

Supporting Information:

Long Live(d) CsPbBr₃ Superlattices: Colloidal Atomic Layer Deposition for Structural Stability

Victoria Lapointe,^a Philippe B. Green,^b Alexander N. Chen,^b Raffaella Buonsanti,^b Marek B. Majewski^{a}*

^a Department of Chemistry and Biochemistry and Centre for NanoScience Research Concordia University 7141 Sherbrooke Street West, Montreal, Quebec, Canada, H4B 1R6

^b Laboratory of Nanochemistry for Energy Research, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, Sion, CH-1950, Switzerland

*E-mail: marek.majewski@concordia.ca

Experimental Methods and Materials

Materials All chemicals were used as received from commercial sources: cesium carbonate (Cs_2CO_3 , 99.9%, Sigma-Aldrich), lead bromide (PbBr_2 , 99.99%, Alfa Aesar), 1-octadecene (ODE, technical grade 90%, Sigma-Aldrich), oleic acid (OLAC, technical grade 90%, Sigma-Aldrich), oleylamine (OLAM, technical grade 70%, Sigma-Aldrich), hexanes (95%, Sigma-Aldrich), octane (anhydrous 99%, Sigma-Aldrich), ethyl acetate (anhydrous 99.8%, Sigma-Aldrich), deuterated toluene (99%, Sigma-Aldrich), trimethylaluminum (TMA, 98% Strem), didodecyldimethylammonium bromide (DDAB, 98%, Sigma-Aldrich), toluene (anhydrous 99.8%, Sigma-Aldrich), silicon substrates (Siegert Wafer).

Synthesis of cesium lead bromide CsPbBr_3 PNCs

A cesium oleate solution was prepared with Cs_2CO_3 (0.22 g, 0.68 mmol), OLAC (0.67 mL, 2.1 mmol) and ODE (8.25 mL, 25.8 mmol) in a three neck round bottom flask. This solution was degassed and heated to 150 °C for 1 hour to let the Cs_2CO_3 dissolve. The solution was then cooled to 130 °C in a nitrogen atmosphere. In another three-neck flask, PbBr_2 (0.28 g, 0.76 mmol), OLAM (2 mL, 6 mmol) and OLAC (2 mL, 6 mmol) was added to ODE (20 mL, 63 mmol) and was degassed at 120 °C for 1 hour. Then the solution was heated to 160 °C under nitrogen and cesium oleate solution (1.6 mL) was injected into this flask swiftly. After 5 seconds, the flask was cooled to room temperature with a water bath to undergo nucleation. The resulting solution turned bright green. This was then centrifuged at 6000 rpm (4140 rcf) for 30 minutes. The supernatant was discarded, and the precipitate was dispersed in approximately 3-4 mL of hexanes. The dispersed precipitate was then purified by the addition of ethyl acetate with a 1:1 volume ratio with hexanes resulting in precipitation. This solution was centrifuged at 6000 rpm (4140 rcf) for 10

minutes. The pellet was then collected, as the supernatant contained unreacted ligands, and it was dissolved in octane in a nitrogen filled glovebox for further synthesis.

Colloidal Atomic Layer Deposition

CAUTION: Concentrated TMA solution is highly pyrophoric, extreme precaution must be taken while manipulating this reagent. All equipment used to prepare this solution (syringes, needles, scintillation vials) was first left overnight in a 100 °C oven to ensure the removal of moisture. The following day it was rinsed with hexanes (3×) before use.

For c-ALD, a 10 mM solution was prepared in a glovebox by diluting the desired amount of the stock TMA solution with anhydrous octane in a scintillation vial. This solution, which was constantly purged with nitrogen, was then transferred to a gas tight syringe (S.G.E. Gas Tight Luer Lock Syringe, 5 mL) with a stainless steel 304 needle (Sigma-Aldrich) that had been evacuated and filled with nitrogen. The PNC solution was held at a positive pressure of nitrogen throughout the synthesis to ensure the constant renewal of nitrogen, replacing any incidentally introduced O₂ and methane generated during the process. The solution was constantly stirred at room temperature.

Each c-ALD step involved the injection of 30 μL of the TMA solution at a rate of 1 mL/hr using a syringe pump (KF Technology NE-1000p programmable single syringe pump) followed by a waiting period of 5 minutes. This was then followed by the bubbling of O₂ which was performed using a mass flow controller at a rate of 1.5 mL/min for 1 min. This step was also followed by a waiting period of 5 minutes. Each addition of TMA counts as one cycle. The last cycle was terminated with a diluted solution of OLAC (5 μL in 200 μL of anhydrous octane).

Terminating ligands such as OLAC and DDAB were introduced using a purged needle and directly injected into the PNC solution. Therefore, the naming of the samples goes as follows: n c-ALD OLAC: $(n - 1)$ TMA/O₂ + TMA/OLAC

After the desired number of cycles, the solution was dried under a constant flow of nitrogen and the PNCs were redispersed in the desired anhydrous solvent such as deuterated toluene or toluene and stored in a nitrogen filled glovebox.

The gas tight syringe was then washed by flowing 15 mL of anhydrous hexanes to avoid alumina formation and avoid clogging the syringe. The clean syringe and long needle were stored in a 60 °C oven. If alumina deposits are observed, 1 M HCl solution was placed in the syringe and left for 1 hr. The syringe was then thoroughly rinsed with hexanes and stored in the oven.

Synthesis of PNC Superlattices (SLs)

To form SLs from similar concentrations of c-ALD treated and untreated PNCs, a 10 mM solution of the stock CsPbBr₃ PNC solution was prepared in a nitrogen filled glove box. This solution was dried using a strong stream of nitrogen until no solvent remained, then was redispersed in 300 μL of toluene and filtered using a 2 μm PTFE filter. Treated PNCs (post c-ALD), were also dried under a strong stream of N₂ right after the c-ALD synthesis, redispersed in 300 μL of toluene and filtered using a 2 μm PTFE filter. These solutions were stored in a nitrogen filled glove box until they were needed.

To induce self-assembly and to make SLs, 15 μL of the concentrated solutions were drop cast on a 0.5 × 1 cm silicon substrate (previously washed with ethanol and acetone) in a glovebox. These were left in the glovebox to slowly evaporate the toluene overnight.

For the stability tests, the CsPbBr₃ SLs were stored under ambient room light in a nitrogen-filled glovebox until subsequent PXRD and SEM analyses where the SLs were exposed to ambient conditions for the duration of the measurements.

Gas phase (g-ALD) Treatment of CsPbBr₃ SLs

First, CsPbBr₃ SLs were synthesized as described. Amorphous AlO_x was deposited in a Savannah-200 ALD system from Cambridge NanoTech Inc. onto these SLs. TMA and ultrapure H₂O were used as aluminum and as oxygen sources, respectively. The chamber was kept at 50 °C with a operating pressure of ~ 0.15 Torr where each deposition cycle consisted of a TMA pulse (0.015 sec), purging (10 sec), H₂O pulse (0.015 sec), purging (10 sec). In total, 25 and 50 cycles of g-ALD were done on the separate CsPbBr₃ SL samples.

Characterization

UV-Vis absorbance measurements were done using a PerkinElmer Lambda 950 spectrophotometer, equipped with a deuterium (ultraviolet range) and tungsten lamp (visible and infrared range). A photomultiplier tube and InGaAs detector was used. The concentrated samples (5 μL) were dissolved in 2 mL of toluene in a clean quartz cuvette to collect this data. A quartz cuvette with toluene was used as a baseline.

The time resolved photoluminescence (TRPL), photoluminescence (PL) and quantum yield (PLQY) measurements were done using a Horiba Jobin Yvon Fluorolog-3 instrument. The PL and PLQY measurements were done using a low-pressure mercury lamp and photomultiplier tube as detector. For liquid samples, the measurements were taken using a quartz cuvette (step size and integration = 1, slit size = 1 nm) and the SL measurements were taken by sticking the silicon

substrates with assembled SLs onto a cut microscope slide with double-sided tape ensuring the silicon substrate completely covered the tape to not influence the PL or PLQY. The blank measurements consisted of a quartz cuvette filled with toluene for liquid samples and a clean silicon substrate stuck onto a microscope slide for solid sample data collection (step size and integration = 1, slit size = 2 nm). For TRPL, a Horiba nanoLED with excitation wavelength of 455 nm and pulse duration of <1.4 ns was employed to selectively excite the CsPbBr₃ NCs and SLs, and the lifetimes were collected at 512 nm as this matched with the maximum emission wavelength of the CsPbBr₃ PNCs. To establish the PL radiative lifetimes, a triexponential fitting function was used to best fit the data and a Riemann sum was used to calculate the average radiative lifetimes of each sample.

Fourier transform infrared spectroscopy (FT-IR) measurements were done using an attenuated total reflectance (ATR) PerkinElmer Two spectrometer. The liquid samples were directly drop-cast on the ATR plate from toluene or octane and left to dry fully before taking the measurement.

