Electronic Supplementary Information

Functionalized hybrid perovskite nanocrystals with organic ligands showing a stable 3D/2D core/shell structure for display and laser applications

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Experiments

Materials

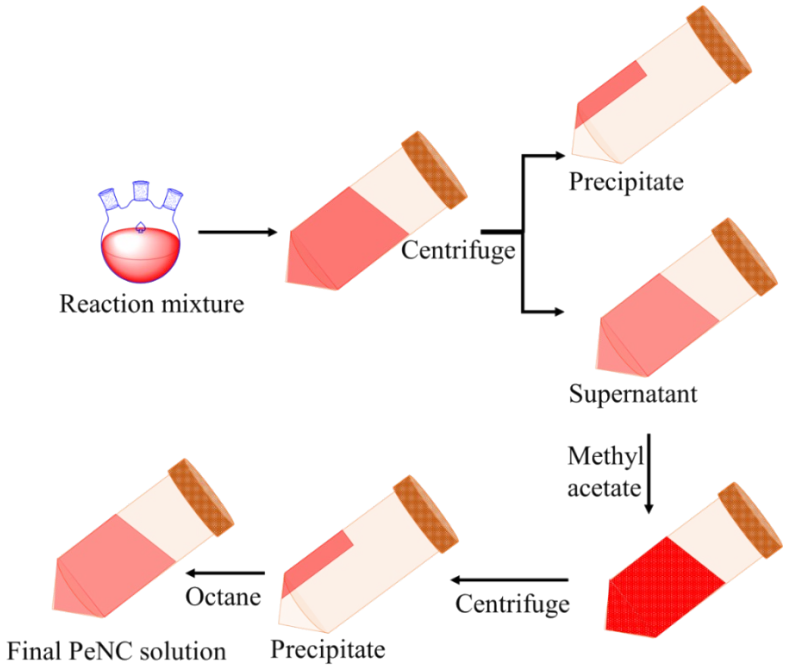
All commercial materials were used without further purification: lead iodide (PbI_2, 99%, Sigma-Aldrich), caesium carbonate (Cs_2CO_3, 99 %, Sigma-Aldrich), formamidinium bromide (FABr, 99 %, Greatcell Solar), butylammonium iodide (BA, Greatcell Solar), phenylethylammonium iodide (PEA, Greatcell Solar), cyclohexylmethylammonium iodide (CHA, Greatcell Solar) and 4-trifluoromethyl-benzylammonium iodide (TFB, Greatcell Solar), oleylamine (OLA, technical grade, 70 %, Sigma-Aldrich), oleic acid (OA, Technical grade, 90 %, Sigma Aldrich), toluene (anhydrous, 99.8 %, Sigma-Aldrich), octane (99.8 %, J. T. Baker). ethylammonium iodide (EA, synthesized in our laboratory) in typical synthesis; hydroiodic acid (HI 57 % in H_2O, Merck) was added in ethylamine.

Preparation of caesium oleate (Cs oleate)

Caesium carbonate (Cs_2CO_3, 0.94 mmol), oleic acid (OA, 3 mL) and octadecene (3 mL) were added to a vial (20 mL). This solution was heated at 150 ^{o}C until the solution become transparent.

Synthesis of perovskite nanocrystals (L1 – L5)

