

Supporting Information for:

Superlattices are Greener on the Other Side: How Light Transforms Self-Assembled Mixed Halide Perovskite Nanocrystals

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1) Materials and Methods

Nanocrystal and Nanocrystal Superlattice Preparation.

Materials. 1-octadecene (ODE, 90%, Sigma-Aldrich), oleic acid (OA, 90%, Sigma-Aldrich), oleylamine (Oam, 70%, Sigma-Aldrich), toluene (99.8% anhydrous, Sigma-Aldrich), hexanes (99% anhydrous, Sigma-Aldrich), tetrachloroethylene (TCE, $\geq 99\%$, Sigma-Aldrich) Cs_2CO_3 (99%, Sigma-Aldrich), PbBr_2 ($\geq 98\%$, Sigma-Aldrich), PbI_2 ($\geq 99.999\%$, trace metal basis, Sigma-Aldrich). All chemicals were used as purchased.

Safety note: lead halides (PbBr_2 and PbI_2) are photosensitive lead poisoning hazards and must be handled and contained inside a glovebox or a fume hood with protection from visible light.

CsPbX₃ (X=Br, I) Nanocrystal Synthesis. CsPbBr_3 and CsPbI_3 NCs were made by a direct synthesis using modified literature methods.¹⁻⁴ Syntheses were performed in 20 mL scintillation vials with an aluminum heating blocks on a hot plate. CsPbBr_3 [CsPbI_3] NCs precursor solutions consisted of 0.072 g PbBr_2 , 5 mL ODE, 500 μL Oam, and 50 μL of OA [0.090 g PbI_2 in 5 mL ODE, 500 μL Oam and 500 μL of OA]. Cs-oleate was produced by dissolving Cs_2CO_3 (0.407 g) in 1.75 mL OA and 15 mL ODE at 120 °C under nitrogen flux for 2 hours. CsPbX_3 precursor solutions were stirred at 120 °C until PbX_2 salts dissolved (~10 minutes), forming transparent clear (X=Br) or yellow (X=I) solutions. Following complete dissolution, the temperature was increased to ~167 °C. Then, the reaction vial was removed from the hot plate and suspended in the air under stirring. The temperature was allowed to cool 157-159 °C at which point 500 μL of Cs-oleate (pre-heated to ~100 °C) was rapidly injected. Upon injection, CsPbX_3 precursor solutions immediately form turbid green/yellow (X=Br) or red/brown (X=I) suspensions, which were allowed to cool to room temperature in air with stirring.

CsPbBr₃ Isolation for Self-Assembly and Halide Exchange. After cooling, CsPbBr_3 NCs were collected by centrifuging the suspension (5000 rpm, 5 mins), decanting the supernatant, and collecting the precipitate. CsPbBr_3 NCs to be used in halide exchange were dispersed in 5 mL of hexanes or toluene (see **Figure S4**), whereas CsPbBr_3 NCs to be used for CsPbBr_3 SL growth were dispersed in 200 μL of TCE.

CsPbI₃ Isolation for Self-Assembly. CsPbI_3 NCs were collected as follows. First, the suspensions were centrifuged (5000 rpm, 5 minutes), and the supernatant was collected. Then, ethyl acetate (5 mL) was added to the supernatant, followed by centrifugation (5000 rpm, 5 minutes). The precipitate was dissolved in 250 μL of toluene and was used for self-assembly.

Halide Exchange: CsPbBr₃ to CsPb(I_{1-x}Br_x)₃. $\text{CsPb(I}_{1-x}\text{Br}_x)_3$ NCs were synthesized via a previously reported halide exchange methodology as opposed to direct synthesis in order to better control $\text{CsPb(I}_{1-x}\text{Br}_x)_3$ NC size distributions.^{3,4} Briefly, PbI_2 (0.500 g) was added to the 5 mL CsPbBr_3 NC dispersions in hexanes or toluene prepared as previously described. These mixtures were vigorously stirred for 48 to 192 hours (see **Figure S4**). Exchange rates (monitored via the PL redshift) appear to depend on the initial concentration (lower concentration leads to faster exchange) and solvent (toluene is nearly 2 \times as fast as hexanes for the same concentration of NCs)

of CsPbBr₃ NCs. **Figure S4** provides before/after absorption along with details (e.g., solvent and exchange time) for the exchange reaction of each SL sample.

CsPb(I_{1-x}Br_x)₃ NCs Isolation for Self-Assembly. Once the desired x-value CsPb(I_{1-x}Br_x)₃ NCs were obtained, the PbI₂ was separated by centrifugation and subsequent filtration through PTFE syringe filters (Sartorius, 0.2 μm pore size). The toluene/hexane was then bubbled off under N₂ flux. The CsPb(I_{1-x}Br_x)₃ NCs were then re-dispersed in 250 μL of TCE (x>0.4) or toluene (x<0.4) to be used for self-assembly. To assess the concentration of the solution used in self-assembly, 40 μL of this solution was then added to 3960 μL of toluene, and absorption spectra were acquired. Optical densities near the band edge ranged from ~0.02 to 0.1.

Self-Assembly of CsPb(I_{1-x}Br_x)₃ (0<x<1.00) Superlattices. Prior to self-assembly, all the NC solutions were filtered through PTFE syringe filters (Sartorius, Minisart[®], 0.2 μm pore size). The solutions were diluted 2× to 5× depending on their initial concentration for the compact NC SL films (for XRD measurements). Solutions were diluted up to 10× for sparse NC SL films (for confocal microscopy). Then, 30 μL aliquots were drop-cast onto 1×1 cm Si substrates (Ted Pella, Inc., 1×1 cm diced Si Wafer, 55 chips/wafer, <100> orientation). Si substrates were enclosed between two glass Petri dishes. The solvent was allowed to slowly evaporate in air (~12 hours x>0.4 [solvent=TCE] and ~6 hours for x<0.4 [solvent=toluene]), after which Si substrates were dried under vacuum to remove excess solvent. The NC SLs samples were stored under vacuum and used for further analysis. We note that solutions can be used for self-assembly for up to two weeks after their isolation, provided that the solution is re-filtered prior to each NC SL sample growth.

Transmission Electron Microscopy (TEM). TEM samples for NC size evaluation were prepared by drop-casting a dilute solution of NCs onto a carbon-coated copper grid (Ted Pella) on top of a paper tissue. TEM samples of SLs were prepared by drop-casting 3 μL of the self-assembly stock solution onto a carbon-coated copper grid. Images were collected with either JEM 1400 Plus JEOL (for NCs) or FEI Titan (for NC SLs) electron microscopes. TEM images were processed using Digital Micrograph[™] and ImageJ software.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). SEM images and EDS spectra of mixed halide NC SLs were acquired using a JEOL 6490LA electron microscope at 25 kV (SEM, EDS) or 15 kV (SEM) accelerating voltages. Collected EDS spectra were analyzed using Analysis Station software ver. 3.8.0.59 (JEOL Engineering Co., Ltd), JED Series AnalysisProgram ver. 3.8.0.37. Quantification of the halide ratio in the EDS spectra was performed via a built-in standardless ZAF quantification method using Cs L, Pb L, Br K, and I L lines.