Nuclear magnetic resonance (NMR) measurements were done using a Bruker Avance III 400 MHz spectrometer equipped with a 5 mm BBFO Z-gradient SmartProbe. ¹H-NMR, DOSY and NOESY spectra were acquired using standard pulse sequences from the Bruker library and the data was processed using Topspin and MNova. DOSY experiments were performed with a pulse field gradient spin-echo PFGSE decay (pulse sequence ledbpgp2s from the Bruker library).

Transmission electron microscopy (TEM) measurements were done using a FEI Tecnai-spirit at 120 kV. The samples were prepared by drop casting 5 μL of a 50-times diluted PNC solution onto carbon-coated copper TEM grids which were placed on a silicone substrate and left for slow solvent evaporation overnight in a fumehood. ImageJ¹ was used to calculate the average PNC size and PNC-to-PNC distances using ~200 particles.

Scanning electron microscopy (SEM) measurements were acquired with a Thermo-Fisher Teneo using an in-lens (Trinity) detector with beam energy ranging from 5 – 15 keV (5 keV for imaging and 15 keV for EDS) and current of 25 pA – 1.6 nA. Samples were imaged on a silicon substrate. ImageJ¹ was used to calculate the average SL size using ~20-30 particles from Figure S18.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) coupled with energy-dispersive X-ray spectroscopy (EDXS) measurements were done using an FEI Tecnai Osiris TEM in the STEM mode with an accelerating voltage of 200 kV. The TEM was equipped with a high brightness XFEG gun and four windowless Super-X silicon drift detectors for EDS. The Bruker Esprit was used for data analysis. The samples were prepared by drop casting 5 μ L of a 50-times diluted PNC solution onto carbon-coated copper TEM grids which were also placed on a silicon substrate and left for slow evaporation overnight in a fumehood.

X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Analytical instrument equipped with a monochromated $K\alpha$ X-ray line of an Al anode. The samples were prepared by drop casting the sample from toluene on a clean silicon substrate. CasaXPS was used to analyze the data. All spectra were referenced at 284.8 eV using the C-C bond of the C 1s orbital.

Powder X-ray diffraction (XRD) measurements were done using a Bruker D8 Advance diffractometer with a Cu $K\alpha$ source equipped with a Lynxeye one-dimensional detector. The diffractometer operated at 40 kV and 40 mA with a Cu $K\alpha$ source with a wavelength of 1.54 Å. The diffraction patterns were collected within a range of 10 – 70 ° 2 θ , using 0.045 increments and 1s integrations. The SL samples were collected on a silicon substrate. Once the SL data was collected, the data was converted from ° 2 θ to q-vector space using the equation $q = \frac{4\pi\sin\theta}{\lambda}$ where

q is the q -vector space (\AA^{-1}), θ is angle (radians), and λ is the X-ray source wavelength (\AA). From this new data, the SL periodicity was estimated using the equation $\Lambda = \frac{2\pi}{\Delta q}$ where Δq is the distance between the fringes (\AA) at $15^\circ 2\theta$ (1.06\AA^{-1}). The d-spacing was estimated by associating it to the center q -vector spacing between the fringes (\AA) at $15^\circ 2\theta$ (1.06\AA^{-1}).²

References

- (1) Schneider, C. A.; Rasband, W. S.; Eliceiri, K. W. NIH Image to ImageJ: 25 Years of Image Analysis. *Nat. Methods* **2012**, *9* (7), 671–675. <https://doi.org/10.1038/nmeth.2089>.
- (2) Toso, S.; Baranov, D.; Altamura, D.; Scattarella, F.; Dahl, J.; Wang, X.; Marras, S.; Alivisatos, A. P.; Singer, A.; Giannini, C.; Manna, L. Multilayer Diffraction Reveals That Colloidal Superlattices Approach the Structural Perfection of Single Crystals. *ACS Nano* **2021**, *15* (4), 6243–6256. <https://doi.org/10.1021/acsnano.0c08929>.

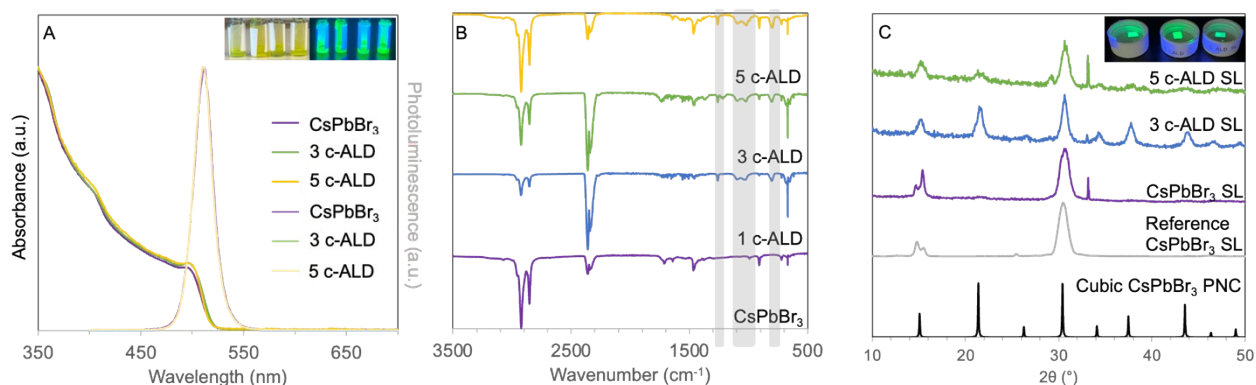


Figure S1. (A) UV-Vis absorbance and photoluminescence spectra of colloidal parent CsPbBr_3 PNCs and *c*-ALD treated PNCs without OLAC termination (inset: photograph of PNC colloids) in toluene, $\lambda_{\text{ex}} = 365 \text{ nm}$; (B) FTIR spectra for parent CsPbBr_3 PNCs and *c*-ALD treated PNCs without OLAC termination. (C) PXRD diffractogram of CsPbBr_3 and *c*-ALD treated PNCs without OLAC termination after undergoing slow evaporation of toluene demonstrating that without OLAC termination PNC colloids do not form SLs as confirmed through the preservation of reflections associated with “unorganized” PNCs.

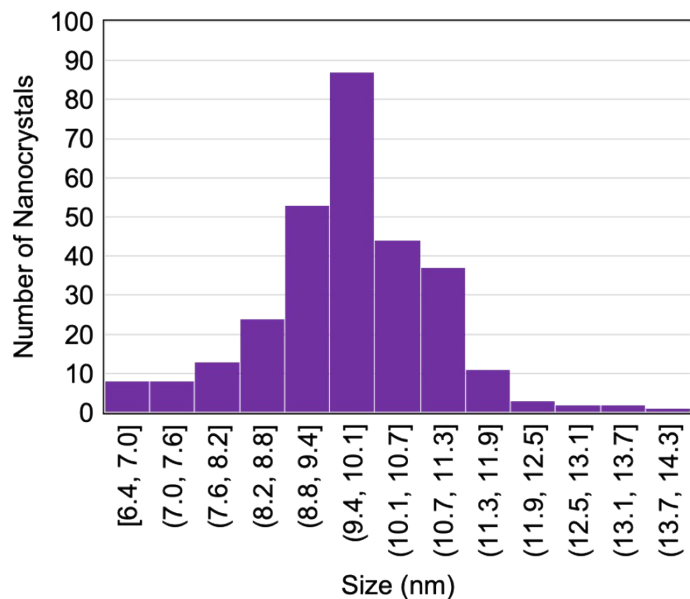


Figure S2. Size distribution for CsPbBr_3 PNCs. Measured using ImageJ from 293 particles.

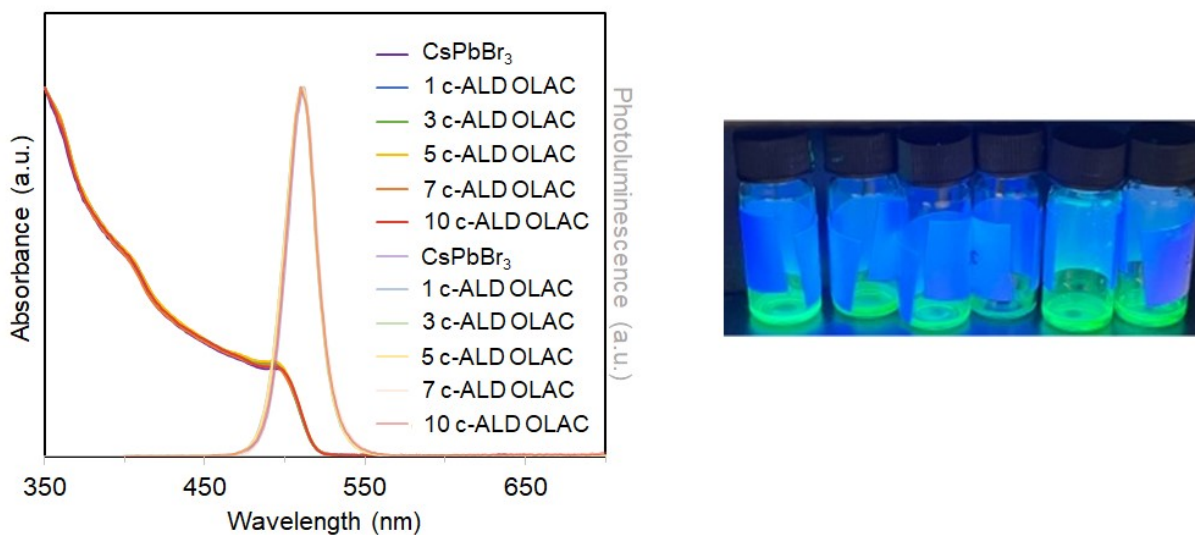


Figure S3. UV-Vis absorbance and photoluminescence spectra of untreated and c-ALD OLAC treated CsPbBr_3 PNCs alongside a photograph of PNC colloids in toluene ($\lambda_{\text{ex}} = 365$ nm).

