-MS results shown in **Table S3**). A slower ion-exchange can be observed in this case, which further confirms the confinement of the halide exchange to the surface of the films without the formation of the $CsCu_2X_3$ intermediate phase.

Cesium incorporated into the layers can be observed where the $CsCu_2X_3$ form is an intermediate phase (60mM soaking solution) or was not detected at all (110 mM soaking solution). In both cases an increase in the cesium content can be observed after 10 minutes of soaking. This might signal that some intermediate phase is also formed in the case of the 110 mM soaking solution, however it is confined to the outermost part of the layers. However, this was not observed from the other materials characterization techniques.

Table S1. Elemental composition of the soaked $Cs_3Cu_2Br_5$ films determined from ICP-MS measurements displayed in atomic percentages. 10 µm thick layers ($Cs_3Cu_2X_5$) were digested after soaking in 30 mM CsI/MeOH solution for different times.

Time (min)	Cu (%)	Br (%)	I (%)	Cs (%)
0	20.1	51.6	0.0	28.3
1	20.3	44.4	11.8	23.5
5	22.5	30.9	33.0	13.6
10	23.3	19.3	44.0	13.4
30	25.7	10.8	51.2	12.3
60	27.5	12.5	47.3	12.7

Table S2. Elemental composition of the soaked $Cs_3Cu_2Br_5$ films determined from ICP-MS measurements displayed in atomic percentages. 10 µm thick layers ($Cs_3Cu_2X_5$) were digested after soaking in 60 mM CsI/MeOH solution for different times.

Time (min)	Cu (%)	Br (%)	I (%)	Cs (%)
1	20.2	40.8	13.7	25.3
5	23.6	28.8	29.6	18.0
10	19.9	15.6	51.8	12.7
30	23.6	8.4	51.9	16.1
60	23.8	7.8	50.4	18.0

Table S3. Elemental composition of the soaked $Cs_3Cu_2Br_5$ films determined from ICP-MS measurements displayed in atomic percentages. 10 µm thick layers ($Cs_3Cu_2X_5$) were digested after soaking in 110 mM CsI/MeOH solution for different times.

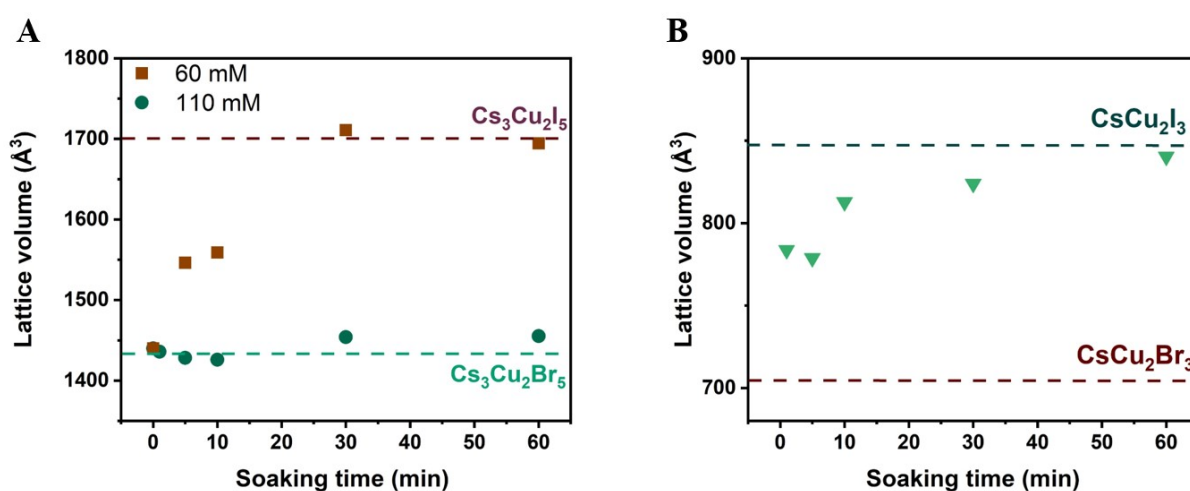| Time (min)	Cu (%)	Br (%)	I (%)	Cs (%)
1	20.1	47.0	6.7	26.2
5	20.2	48.1	7.6	24.1
10	20.6	36.8	20.7	21.9
30	17.5	36.4	21.0	25.1
60	15.8	34.6	26.9	22.8

Figure S5. The effect of the exchange solution concentration on the lattice volume in the case **A:** of 60 and 110 mM CsI/MeOH concentration and the unit cell is Pnma. **B:** of 30 mM CsI/MeOH concentration and Cmcm unit cell.