Ensemble CsPb(I_{1-x}Br_x)₃ NC Absorbance and Photoluminescence (PL). Absorbance and PL spectra of diluted CsPb(I_{1-x}Br_x)₃ NC solutions were recorded in toluene using a Cary 300 spectrophotometer and Cary Eclipse spectrofluorimeter, respectively. The spectra were measured in 10x4 mm quartz cuvettes (Hellma Analytics, 114F) on freshly diluted samples. The excitation wavelength for PL measurements was 400 nm in all cases, with 2.5-5 nm excitation and emission

slit widths. Reported PL spectra in units of eV were obtained by converting the wavelength scale to energy using appropriate fundamental constants and by multiplying each intensity by λ^2 .

Photostability tests of NCs in solution and SLs. The photostability experiments were performed using a fiber-coupled 385 nm LED (Thorlabs, M385FP1) or 470 nm LED (Thorlabs M470L2). The series of PL spectra for *in situ* measurements were collected using a fiber spectrometer (AvaSpec-2048-USB2-UA) equipped with an optical fiber (Thorlabs, M28L01, 400 μm , 0.39NA, TP01465305, 400-2200 nm wavelength range). The incident power was measured using a Thorlabs PM100D power meter equipped with a Thorlabs S120VC sensor. The area of the illuminated spot on the samples was estimated by measuring the diameter of the spot (typically a circle) with a ruler (e.g., by placing a piece of fluorescent paper at the sample position and noting the dimensions of the illuminated spot). A 405 nm CW diode laser was used for experiments described in **Figure 5** main text and **Figure S16**.

Confocal laser scanning microscopy (CLSM). CLSM of mixed halide NC SLs grown on Si substrates was performed using a Nikon A1 CLSM equipped with a Plan Apo 40x DIC M N2 objective (NA = 0.6) and CW 405 nm laser source (solid-state laser, Coherent, 1170506) with a maximum power of ~ 88 mW (100%) at the sample. The imaging of isolated NC SLs (**Figure 2b-e** insets, **Figure 4a** in the main text, and **Figure S6**) was performed at 1% incident laser power and the fastest scan rate (scan area $\sim 14.3 \mu\text{m} \times \sim 14.3 \mu\text{m}$, scan size 512 x 512 pixels, acquisition speed 1 frame per second, $\sim 2.2 \mu\text{s}$ dwell time per pixel) to minimize photoinduced changes. The sequence of brief, intense laser exposures (“rounds”) discussed in the main text (**Figure 4**, **Movie S1**) was carried out using 100% incident laser power and a medium scan rate (1 round = 10 consecutive frames with the following settings per frame: scan area $\sim 14.3 \mu\text{m} \times \sim 14.3 \mu\text{m}$, scan size 512 x 512 pixels, acquisition speed 0.25 frames per second, $\sim 12.1 \mu\text{s}$ dwell time per pixel). The spectral information was captured with a 32-channel detector covering 470-660 nm spectral range. Control experiments with a spectral range extending to ~ 740 nm were performed to check for the presence/formation of photoproducts with a deep red emission (e.g., pure CsPbI₃), and those were not observed in any of the studied mixed halide compositions. The spectrally resolved imaging data were acquired using Nikon NIS-Elements High Content Analysis ver. 4.30.02 and stored as *.nd2 files. To view, process, obtain “true” color (RGB) images of the SLs, and to extract the spectral data, the *.nd2 files were processed using a combination of Nikon NIS-Elements Viewer ver. 4.20.00 and ImageJ ver.1.51j8⁵ (upgraded with a Nikon ND2 Reader plugin)⁶ software.

θ :2 θ X-Ray Diffraction. Static XRD patterns were acquired with a PANalytical Empyrean X-ray diffractometer equipped with a 1.8kW CuK α ceramic X-ray tube, PIXcel^{3D} 2 \times 2 area detector and operating at 45 kV and 40 mA. All diffraction patterns were collected in the air at room temperature. The *in situ* XRD patterns were recorded on a Rigaku SmartLab X-ray diffractometer equipped with a 9 kW CuK α rotating anode and a five-axis goniometer, operating at 40 kV and 150 mA. All XRD patterns were collected over the angular range of 1 $^\circ$ to 40 $^\circ$ 2 θ . The total X-Ray exposure time for each pattern was ~ 10 minutes. An initial SL θ :2 θ pattern was collected prior to illumination. Then, subsequent XRD patterns were collected every three hours for 21 hours under CW illumination from a fiber-coupled 385 nm LED ($I_{\text{exc}} = 75 \text{ mW cm}^{-2}$) to monitor shifting of the Bragg reflections. Then, the diode was turned off, and the sample was

allowed to rest in the dark. A final XRD pattern was acquired after 20 hours in the dark to monitor potential recovery.

Potato Starch-Potassium Iodide Indicator Test.

Materials: potassium iodide (puriss., Sigma-Aldrich, cat. no. 30315, Lot SZBA2220), starch from potato (Sigma-Aldrich, cat. no. S2004-500G, Lot BCBN5836V), iodine (ACS reagent, $\geq 99.8\%$, Sigma-Aldrich, cat. no. 207772-100G).

Safety note: Iodine (I_2) and its vapors are toxic oxidizing agents, which cause burns by all exposure routes and may cause an allergic reaction. All operations with I_2 or its sources must be carried out in a well-ventilated fume hood using personal protective equipment.

Control Test. The qualitative test for iodine (I_2) evolution from mixed halide NCs used for SLs was performed using a potassium iodide (KI) and starch test.⁷ Specifically, small pieces cut out of a paper tissue (Kimtech Kimwipes, Kimberly-Clark), roughly ~ 2 cm by ~ 2 cm, were individually wet with a 10 μ L drop of the colorless aqueous suspension of potato starch and KI (40 mg of KI, 40 mg of potato starch, dissolved in 1 ml of deionized water) and left to dry, producing an I_2 indicator paper (**Figure S15a**). The performance of the paper was tested by placing one piece in a closed vial next to the small piece of pure I_2 (**Figure S15b**). Immediately after placing the indicator paper, it started to turn dark – indicating a reaction of I_2 vapors with KI/starch and formation of I_3^- /starch complex known for its deep color (brown in **Figure S15c,d**).⁷ The reaction was accelerated by a gentle heating of the vial, which led to an increase in the I_2 vapor pressure and further darkening of the indicator paper (**Figure S15c**). For comparison, the non-reacted paper and a paper exposed to I_2 vapor are shown side by side in **Figure S15d**.

Test on illuminated mixed halide NC SLs. A piece of Si wafer covered with a thick film of $CsPb(I_{0.64}Br_{0.36})_3$ NC SLs was placed in a quartz cuvette with a piece of KI/starch paper immediately above the Si wafer (**Figure S16a**). The cuvette was closed with an air-tight cap, and the NC SLs sample was illuminated with a focused blue LED source ($\lambda_{exc}=470$ nm; $I_{exc}\sim 100$ mW cm^{-2}) for 20 hours. The KI/starch paper slowly acquired a yellow color (**Figure S16b,c**) indicative of the I_3^- /starch complex formation because of I_2 evolution.