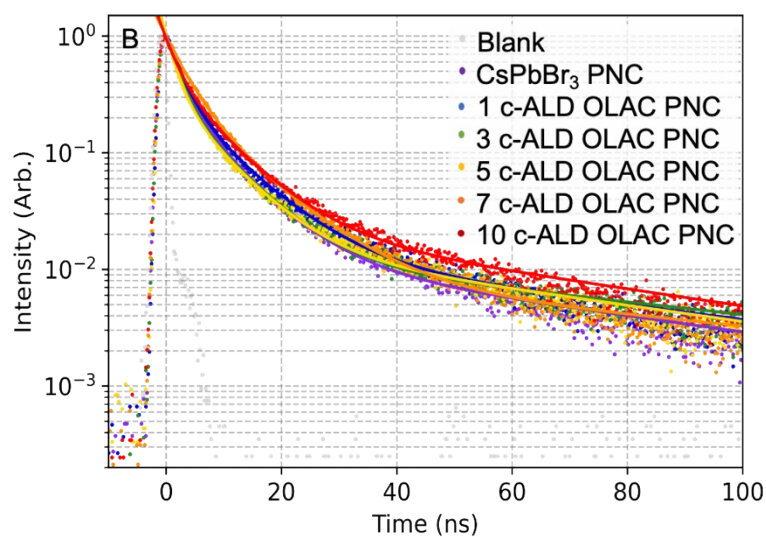


Figure S4. Time-resolved photoluminescence decay traces and corresponding fits of untreated and *c*-ALD OLAC treated CsPbBr_3 PNCs $\lambda_{\text{ex}} = 455$ nm. Toluene was used as a blank.

Table S1. Photophysical data for *c*-ALD OLAC treated CsPbBr_3 PNCs

Sample	Bandgap (nm)	Max λ_{em} (nm)	FWHM (nm)	QY (%)	PL lifetime (ns)
CsPbBr_3	498	512	22	44	22.8
1 <i>c</i> -ALD OLAC	495	510	23	62	23.4
3 <i>c</i> -ALD OLAC	495	511	23	52	29.5
5 <i>c</i> -ALD OLAC	498.5	511	23	62	24.0
7 <i>c</i> -ALD OLAC	498.5	512	23	54	22.8
10 <i>c</i> -ALD OLAC	499	510	23	45	24.5

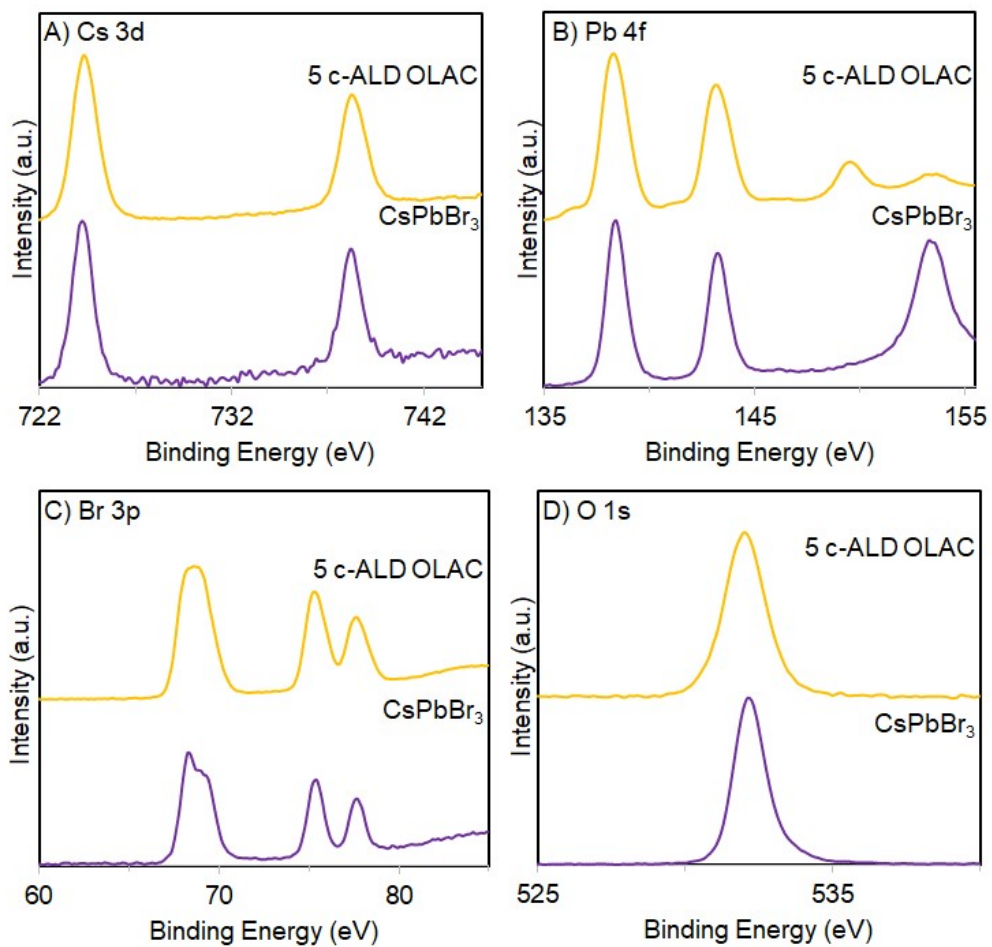


Figure S5. XPS spectra of untreated CsPbBr_3 and 5 c-ALD OLAC PNCs for Cs 3d (A), Pb 4f (B), Br 3p (C), O 1s (D) core-level regions.

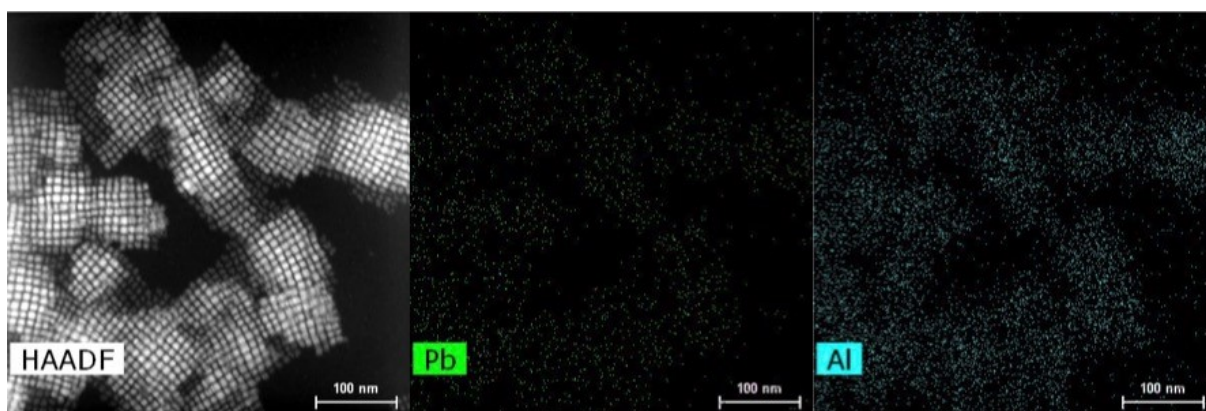


Figure S6. *STEM-EDS Micrograph and mapping of c-ALD 5 OLAC SL sample (The solution was diluted 50x in order before depositing onto TEM grid).*