Modified perovskite nanocrystals (PeNC) were synthesized with a novel hot-addition method (HAM) introduced here. To prepare the reference PeNC (L0), we added PbI_2 (1.88 mmol) and octadecene (40 mL) in a round-bottom flask (RB, 50 mL). The mixed PbI_2/octadecene suspension was stirred and heated at 100 °C under vacuum for 1 h to remove water. Afterward, OA (5 mL) and OLA (5 mL) were added to the RB to dissolve PbI_2; the solution became clear. At 140 °C, FABr (1.88 mmol) dissolved in IPA (3 mL) was added; after addition, the solution in the RB changed to turbid orange and then to light yellow as the temperature increased. The solution of caesium oleate (6 mL) was injected into the RB at 200 °C; RB was immediately immersed in an ice bath to suppress further growth of the PeNC to a black phase. To prepare the modified PeNC (L1 – L5), we added organic ammonium iodide salt cation (L*n*I, *n* = 1 – 5, 1.88 mmol) solutions in IPA at 150 °C after addition of FABr before injection of Cs-oleate. After the reaction became completed, the solution was centrifuged at 9000 rpm for 40 min; the precipitate containing particles of large size was discarded. Methyl acetate was added to the supernatant in ratio 1:3 to precipitate PeNC. These PeNC precipitates were collected on centrifugation; octane was added to obtain the final PeNC solutions (Scheme S1).



Scheme S1. Schematic representation of the PeNC purification

Characterizations

The size and shape of PeNC were characterized with a scanning transmission electron microscope (Cs-corrected STEM, JEOL ARM 200F, corrected for spherical aberration); a X-ray diffractometer (Bruker AXS, D8 Advance, Cu Kα irradiation, λ = 154.18 pm) generated X-ray diffraction (XRD) patterns of the PeNC coated on glass substrates; elemental analysis and surface composition were determined with X-ray photoelectron spectra (XPS) (Thermo K-α Surface Analysis); an absorption spectrometer (V-780 JASCO) was used to record absorption spectra for PeNC in range 300-800 nm; photoluminescence (PL) spectra were recorded in range 500-700 nm with excitation at 375 nm (LDH-635, PicoQuant). The PL transients were recorded with a time-correlated single-photon-counting (TCSPC) system (Fluotime 200, PicoQuant, excitation at 375 nm) from a picosecond pulsed-diode laser (LDH-375, PicoQuant, FWHM ~70 ps). An ion TOF-SIMS instrument was used to analyze the surface of the PeNC.

Femtosecond transient absorption spectral (TAS) experiments were performed with a pump-probe spectrometer (Excipro, CDP systems) in combination with an ultrashort pulse Ti:sapphire amplified laser system (Legend USP, 795 nm, 1 kHz, 3 mJ, 35 fs). The pump pulses were generated from an optical parametric amplifier (TOPAS-C). The pump wavelengths for TAS experiments and optical gain experiments were 640 and 395 nm, respectively. The source of the probe pulse was a white-light continuum generation obtained on pumping a sapphire crystal (thickness 3 mm) with a fundamental laser pulse (795 nm) of small energy; the generated white light was limited to range 450–750 nm using a short-pass filter. The cross correlation of the laser system was about 150 fs. The transient spectra were recorded on varying the optical delay between pump and probe pulses using a translational stage. The pump-probe experiments were performed on drop-cast samples in an ethyl-cellulose matrix (thickness ~5 μm) on a 25-mm glass substrate (BK7) while the sample substrate rotated during measurement to avoid photobleaching and thermally induced artifacts. The transient spectra about time zero were corrected for chirp on measuring the optical Kerr signal from blank substrates.