2) Supplemental Figures and Table

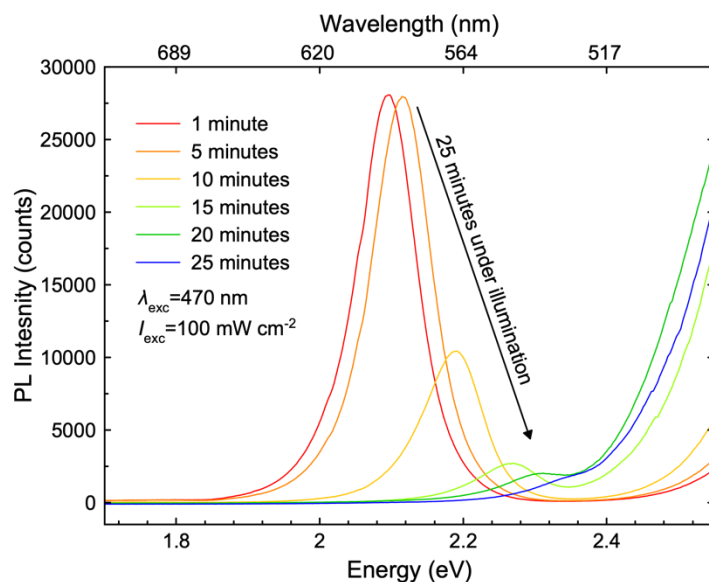


Figure S1. PL spectra of $\text{CsPb}(\text{I}_{0.64}\text{Br}_{0.36})_3$ NCs in toluene during 25 minutes of CW illumination (LED source, $\lambda_{\text{exc}}=470$ nm; $I_{\text{exc}}=100$ mW cm^{-2}). Spectra shown in 5 minutes increments.

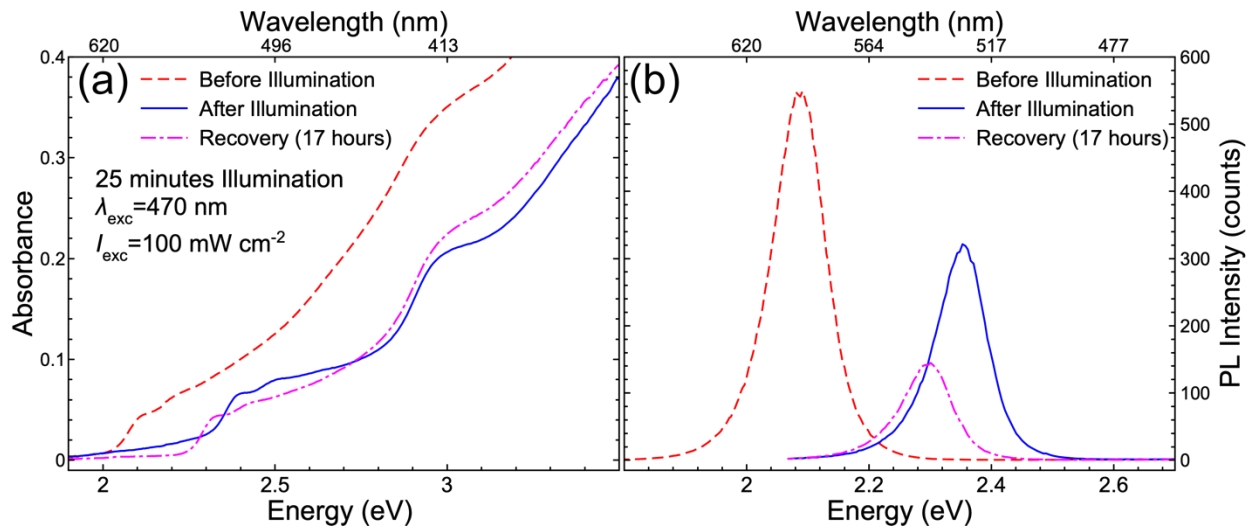


Figure S2. (a) Absorption and (b) PL spectra of $\text{CsPb}(\text{I}_{0.64}\text{Br}_{0.36})_3$ NCs in toluene before (dashed red lines) and after (solid blue lines) 25 minutes of CW illumination (LED source, $\lambda_{\text{exc}}=470$ nm; $I_{\text{exc}}=100$ mW cm^{-2}). Dashed-dotted magenta lines in (a, b) were acquired after the NC ensemble was stored in the dark for 17 hours.

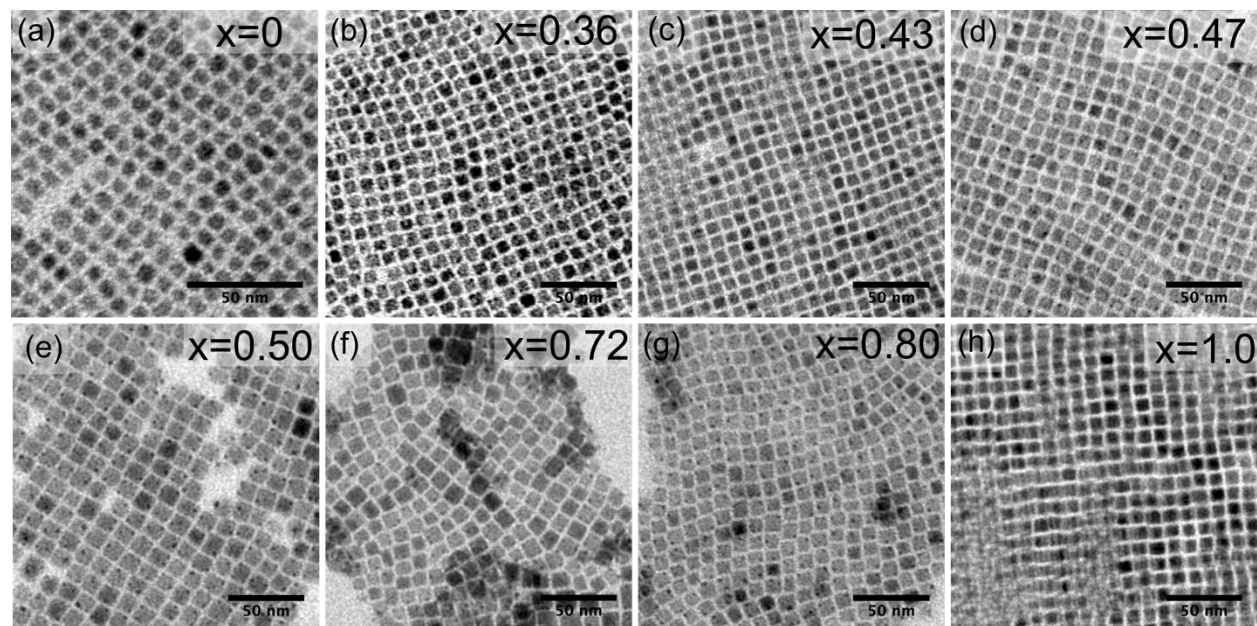


Figure S3. Representative transmission electron microscopy images (TEM) of all mixed halide NCs used in the NC SL growth [(a) $x=0.00$, (b) $x=0.36$, (c) $x=0.43$, (d) $x=0.47$, (e) $x=0.50$, (f) $x=0.72$, (g) $x=0.80$ and (h) $x=1.00$]. Scale bars are 50 nm.