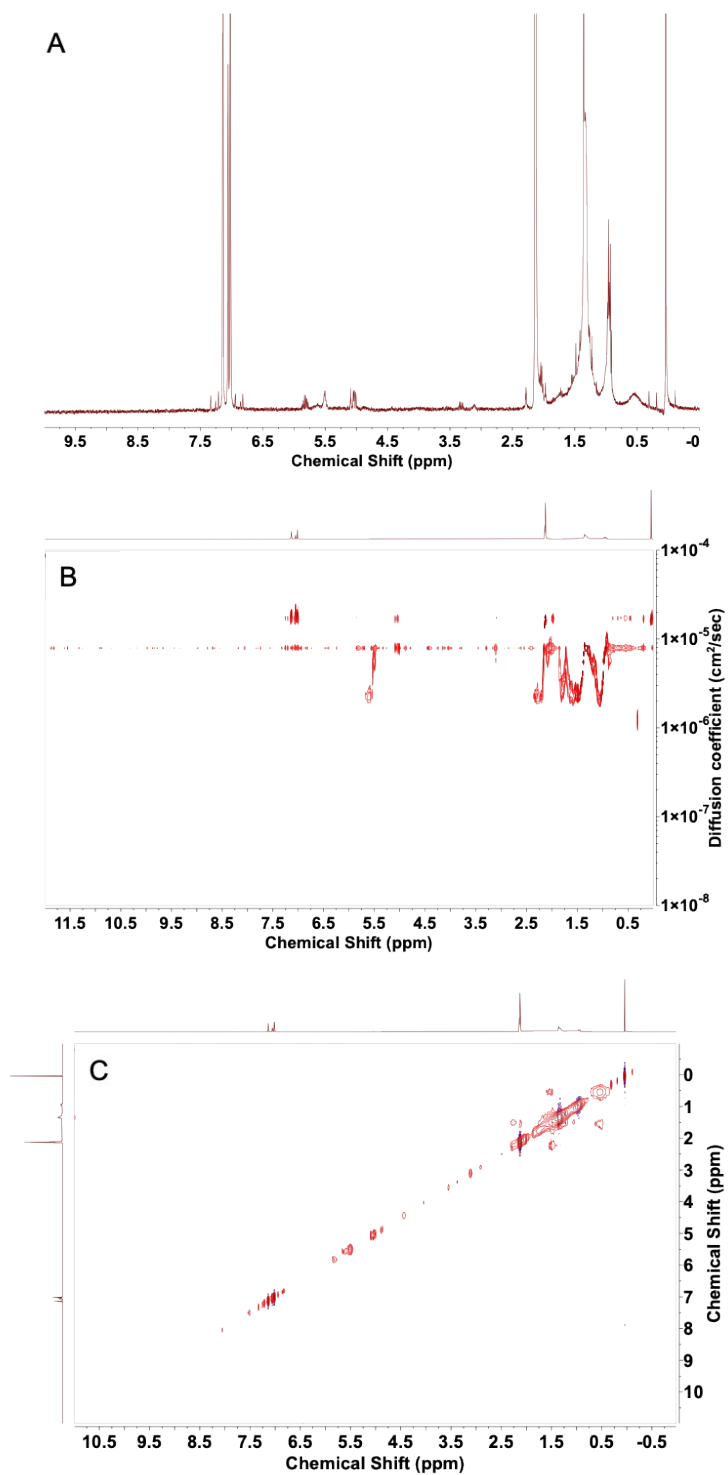


Figure S7. (A) ^1H NMR, (B) DOSY and (C) NOESY of untreated CsPbBr_3 PNC in toluene-d_8 (400 MHz).

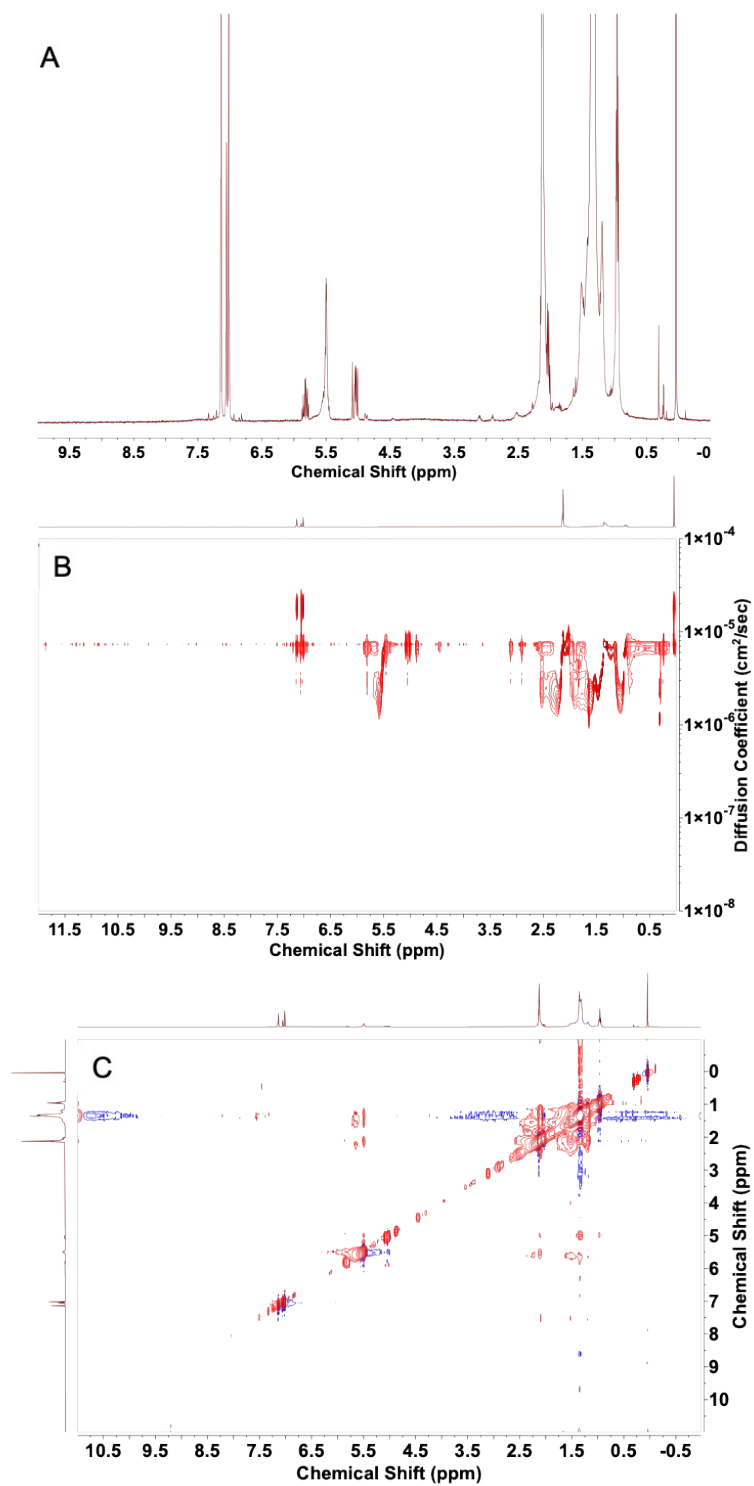


Figure S8. (A) ¹H NMR, (B) DOSY and (C) NOESY of 5 c-ALD OLAC PNC in toluene-d₈ (400 MHz).

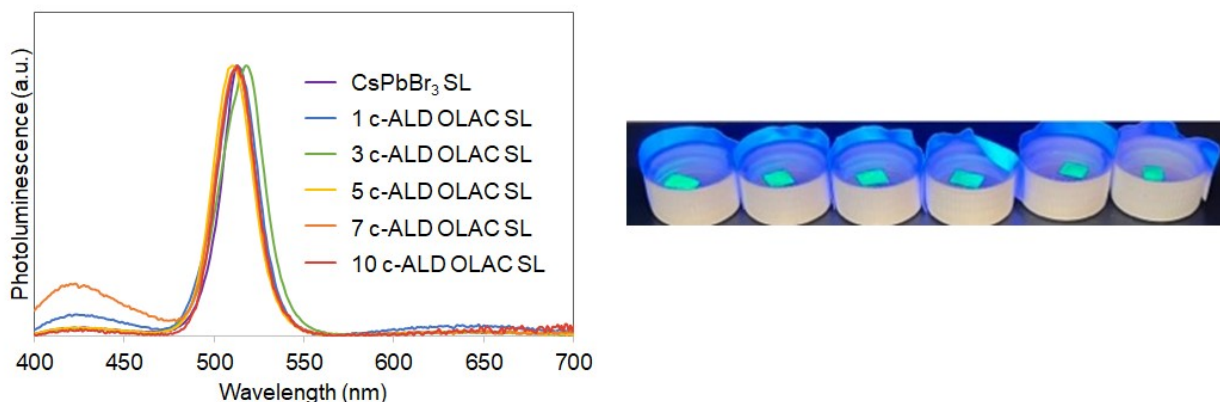


Figure S9. Normalized photoluminescence spectra of SLs assembled from untreated and *c*-ALD OLAC treated CsPbBr₃ PNCs alongside photograph of SLs as assembled on Si substrates ($\lambda_{ex} = 365$ nm). The emission of 425 nm corresponds to the integrating sphere.