Table S4. Elemental composition of the soaked $Cs_3Cu_2Br_5$ films determined from EDX measurements displayed in atomic percentages. 10 µm thick layers ($Cs_3Cu_2X_5$) on glass substrates were used after soaking in 30 mM CsI/MeOH solution for different times. The layers were measured at three different places.

Time (min)	Cu (%)	Br (%)	I (%)	Cs (%)
1	25.0 ± 3.5	30.0 ± 1.0	18.0 ± 1.3	24.0 ± 1.5
5	29.0 ± 4.2	18.4 ± 0.1	31.5 ± 0.1	18.0 ± 0.1
10	30.0 ± 1.8	10.0 ± 0.3	40.8 ± 0.4	19.0 ± 2.9
30	31.0 ± 0.5	6.5 ± 0.5	45.0 ± 0.8	17.0 ± 0.2
60	30.0 ± 0.5	7.0 ± 2.3	44.0 ± 2.8	17.5 ± 0.2

Table S5. Elemental composition of the soaked $Cs_3Cu_2Br_5$ films determined from EDX measurements displayed in atomic percentages. 10 µm thick layers ($Cs_3Cu_2X_5$) on glass substrates were used after soaking in 60 mM CsI/MeOH solution for different times. The layers were measured at three different places.

Time (min)	Cu (%)	Br (%)	I (%)	Cs (%)
0	19.5 ± 0.1	44.8 ± 0.1	0.00 ± 0.0	35.6 ± 0.1
5	24.0 ± 2.2	23.0 ± 1.8	27.0 ± 1.7	27.0 ± 2.2
10	24.0 ± 1.3	15.8 ± 0.4	34.3 ± 0.1	26.0 ± 1.7
30	21.0 ± 1.4	7.3 ± 0.1	44.4 ± 0.3	27.0 ± 1.1
60	19.2 ± 0.5	4.8 ± 0.2	47.2 ± 0.7	28.8 ± 0.1

Table S6. Elemental composition of the soaked $Cs_3Cu_2Br_5$ films determined from EDX measurements displayed in atomic percentages. 10 µm thick layers ($Cs_3Cu_2X_5$) on glass substrates were used after soaking in 110 mM CsI/MeOH solution for different times. The layers were measured at three different places.

Time (min)	Cu (%)	Br (%)	I (%)	Cs (%)
1	19.9 ± 0.5	39.5 ± 1.1	6.0 ± 0.9	35.0 ± 0.4
5	21.3 ± 0.9	37.6 ± 0.8	8.0 ± 0.7	33.0 ± 0.9
10	20.0 ± 0.5	37.8 ± 0.5	8.0 ± 0.9	35.0 ± 0.4
30	19.4 ± 1.1	36.2 ± 0.9	10.0 ± 0.8	34.0 ± 1.2
60	19.0 ± 0.7	29.0 ± 1.0	18.0 ± 1.4	33.0 ± 1.5

Table S7 Layer mass before halide exchange and after halide exchange in 30 mM CsI/MeOH exchange solutions.

Time (min)	Mass Before soaking (mg)	After soaking (mg)
1	4.323	4.317
5	3.950	3.941
10	4.261	4.240
30	4.529	4.517
60	4.448	4.438