Table 1. SEM-EDS, TEM, Absorption, Emission and XRD data for $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ ensemble NCs and NC SLs.

x^*	Avg. NC Edge Length, l (nm)**	NC Size-Distribution (nm)**	NC $E_{\text{PL,Max}}$ (eV)	NC PL FWHM (meV)	NC E_{g} (eV)	SL $E_{\text{PL,Max}}$ (eV)	Single SL PL FWHM (meV)	SL (200) Bragg Angle 2θ ($^\circ$)	SL Periodicity, Λ (nm)
0	9.5	2.4	1.82	101	1.86	1.84	120	28.77	11.9
0.36	8.7	0.9	2.04	101	2.09	2.01	107	29.37	10.7
0.43	8.5	0.9	2.08	113	2.11	2.10	109	29.60	10.2
0.47	9.2	1.0	2.09	112	2.12	2.11	113	29.84	11.4
0.50	11.6	1.6	2.11	97	2.16	2.10	120	29.74	13.7
0.72	10.4	1.1	2.24	90	2.28	2.25	109	30.02	12.9
0.80	9.6	0.9	2.29	88	2.36	2.32	133	30.24	12.3
1.00	9.3	0.5	2.42	85	2.46	2.41	95	30.48	11.2

* x quantified by SEM-EDS on compact NC SL films. ** l and size-distributions quantified from TEM imaging.

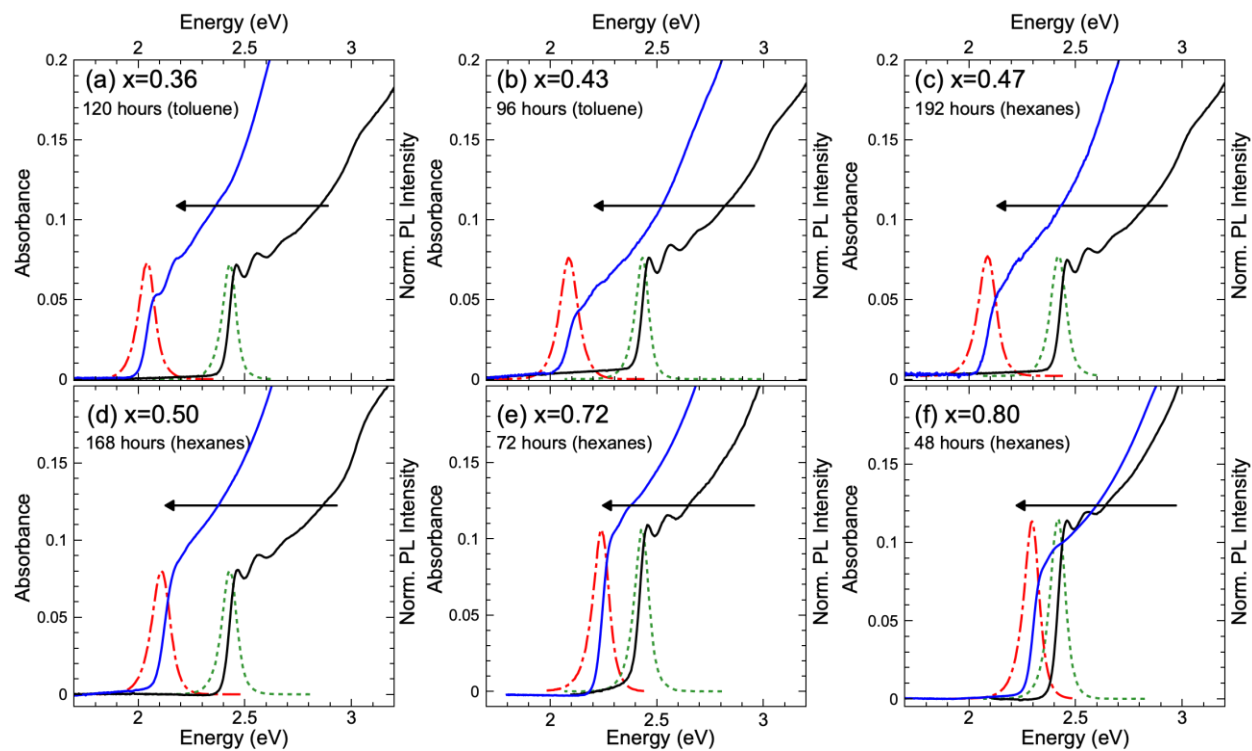


Figure S4. Absorption (solid blue lines) and emission (dashed-dotted red lines) spectra in toluene of the six mixed halide NC solutions employed in self-assembly [(a) $x=0.36$, (b) $x=0.43$, (c) $x=0.47$, (d) $x=0.50$, (e) $x=0.72$ and (f) $x=0.80$]. Given adjacent to each mixed halide NC ensembles in each panel are absorption (solid black lines) and emission (dashed green lines) spectra of the corresponding parent CsPbBr₃ NC ensembles (i.e., before anion exchange). The time and solvents used in the halide exchange reactions are provided within each panel.

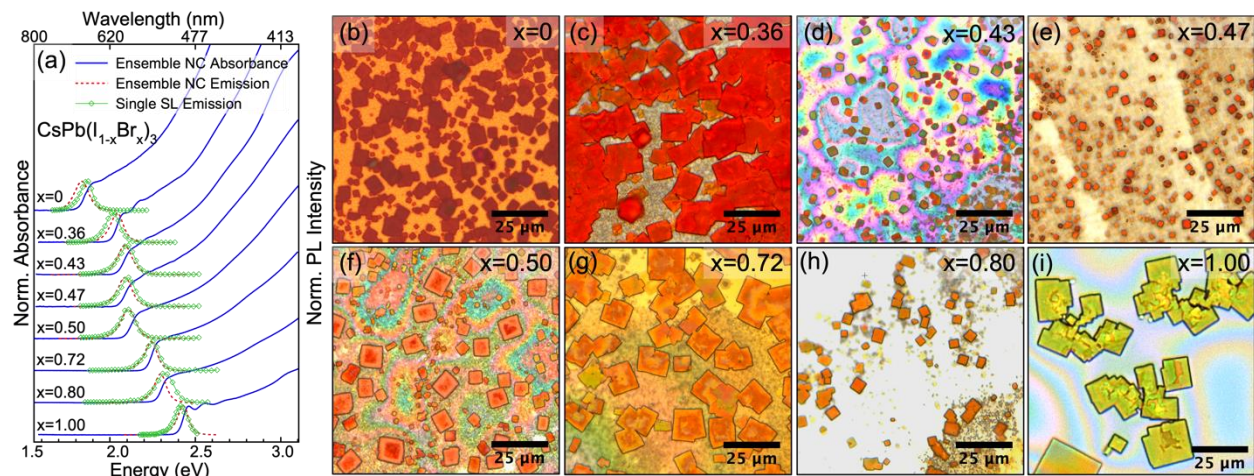


Figure S5. (a) Absorption (solid blue lines) and emission (dashed red lines) of ensemble $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ ($0 < x < 1.00$) NC dispersions in toluene. Corresponding single SL emission spectra represented by open green diamonds/solid lines. SEM-EDS determined x values given adjacent to each set of spectra. All emission spectra are normalized to 1.0 at their peak maxima. Absorption spectra are normalized to 1.0 at their band edge energies, which are reported in **Table S1**. Optical densities for absorption spectra in (a) are reported in **Figure S4**. Spectra offset for clarity. Optical microscopy images of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ SLs for $x=0$ (b), $x=0.36$ (c), $x=0.43$ (d), $x=0.47$ (e), $x=0.50$ (f), $x=0.72$ (g), $x=0.80$ (h) and $x=1.00$ (i).