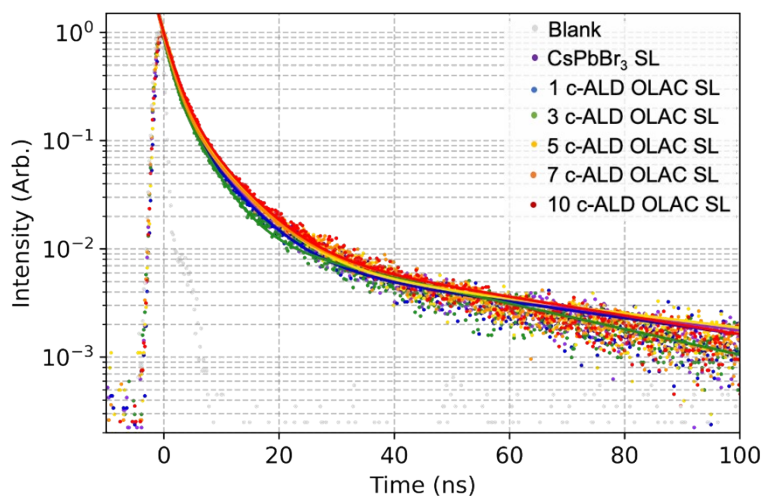


Figure S10. Time-resolved photoluminescence decay traces and corresponding fits of SLs assembled from *c*-ALD OLAC treated CsPbBr₃ PNCs $\lambda_{ex} = 455$ nm. A Si substrate was used as a blank.

Table S2. Photophysical data for SLs assembled from *c*-ALD OLAC treated CsPbBr₃ PNCs.

Sample	Max λ_{em} (nm)	FWHM (nm)	QY (%)	PL Lifetime (ns)
CsPbBr ₃ SL	513	22	10	19.5
1 <i>c</i> -ALD OLAC SL	513	26	6	14.3
3 <i>c</i> -ALD OLAC SL	518	28	11	22.3
5 <i>c</i> -ALD OLAC SL	510	25	15	22.8
7 <i>c</i> -ALD OLAC SL	512	25	24	19.5
10 <i>c</i> -ALD OLAC SL	513	25	40	17.2

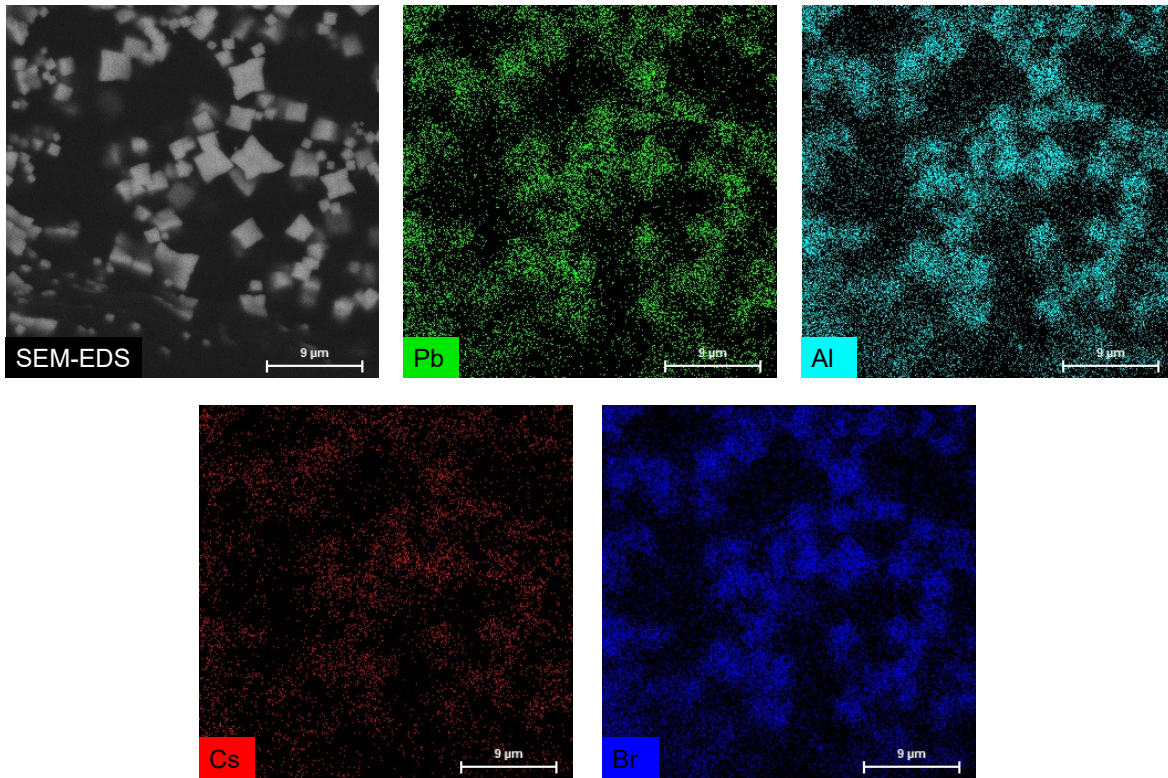


Figure S11. SEM-EDS micrographs and elemental mapping of a *c*-ALD 5 OLAC SL sample.

Table S3. *Calculated structural SL parameters.*

Sample	SL periodicity Λ (nm)	d-spacing d (nm)
CsPbBr ₃ SL	13.15	0.5888
1 c-ALD OLAC SL	14.09	0.5793
3 c-ALD OLAC SL	13.15	0.5802
5 c-ALD OLAC SL	12.33	0.5776
7 c-ALD OLAC SL	11.60	0.5785
10 c-ALD OLAC SL	11.60	0.5819
5 c-ALD DDAB SL	16.43	0.5879

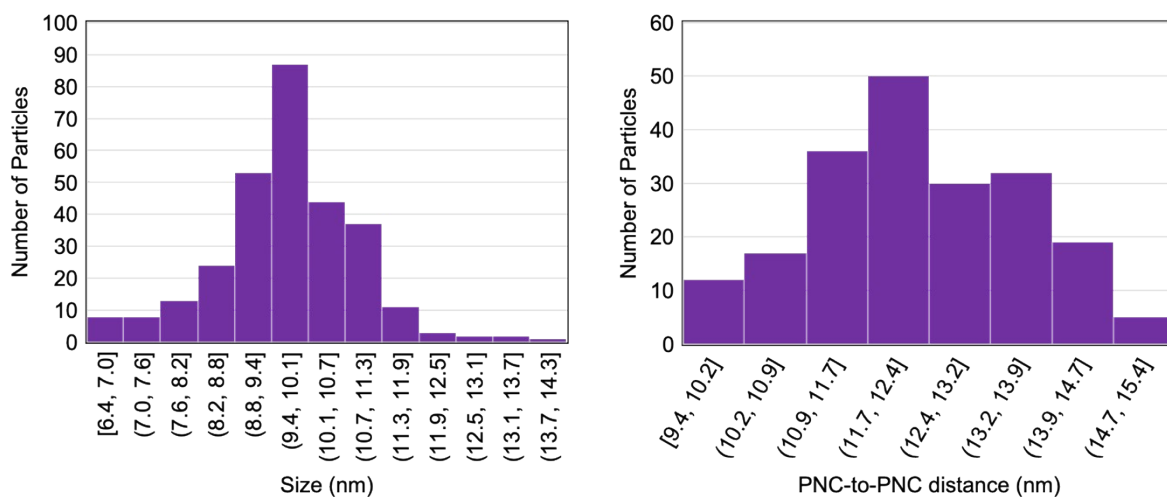


Figure S12. Size distribution for (A) PNC size measured with ImageJ using 293 particles and (B) PNC-to-PNC distance measured with ImageJ using 201 particles of CsPbBr₃ PNCs within the SL formation.

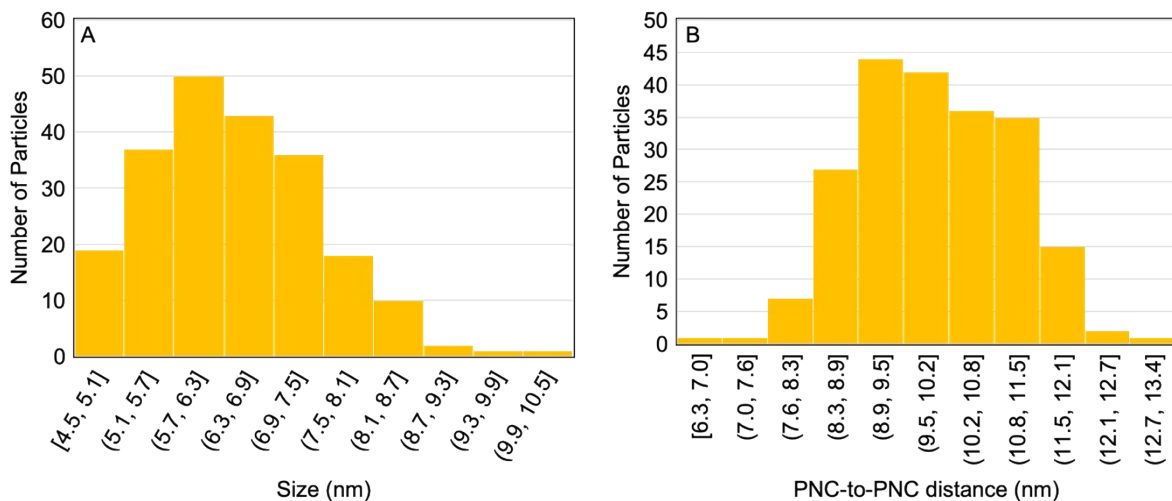


Figure S13. Size distribution for (A) PNC size measured with ImageJ using 217 particles and (B) PNC-to-PNC distance measured with ImageJ using 211 particles of 5 *c*-ALD OLAC PNCs within the SL formation