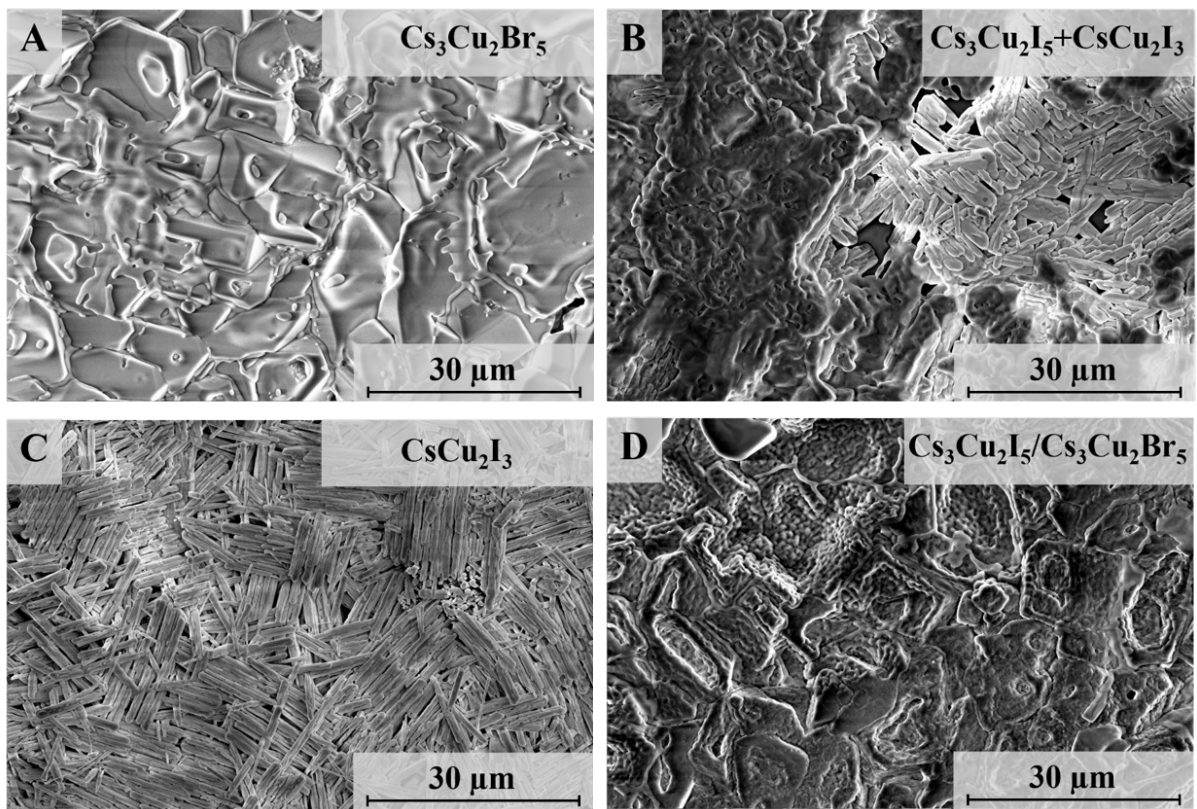**Figure S6.** Top-down SEM images of the different morphologies obtained by the soaking method. **A:** $Cs_3Cu_2Br_5$ starting material. **B:** after 10 min soaking in 60 mM CsI/MeOH. **C:** 10 min soaking in 30 mM CsI/MeOH **D:** 10 min in 110 mM CsI/MeOH.