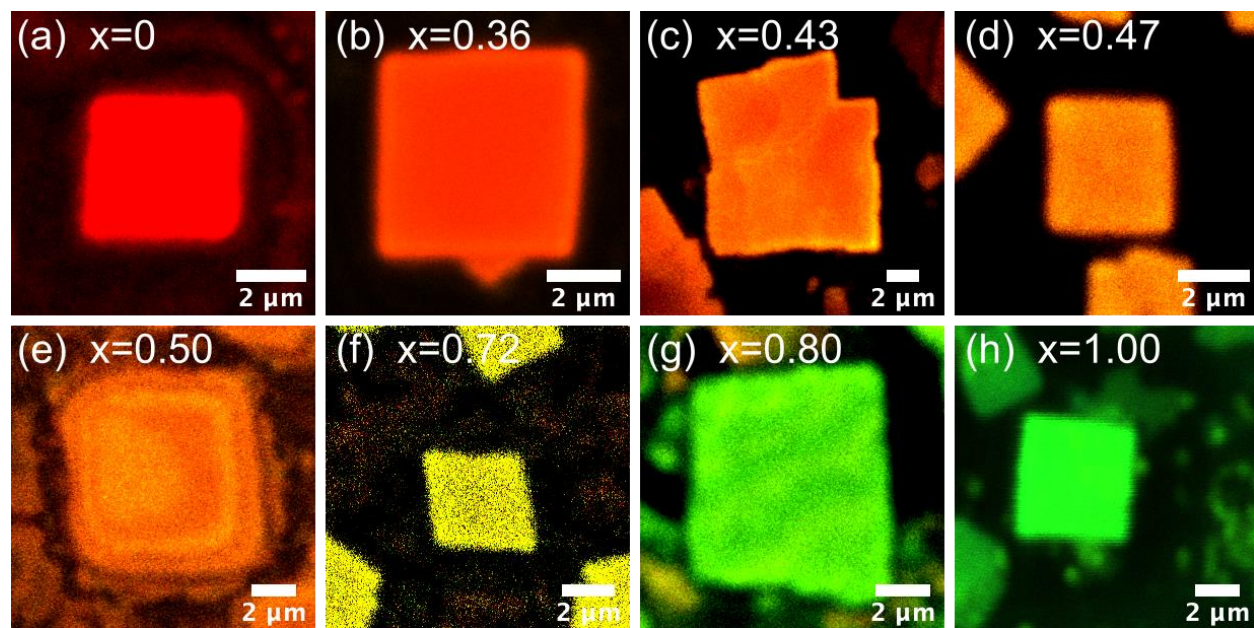


Figure S6. Spatially-resolved PL maps of individual $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ NC SLs [(a) $x=0.00$, (b) $x=0.36$, (c) $x=0.43$, (d) $x=0.47$, (e) $x=0.50$, (f) $x=0.72$, (g) $x=0.80$ and (h) $x=1.00$].

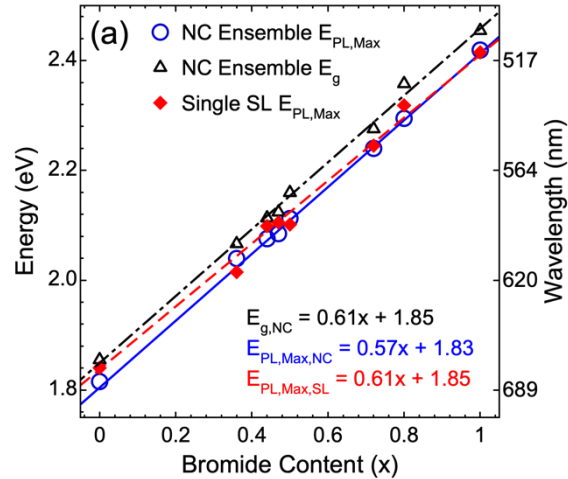


Figure S7. Calibration curves based on E_g and $E_{PL,Max}$ for $CsPb(I_{1-x}Br_x)_3$ NC solutions (dashed-dotted black line/triangles and solid blue line/circles) and single $CsPb(I_{1-x}Br_x)_3$ NC SLs (dashed red line and diamonds). Equations from linear fits to data provided within.

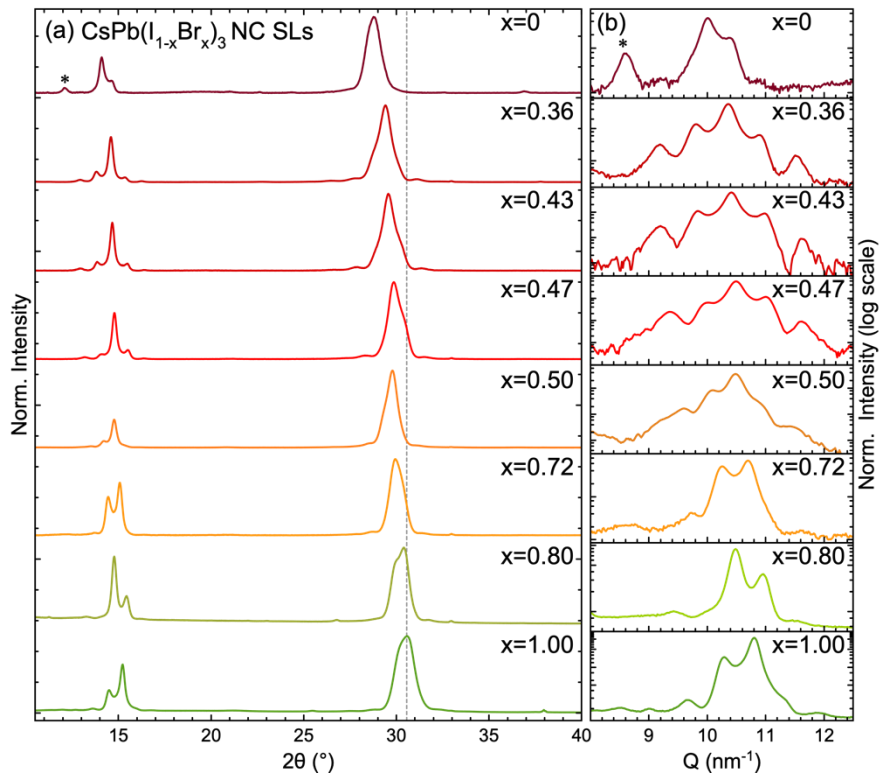


Figure S8. (a) $\theta:2\theta$ XRD patterns of compact $CsPb(I_{1-x}Br_x)_3$ NC SL films. Corresponding x -values are given adjacent to each pattern. Dashed grey line indicates the approximate (200) peaks position for the $x=1.00$ NC SLs. Patterns are vertically offset for clarity. (b) Zoomed-in view of the $\sim 15^\circ$ 2θ ($CuK\alpha$) peaks in (a), which are replotted in logarithmic intensity scales versus scattering vectors ($Q=[4\pi/\lambda_{Cu}]\sin[\theta]$). Related x -values are given within each panel. Asterisks in the $x=0$ patterns indicate peaks originating from Cs_4PbI_6 NC impurities.