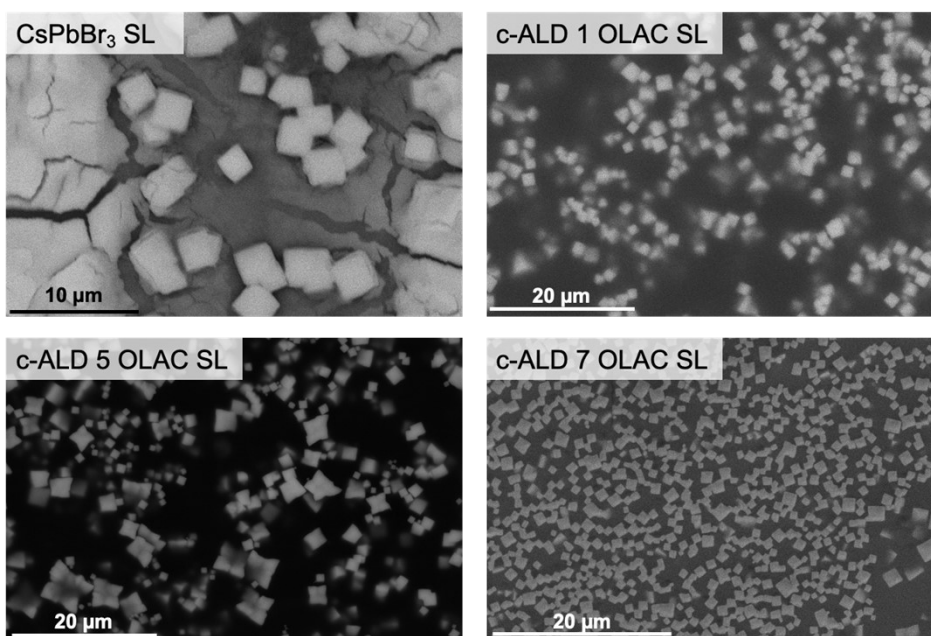


Figure S14. SEM micrographs of untreated and *c*-ALD OLAC treated CsPbBr_3 SLs, at lower magnification to show ordered SLs over larger areas on the silicon substrate.

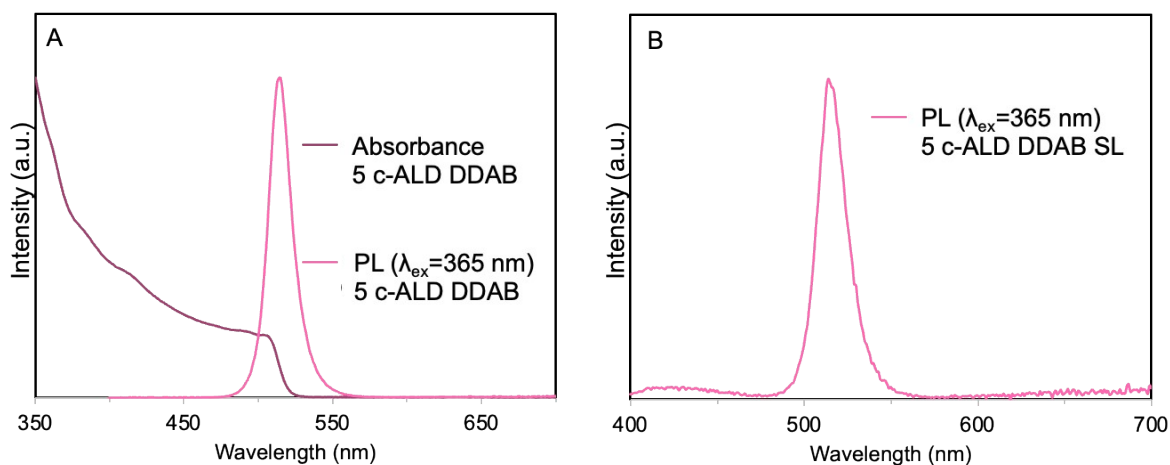


Figure S15. (A) UV-Vis absorbance and photoluminescence for 5 c-ALD DDAB treated CsPbBr₃ PNCs and (B) photoluminescence of the corresponding SL, $\lambda_{ex} = 365$ nm in toluene (for the colloids) or on a silicon substrate for the SL.

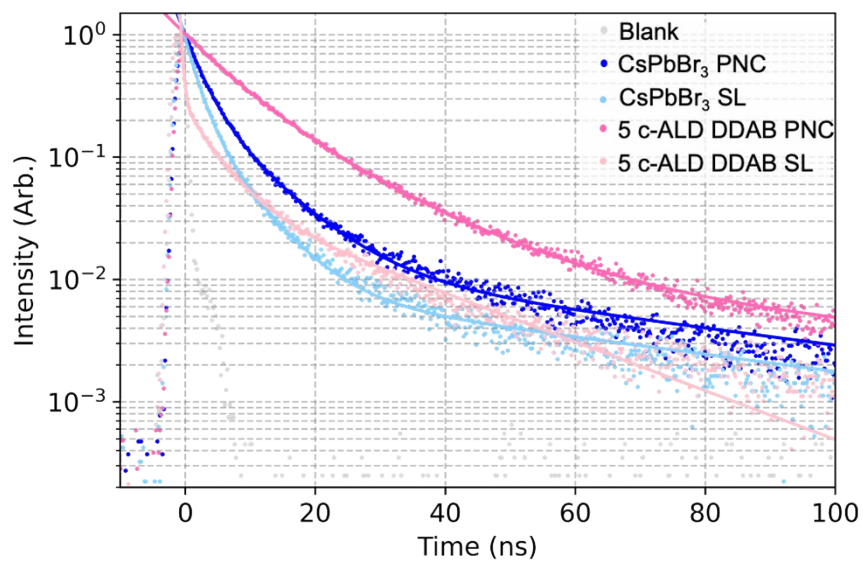


Figure S16. Time-resolved photoluminescence decay traces and corresponding fits of c-ALD OLAC treated CsPbBr₃ PNCs, $\lambda_{ex} = 455$ nm.

Table S4. Photophysical data for 5 *c*-ALD DDAB PNCs and SLs

Sample	Bandgap (nm)	Max λ_{em} (nm)	FWHM (nm)	QY (%)	PL Lifetime (ns)
CsPbBr ₃ PNC	498	513	17	47	22.6
CsPbBr ₃ SL		515	17.5	21	14.6
5 <i>c</i> -ALD DDAB PNC	505.5	515	18	98	22.9
5 <i>c</i> -ALD DDAB SL		514	19.5	39	28.5

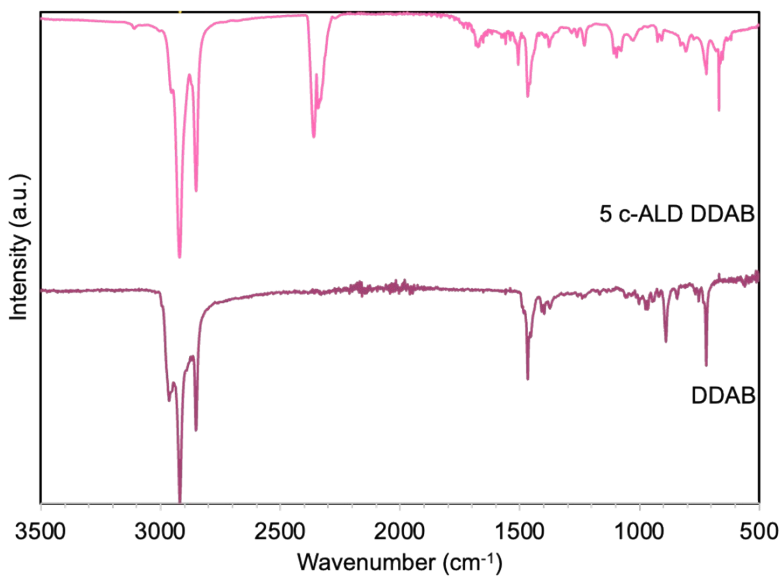


Figure S17. FTIR spectra for the DDAB ligand and 5 *c*-ALD DDAB PNCs.