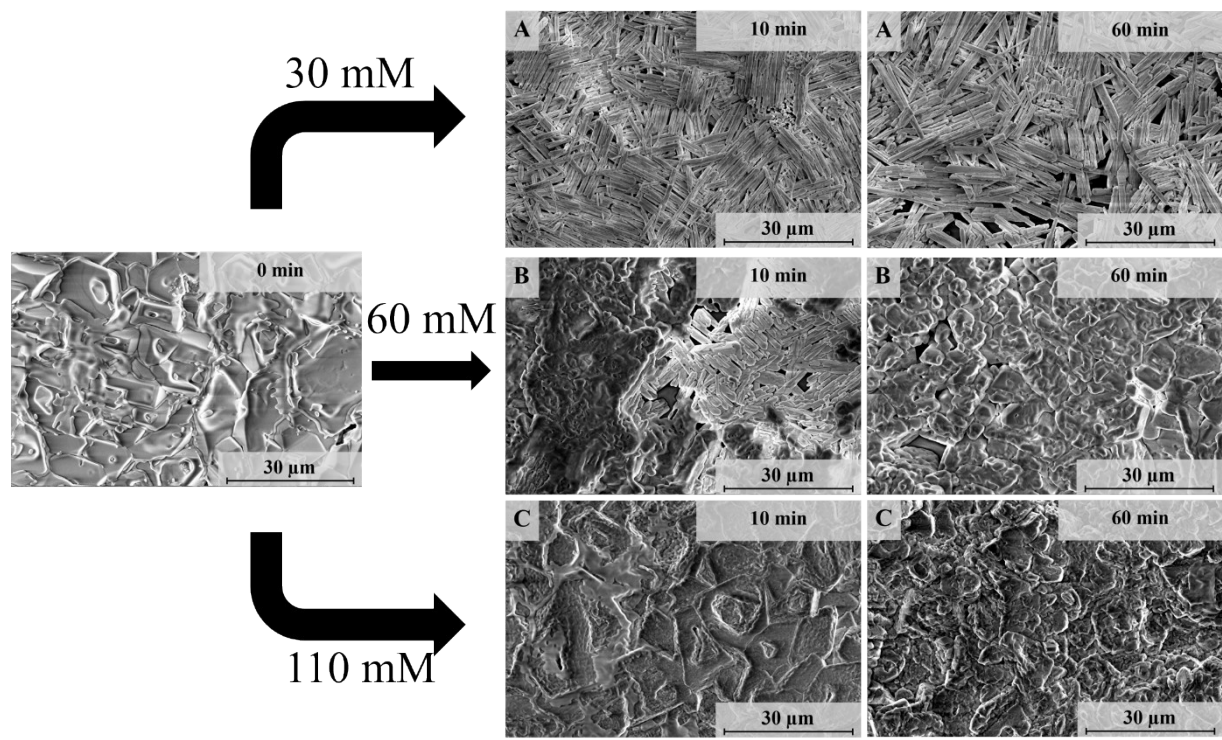
Figure S7. SEM images of the $Cs_3Cu_2Br_5$ starting material on glass substrate the layers after exchange with a) 30 mM b) 60 mM c)110 mM CsI/MeOH solution.
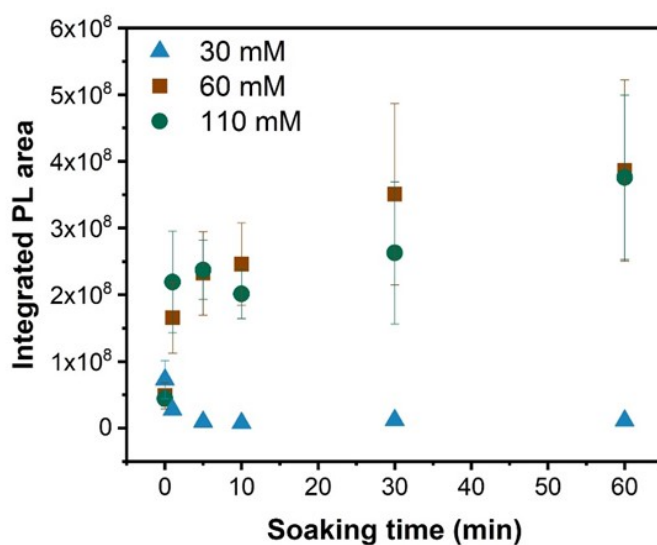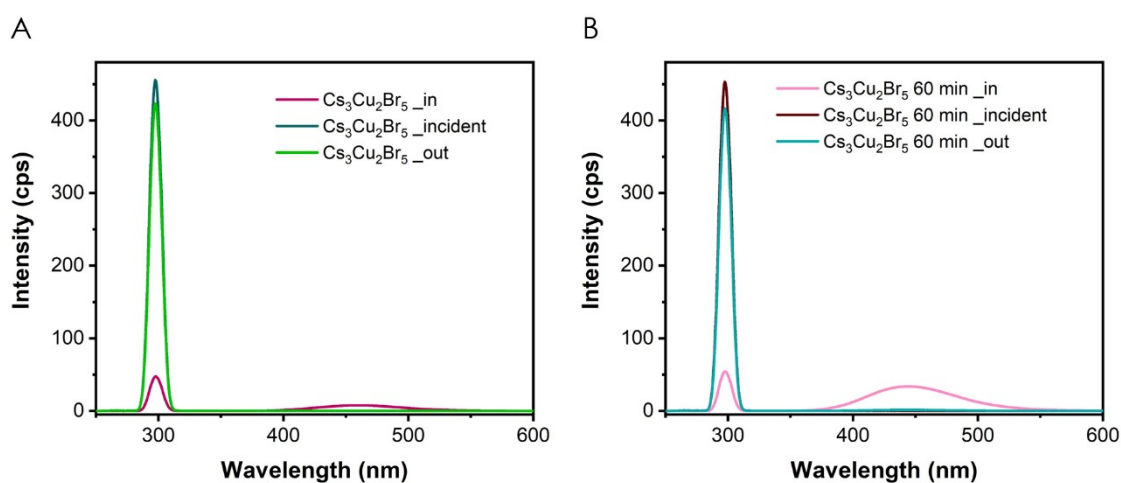