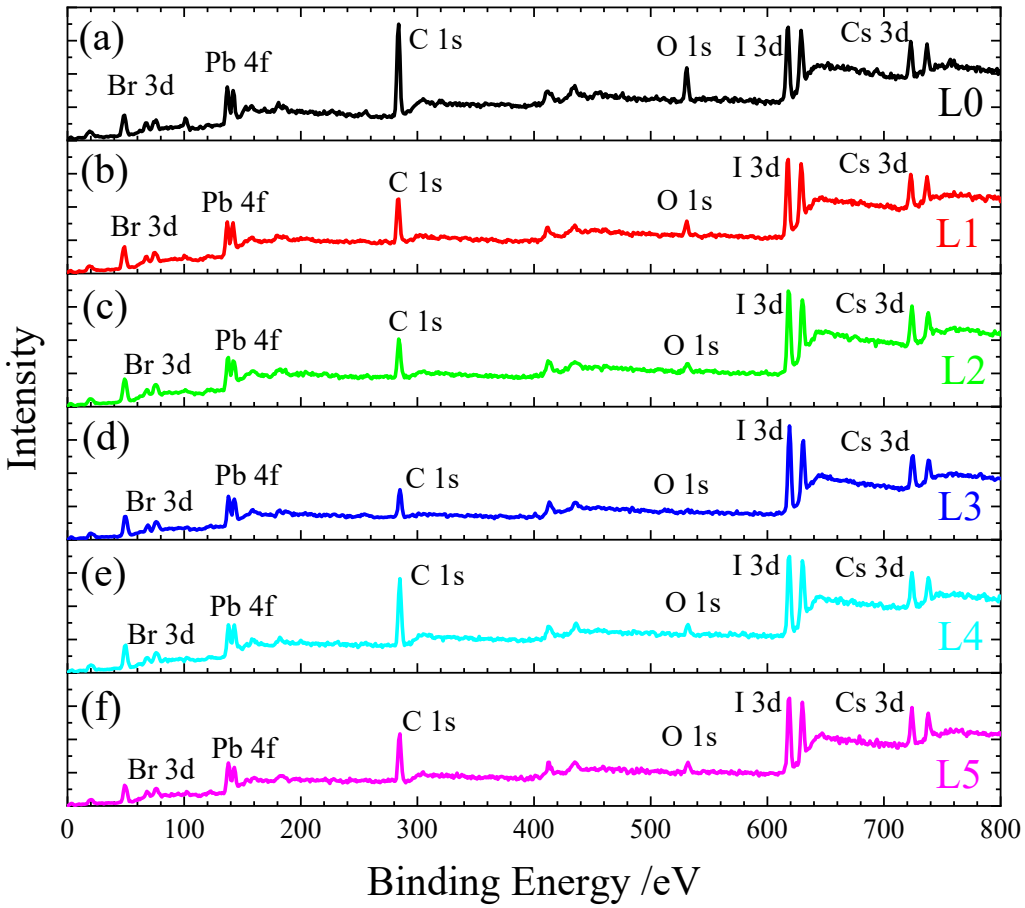


Figure S1. X-ray photoelectron spectra (XPS) of the thin-film PeNC (a) L0, (b) L1, (c) L2, (d) L3, (e) L4 and (f) L5 fabricated with the drop-casting method.