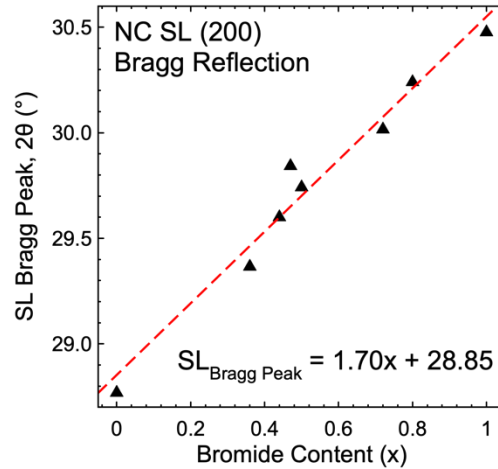


Figure S9. Composition calibration curves based on the (200) pseudocubic peaks positions of $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ NC SLs XRD patterns. Equation from linear fit (dashed red line) to the data is provided within.

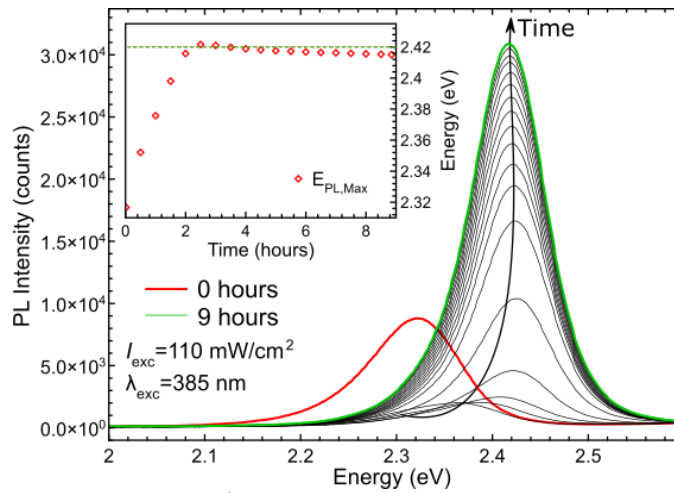


Figure S10. Time-evolved emission spectra in $1/2$ -hour segments (light grey lines) of an $\text{CsPb}(\text{I}_{0.28}\text{Br}_{0.72})_3$ NC SL film over 9 hours of CW illumination ($\lambda_{\text{exc}}=385$ nm, $I_{\text{exc}}=110$ mW cm^{-2}). Initial spectra in red and final spectra in green. Inset: $E_{\text{PL,Max}}$ versus time. The dashed green line represents the emission energy of a single CsPbBr_3 SL ($x=1.00$).

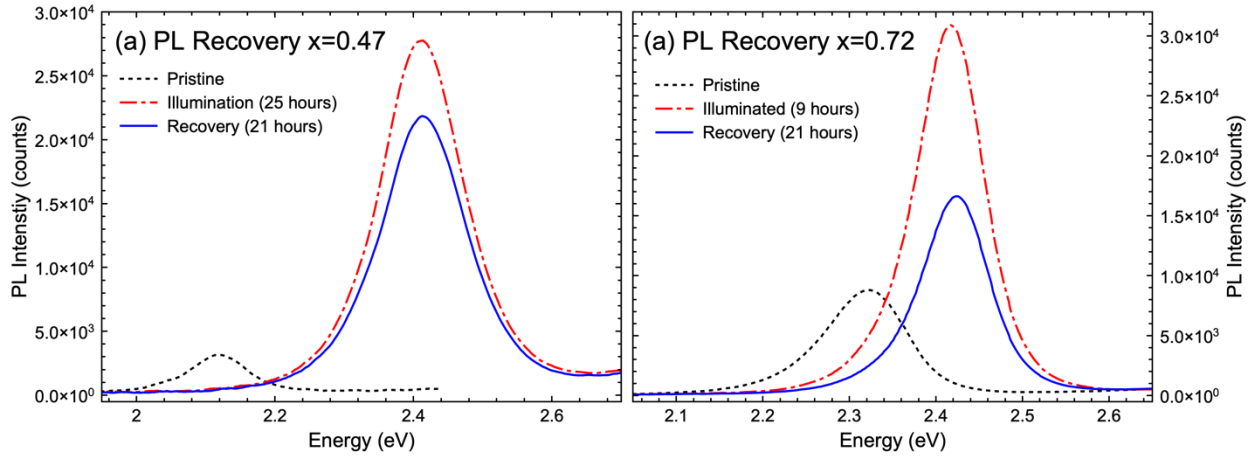


Figure S11. PL spectra of (a) $x=0.47$ and (b) $x=0.72$ $\text{CsPb}(\text{I}_{1-x}\text{Br}_x)_3$ NC SL films before (dashed black lines) and after (dashed-dotted red lines) prolonged CW illumination ($\lambda_{\text{exc}}=385$ nm, $I_{\text{exc}}=110$ mW cm^{-2}). Solid blue lines plot PL spectra of the illuminated NC SL films after 21 hours of recovery in the dark.

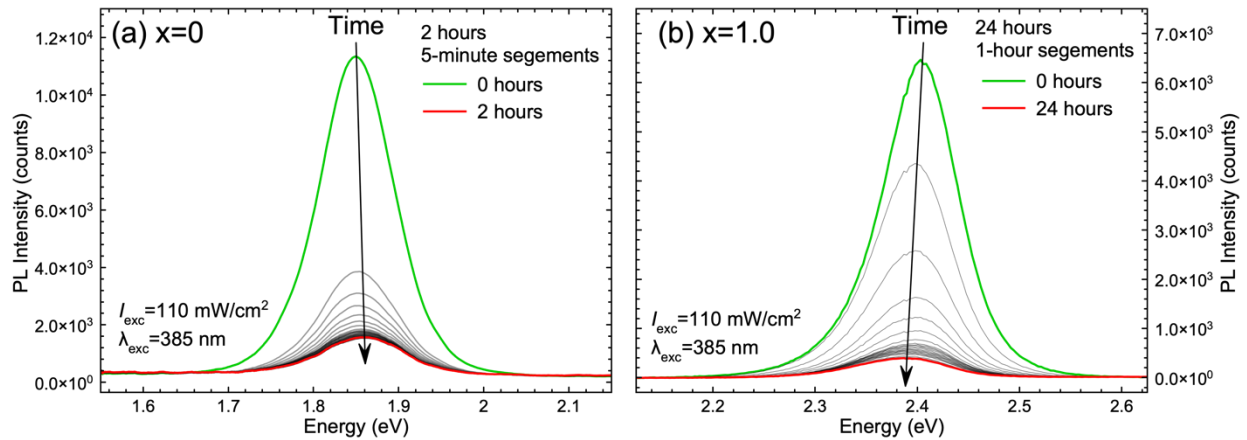


Figure S12. Time-evolved emission spectra of (a) CsPbI_3 and (b) CsPbBr_3 NC SL films during CW illumination ($\lambda_{\text{exc}}=385$ nm, $I_{\text{exc}}=110$ mW cm^{-2}).