Figure S8. The integrated PL intensity of the layers after halide exchange. The excitation

wavelength is 290 nm.

Figure S9. Absolute PLQY determination of **A:** $Cs_3Cu_2Br_5$ and **B:** $Cs_3Cu_2Br_5$ sample after soaking in 60 mM CsI/MeOH solution for 60 min, with a nominal thickness of 10 μm. The excitation wavelength was 300 nm in both cases.

Three measurements were carried out for each sample: (i) the sphere itself without the sample, with the 290 nm excitation light (denoted as incident), (ii) the layer was placed in the sphere but out of the path of the incident beam (denoted as out), and (iii) the layer was placed in the sphere in the path of the incident beam (denoted as in). From these measurements we could calculate the PLQY% with **eq. 1.** Where, S_0 is the integrated peak area of incident light, S_1 is the number of unabsorbed photons, and S_2 is the area of the emission peak.

$$PLQY\% = \frac{Number\ of\ photons\ emitted\ by\ the\ sample}{Number\ of\ photons\ absorbed\ by\ the\ sample} * 100\% = \frac{S_2}{S_0 - S_1} * 100\% \quad (1)$$

Table S8. Fitting parameters of the PL decay curves in case of the starting material $Cs_3Cu_2Br_5$ and after soaking in 60 mM CsI/MeOH solution.

Time (min)	y0 (cps)	A1 (cps)	t1 (μs)	A2 (cps)	t2 (μs)	A3 (cps)	t3 (μs)
0	19.3 ± 0.8	800.0 ± 0.1	0.0251 ± 0.0006	127.0 ± 4.0	0.350 ± 0.017	156.2 ± 0.7	10.7 ± 0.2
1	11.4 ± 0.3	448.0 ± 7.0	0.0969 ± 0.0029	441.0 ± 5.0	0.713 ± 0.011	149.0 ± 2.0	5.4 ± 0.1
10	1.4 ± 0.1	141.0 ± 8.0	0.18 ± 0.02	758.0 ± 12.0	0.872 ± 0.019	59.0 ± 17.0	2.3 ± 0.3
30	2.6 ± 0.1	318.0 ± 6.0	0.138 ± 0.004	612.0 ± 5.0	0.775 ± 0.011	67.0 ± 4.0	3.2 ± 0.1
60	1.2 ± 0.1	387.0 ± 30	0.54 ± 0.02	584.0 ± 31.0	1.127 ± 0.020		

Table S9. Intensity and amplitude averaged lifetime of the soaked layers.

Time (min)	Intensity avereaged lifetime (us)	Amplitude avereaged lifetime (us)
0	10.31 ± 0.43	1.60 ± 0.03
1	3.93 ± 0.43	1.12 ± 0.02
10	1.09 ± 0.16	0.86 ± 0.05
30	1.45 ± 0.09	0.73 ± 0.02
60	0.99 ± 0.07	0.89 ± 0.06

Table S10. PLQY% measurements for the reference $Cs_3Cu_2Br_5$ film and the halide exchanged samples after 1 year of storage under ambient conditions.

Soaking solution	Soaking time	Internal Quantum Efficiency (%)	Internal Quantum Efficiency 1 year later (%)
None	-	13.7	13.8
30 mM	30 min	0.5	0.4
30 mM	60 min	1.0	1.8
60 mM	30 min	35.8	21.1
60 mM	60 min	64.6	56.0
110 mM	30 min	34.1	28.4
110 mM	60 min	37.3	24.1

References

1   B. H. Toby, R. B. Von Dreele, *J. Appl. Crystallogr.,* 2013, **46**, 544–549.