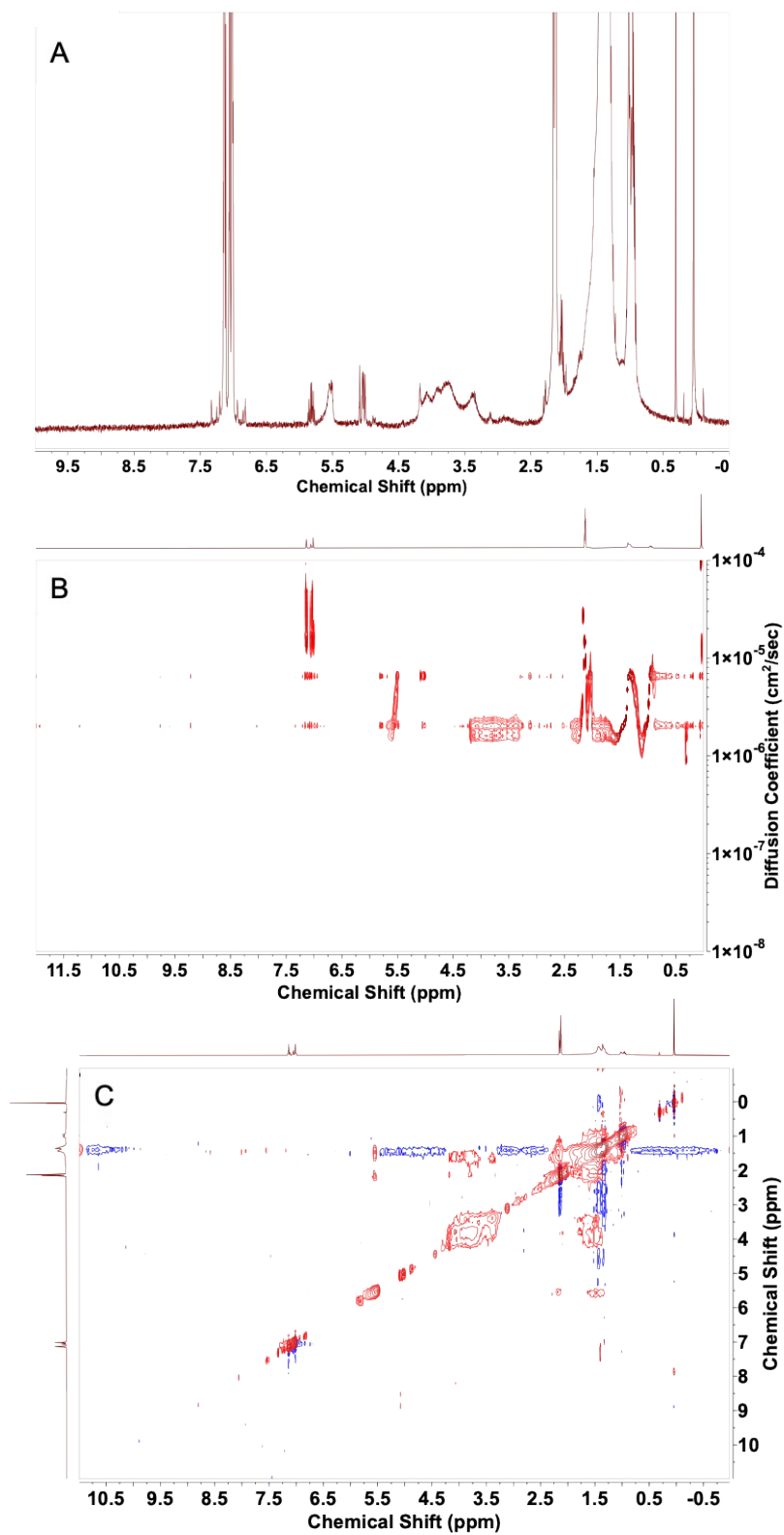


Figure S18. (A) ¹H NMR, (B) DOSY and (C) NOESY of 5 c-ALD DDAB PNCs in toluene-d₈ (400 MHz).

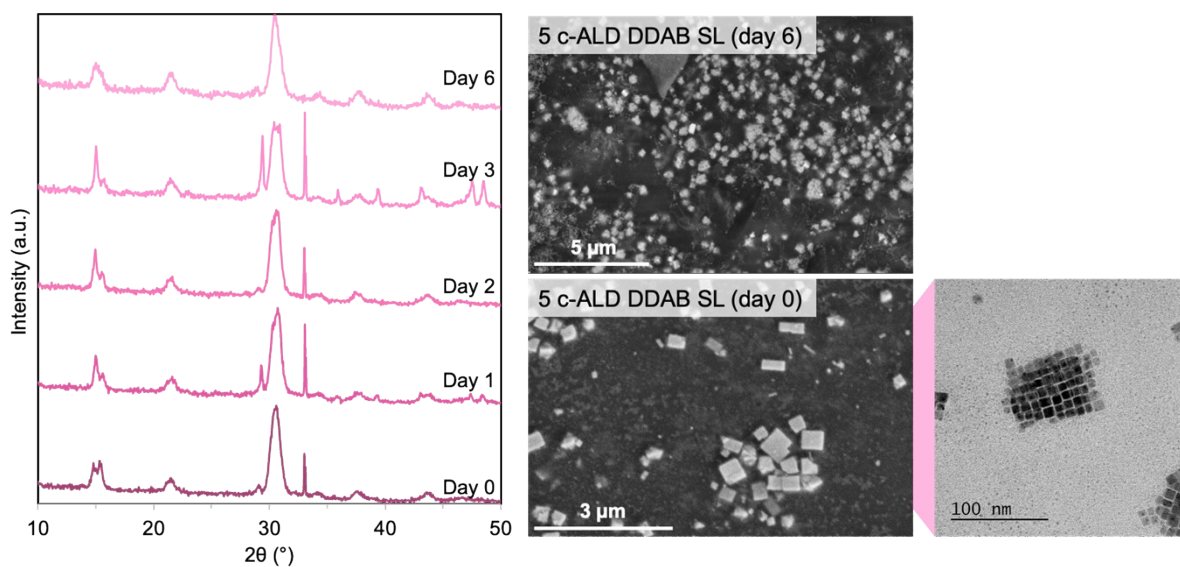


Figure S19. PXRD diffractograms (over time), SEM micrographs (over time) and STEM micrographs for 5 c-ALD DDAB SLs.

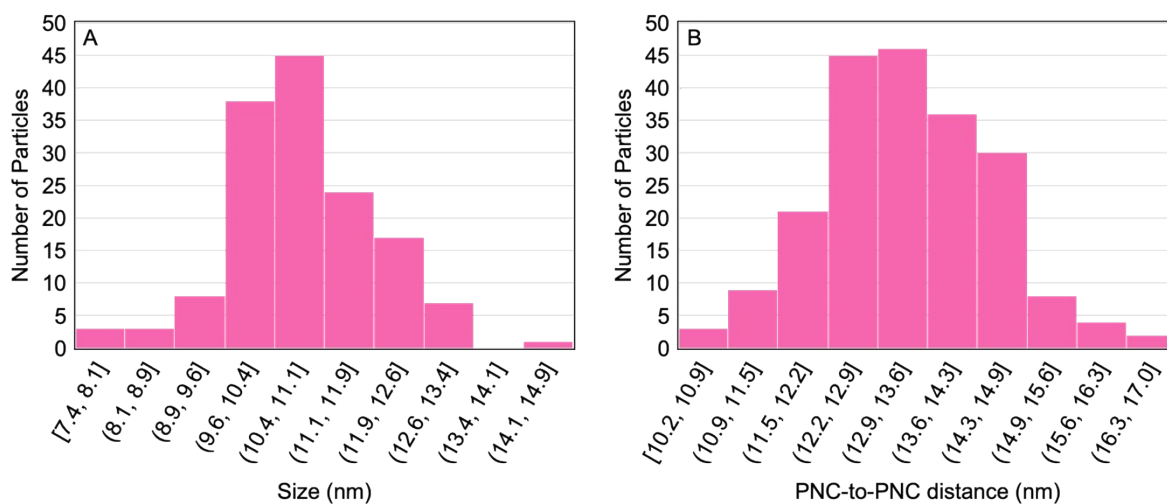


Figure S20. Size distribution for (A) PNC size measured with ImageJ using 146 particles and (B) PNC-to-PNC distance measured with ImageJ using 204 particles of 5 c-ALD DDAB PNCs within the SL formation

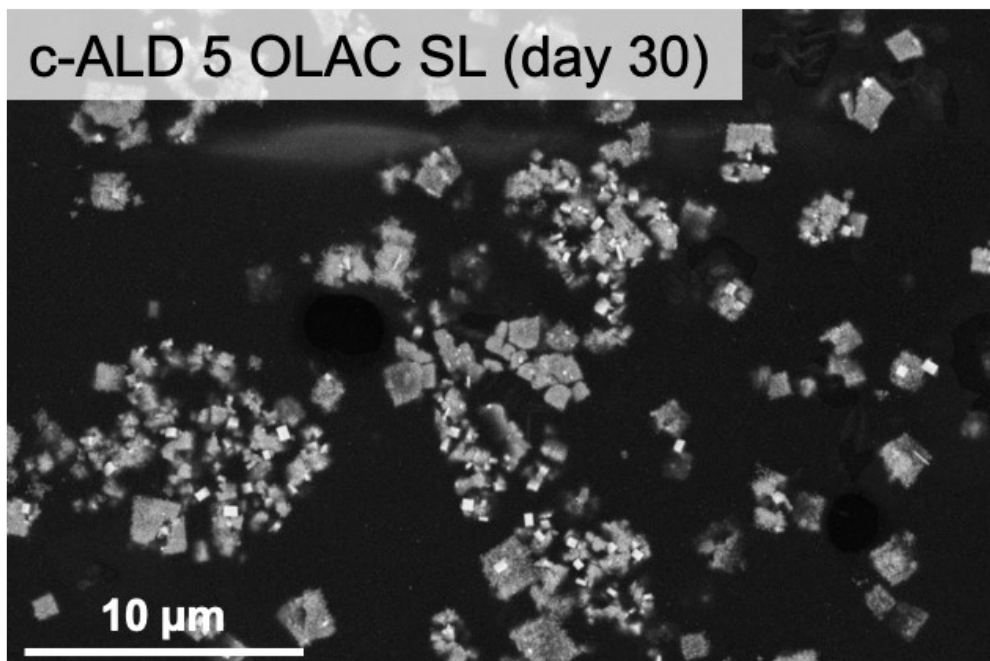


Figure S21. SEM micrograph of 5 c-ALD OLAC SLs after 30 days, which start showing signs of aging.