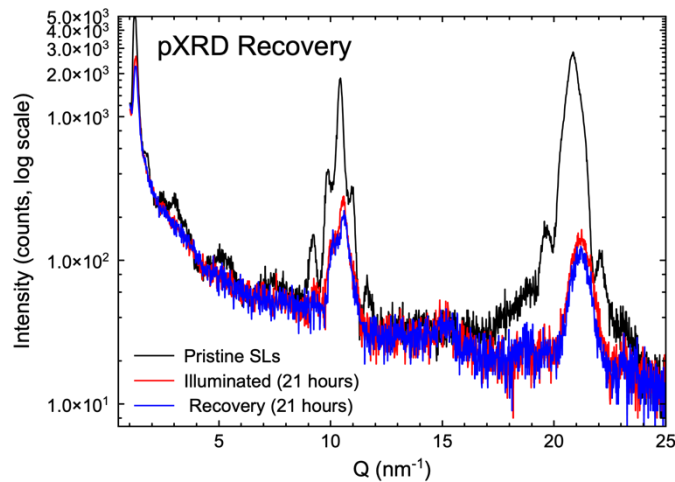


Figure S13. XRD patterns of $\text{CsPb}(\text{I}_{0.53}\text{Br}_{0.47})_3$ NC SL film before (black line) and after (red line) prolonged CW illumination ($\lambda_{\text{exc}}=385$ nm, $I_{\text{exc}}=110$ mW cm^{-2}). XRD patterns after 21 hours in the dark of the same NC SL film (blue line).

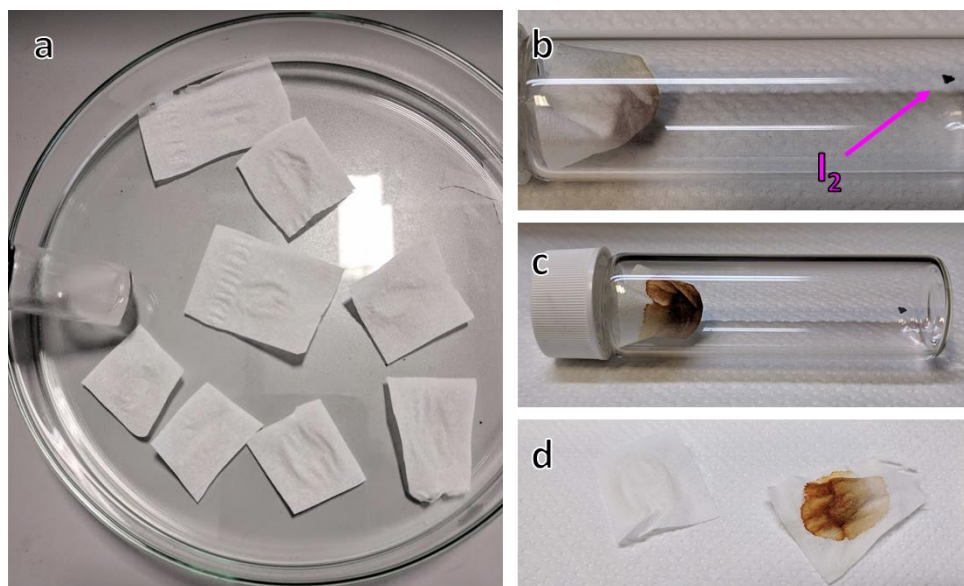


Figure S14. KI/starch indicator paper test for I_2 . (a) A Petri dish with eight pieces of paper tissue each drying 10 μ L of the KI/starch aqueous suspension (40 mg/ml of each component in water, the vial with the suspension is visible on the left); (b) a photograph capturing the color change of dried KI/starch paper after it was placed in the vicinity of a small piece of I_2 in a closed vial; (c) the same setup as in (b), but after gentle heating of the right side of the vial where a piece of I_2 is located; (d) non-reacted and reacted pieces of KI/starch indicator paper are shown side by side for comparison.

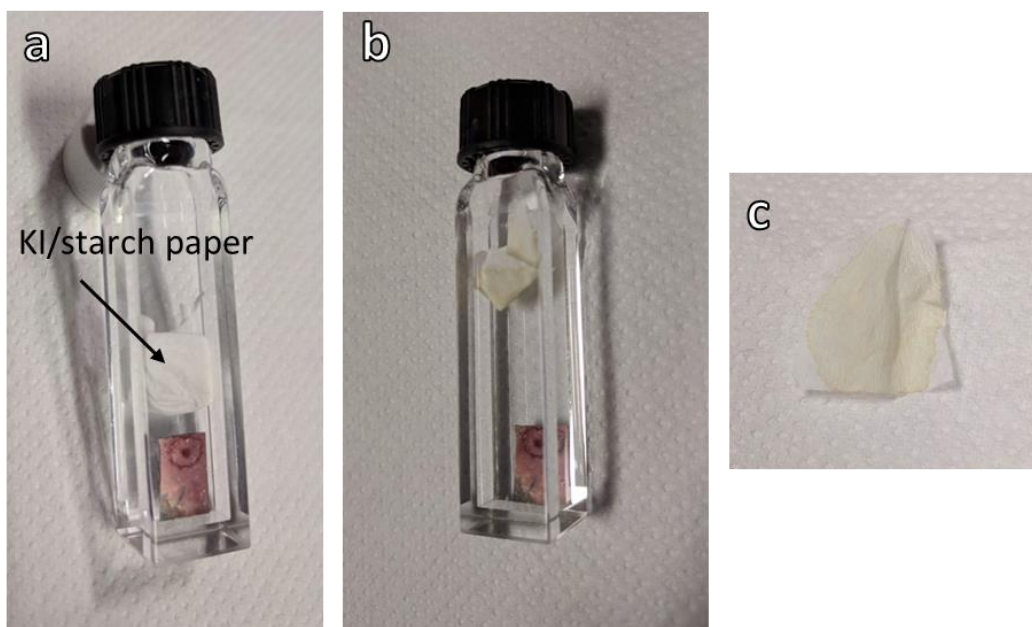


Figure S15. KI/starch test on a thick film of $CsPb(I_{0.64}Br_{0.36})_3$ NC SLs ~ 20 hrs of illumination ($\lambda_{exc}=470$ nm; $I_{exc}=mW\ cm^{-2}$): (a) cuvette with a SL sample and a starch paper before the test; (b) after the test; (c) KI/starch paper turned light yellow as a result of reaction with sublimated I_2 expressed by the sample under the light.