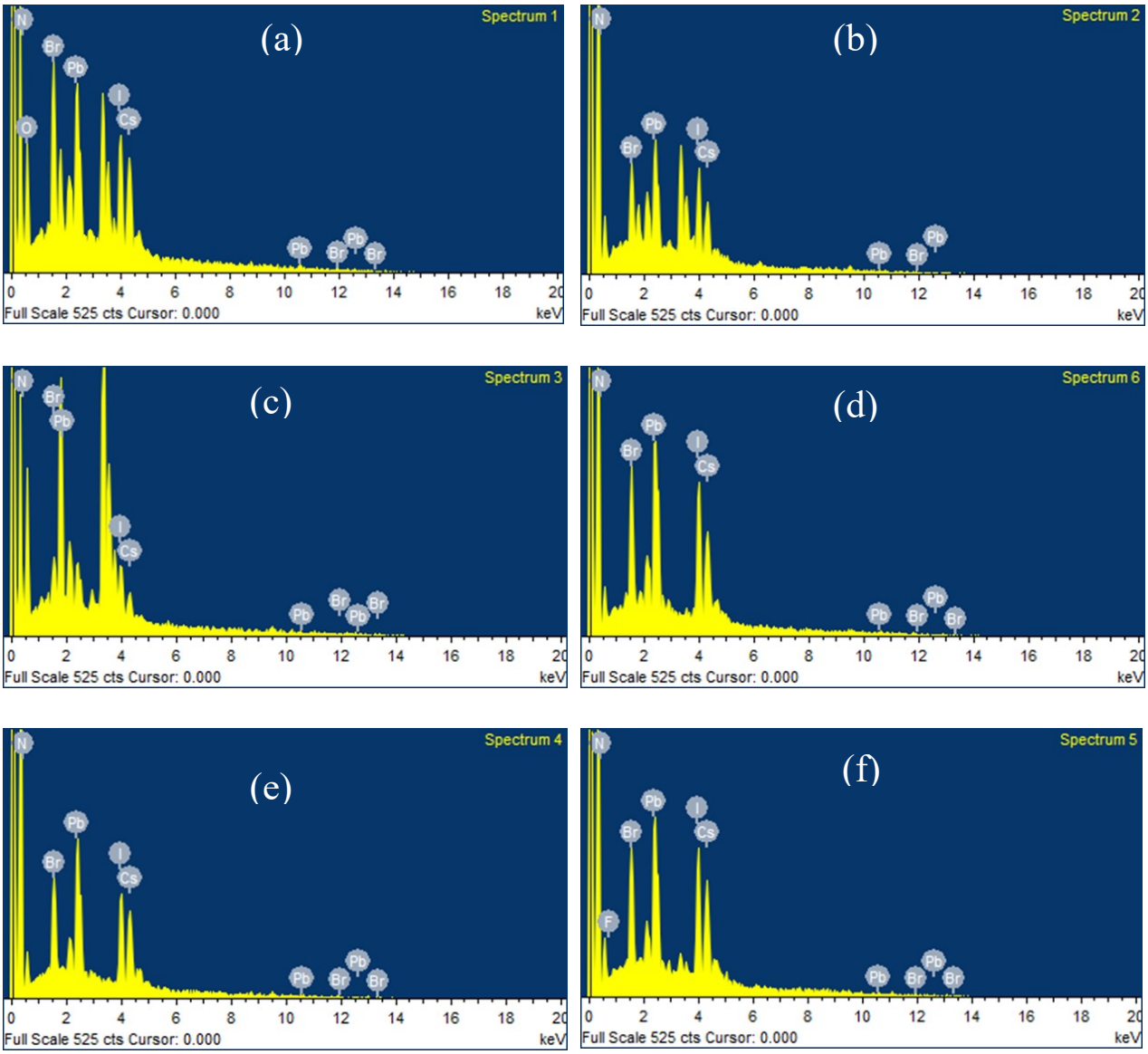


Figure S2. Energy dispersive X-ray spectra (EDAX) of thin-film PeNC (a) L0, (b) L1, (c) L2, (d) L3, (e) L4 and (L5) fabricated with the drop-casting method