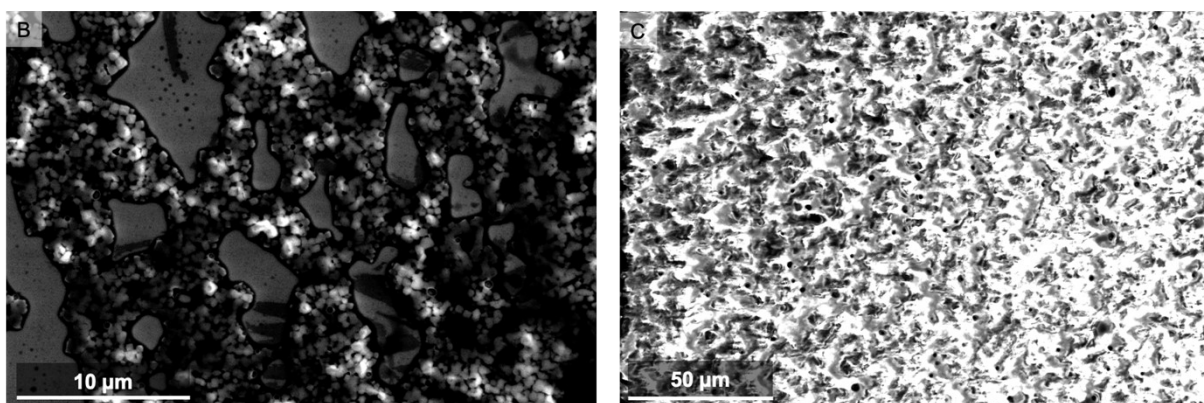
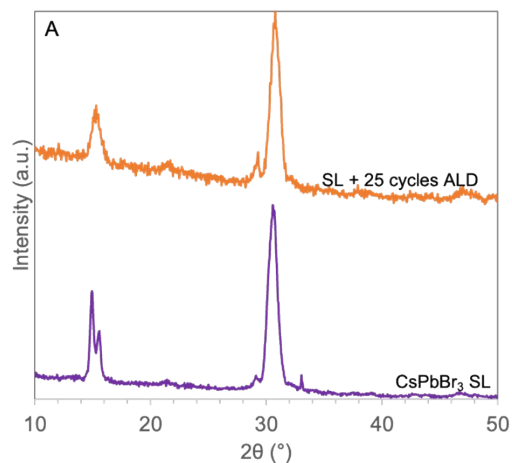


Figure S22. (A) PXRD diffractograms of untreated CsPbBr₃ SL and CsPbBr₃ SL with 25 cycle g-ALD cycles, (B) and (C) SEM micrographs of CsPbBr₃ SL with 25 cycle g-ALD cycles at high and low magnification.

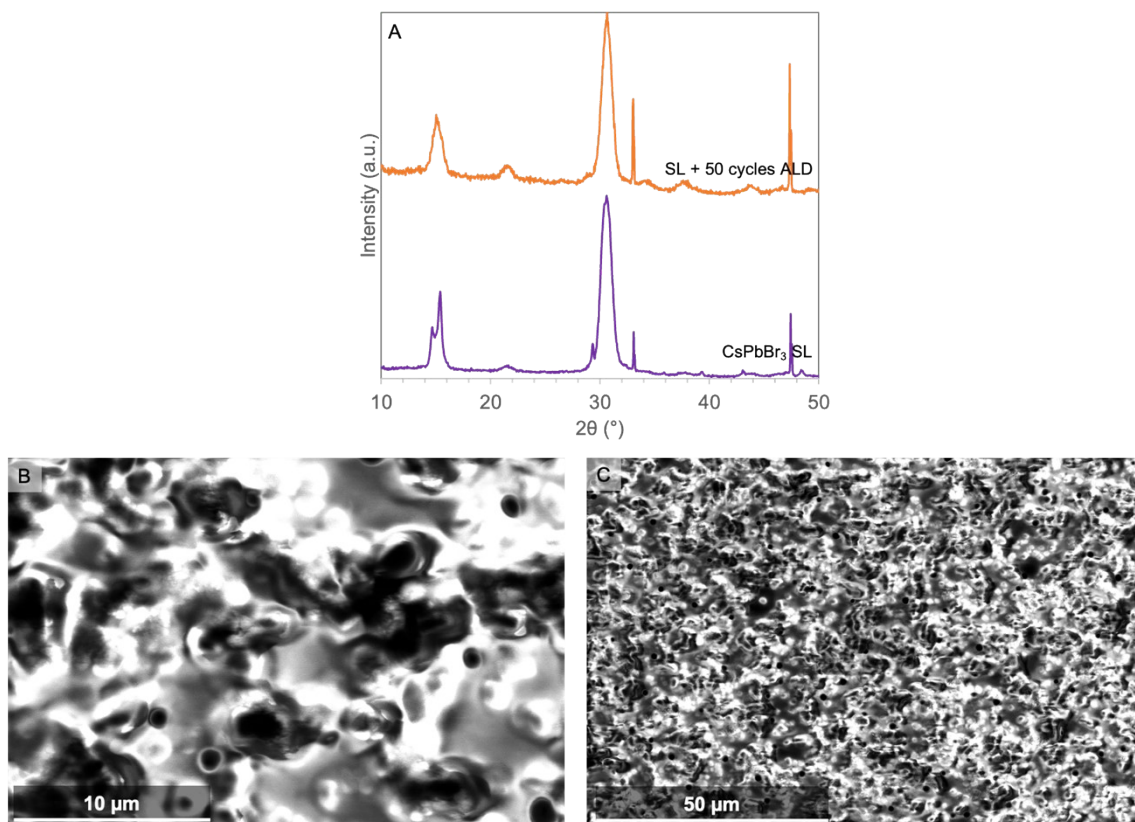


Figure S23. (A) PXR D diffractograms of untreated CsPbBr_3 SL and CsPbBr_3 SL with 50 cycle g-ALD cycles, (B) and (C) SEM micrographs of CsPbBr_3 SL with 50 cycle g-ALD cycles at high and low magnification.

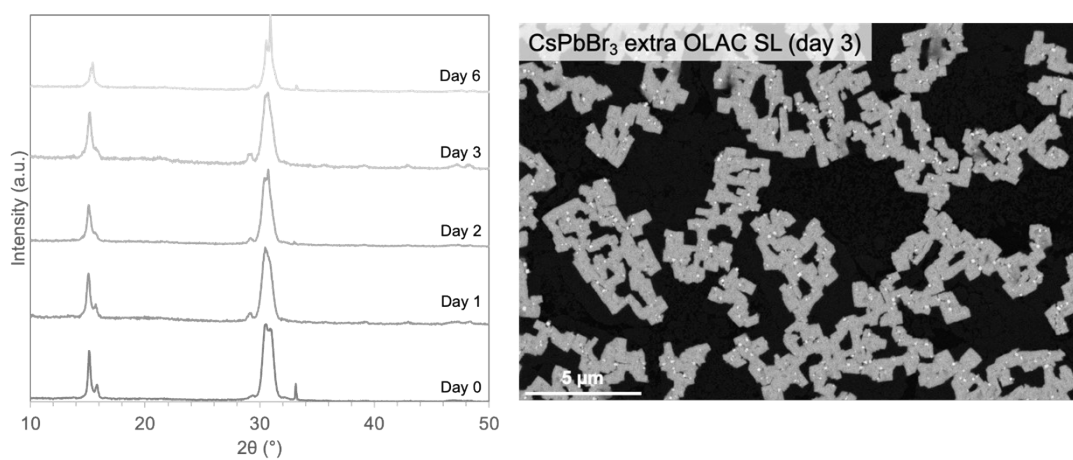


Figure S24. PXR D diffractograms and SEM micrographs of CsPbBr_3 SL with extra OLAC added.