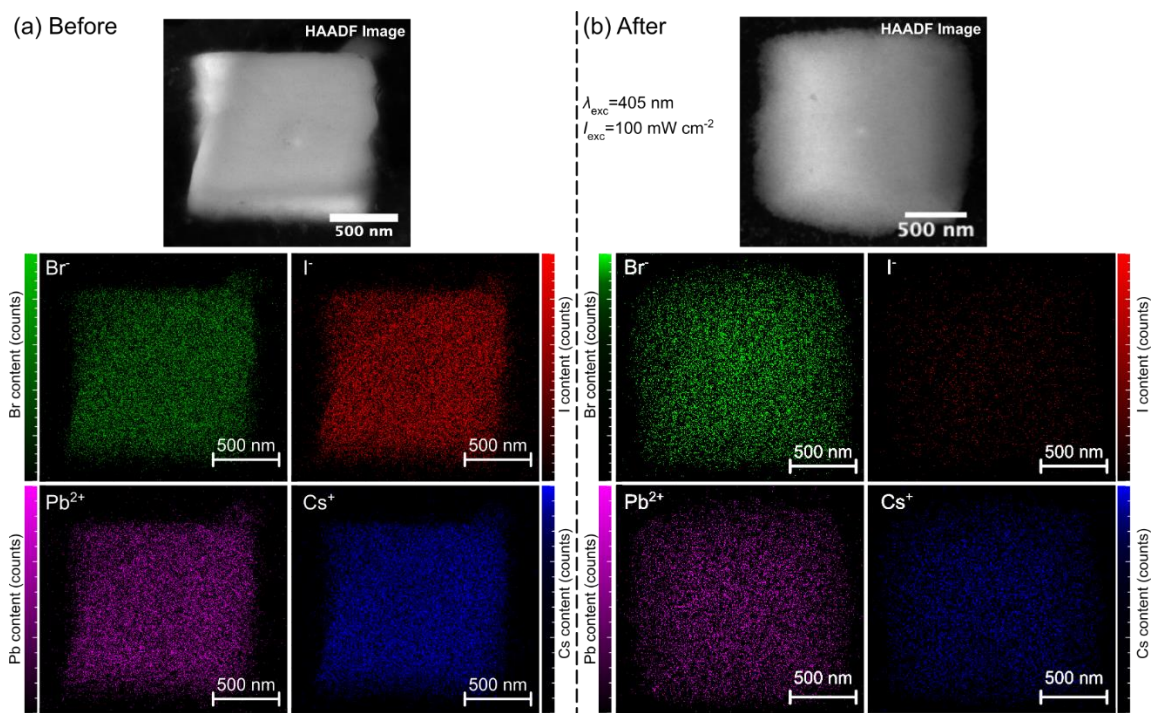


Figure S16. HAADF images (top row) and TEM-EDS maps (middle and bottom rows) for Br⁻, I⁻, Pb²⁺, and Cs⁺ elemental distribution of two different CsPb(I_{0.50}Br_{0.50})₃ NC SLs collected from the same TEM grid (a) before and (b) after illumination ($\lambda_{exc}=405$; $I_{exc}=100$ mW cm⁻², ~24 hours).

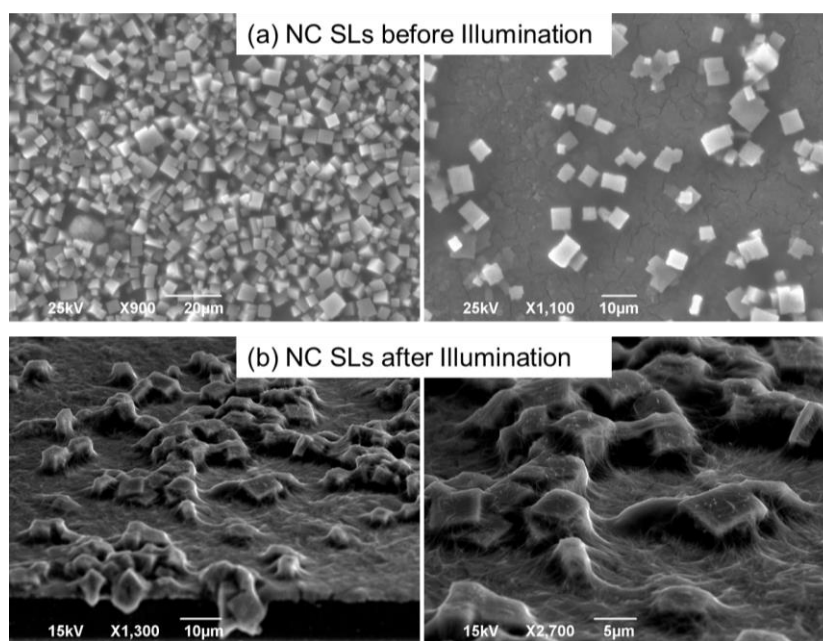


Figure S17. SEM images of (a) freshly made and (b) illuminated (LED source, $\lambda_{exc}=470$ nm; $I_{exc}=100$ mW cm⁻², 20 hours) samples of CsPb(I_{0.64}Br_{0.36})₃ NC SLs. The freshly prepared sample features NC SLs with clearly distinguishable edges while illuminated NC SLs have an overcoating layer attributed to the amorphous products of the NC degradation, as discussed in the main text. The amount of visible amorphous layer observed in SEM experiments varies with the density of NC SLs in the sample (i.e. the denser the NC SLs area, the more visible the amorphous layer).

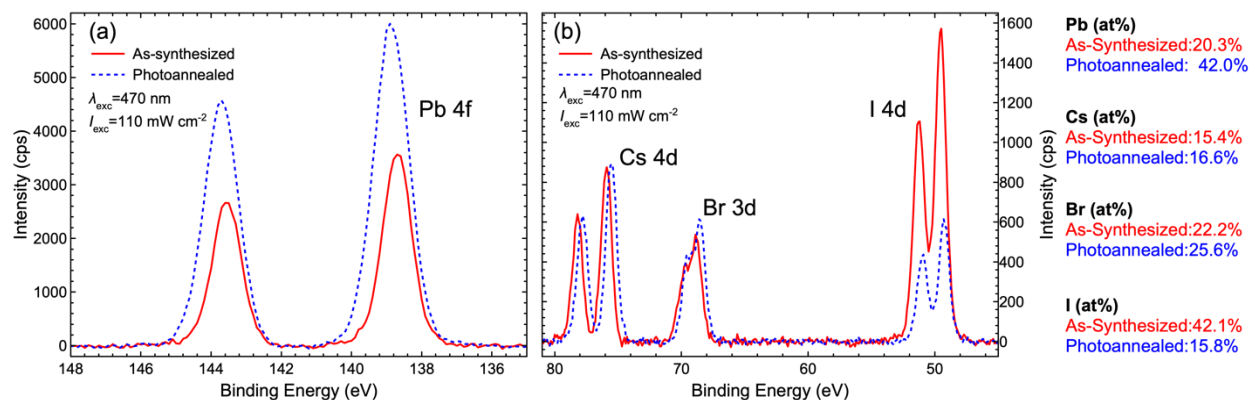


Figure S18. XPS results as-synthesized (solid red lines) and illuminated (dashed blue lines, $\lambda_{\text{exc}}=470$ nm; $I_{\text{exc}}=110$ mW cm⁻², 20 hours) replicas of thick films of CsPb(I_{0.64}Br_{0.36})₃ NC SLs. Pb 4f binding energy in (a). Cs 4d, Br 3d, and I 4d binding energies in (b). Atomic % for each element of each replica listed to the right of the panel (b).

3) References

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