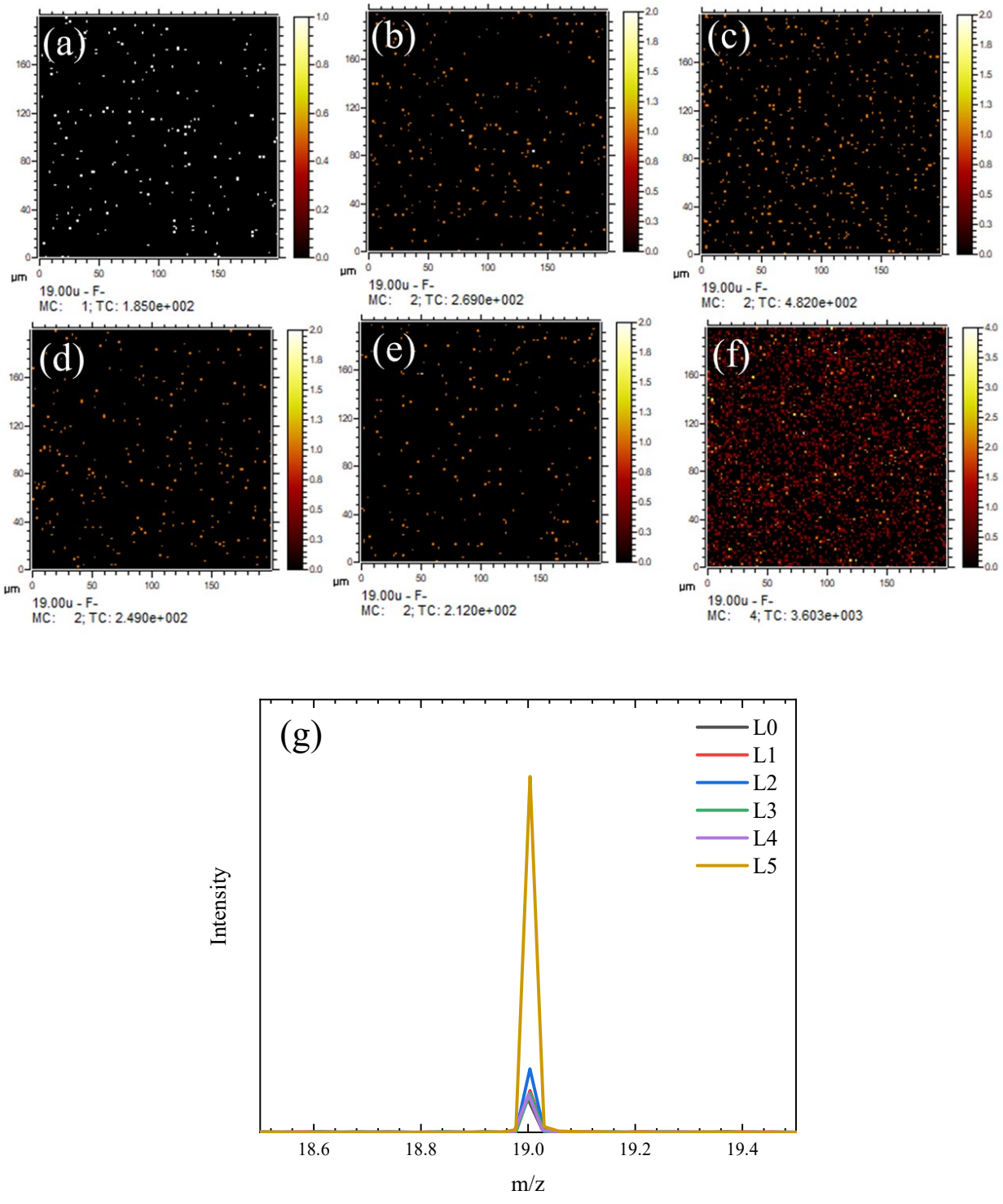


Figure S3. TOF-SIMS images of thin-film samples (a) L0, (b) L1, (c) L2, (d) L3, (e) L4 and (f) L5, and (g) TOF-SIMS mass spectra showing the surface ion density of fluorine on PeNC.

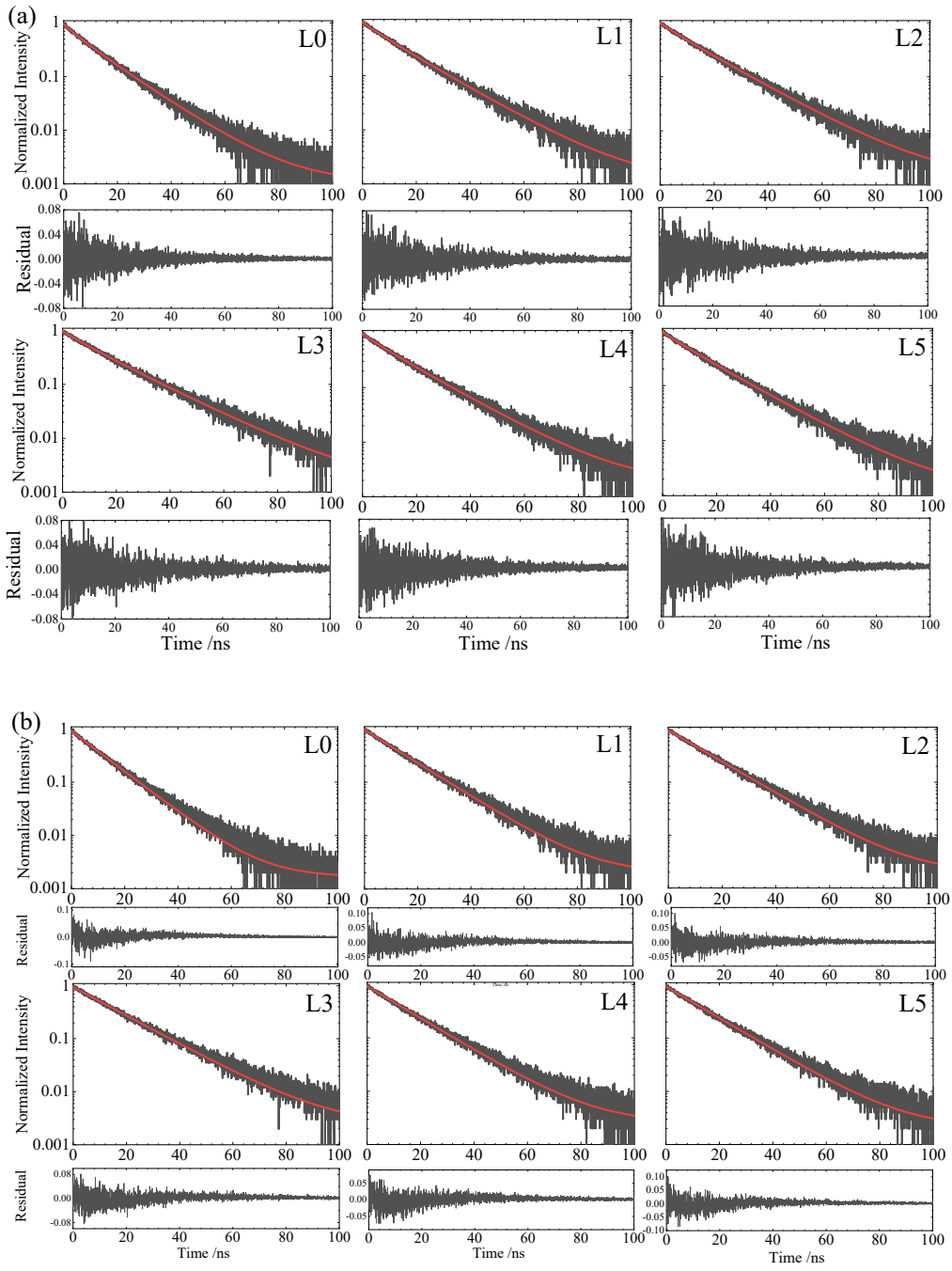


Figure S4. Photoluminescence decay profiles and residual plots of fits using models according to (a) stretched-exponential-decay and (b) single-exponential-decay functions.

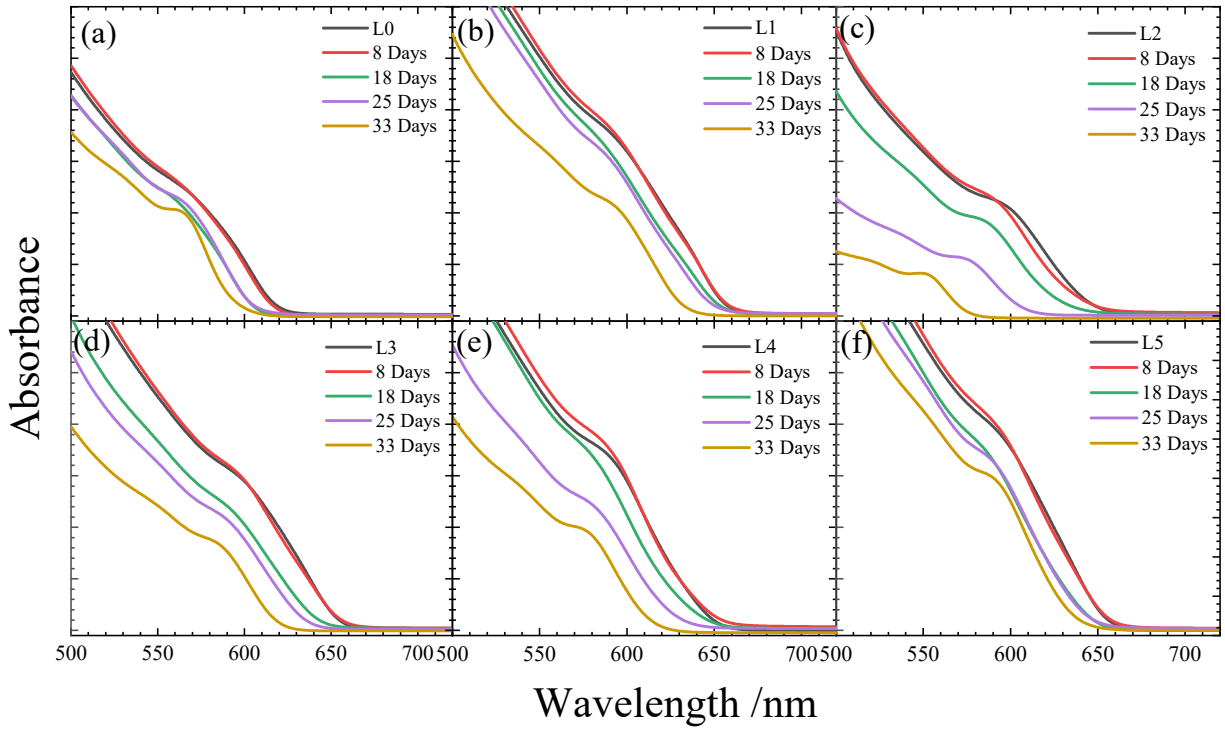


Figure S5. UV-vis spectra showing stability results under ambient air conditions (RH ~60 %) for octane solutions of PeNC (a) L0, (b) L1, (c) L2, (d) L3, (e) L4 and (f) L5.

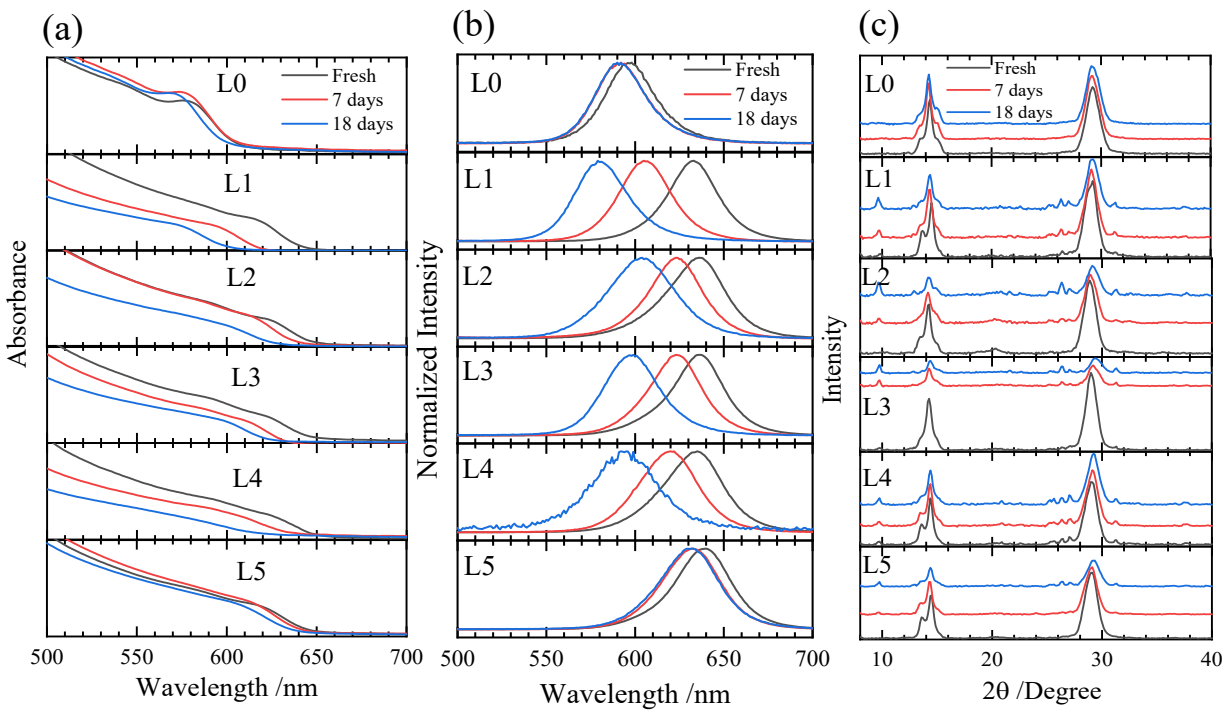


Figure S6. Tests of stability of PeNC films showing (a) UV-vis spectra, (b) PL spectra and (c) XRD patterns of samples L0-L5 stored under ambient air conditions (RH ~30 %) for periods up to 18 days. The diffraction signals at 2θ ~10° in (c) indicate the formation of a 2D-perovskite structure for samples L1-L5.

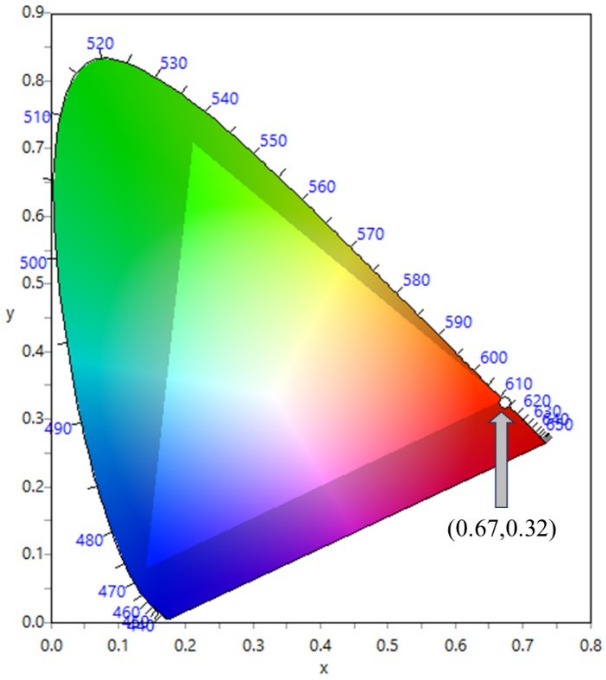


Figure S7. NTSC 1953 colour gamut and Commission Internationale de l'Enclairage (CIE) coordinates of 14-day-old L5 sample simulated using OSRAM software.

Table S1. Surface elemental composition determined from XPS analysis

Sample	Cs/Pb	I/Br	I+Br/Pb	$FA_{(x)}$ [a]	$Br_{(y)}$ [a]	$I_{(3-y)}$ [a]
L0	0.94	1.18	3.65	0.06	1.37	1.63
L1	1.02	1.54	4.22	-	1.18	1.82
L2	1.03	1.86	3.73	-	1.05	1.95
L3	0.88	1.84	3.38	0.12	1.06	1.94
L4	1.04	2.02	3.82	-	0.99	2.01
L5	0.88	1.59	3.57	0.12	1.16	1.84

[a] The values were determined according to the crystal structure $Cs_{1-x}FA_xPbBr_yI_{3-y}$.

Table S2. Elemental composition determined by EDX analysis

Sample	Cs/Pb	I/Br	I+Br/Pb	$FA_{(x)}$[a]	$Br_{(y)}$[a]	$I_{(3-y)}$ [a]
L0	0.98	1.15	3.51	0.02	1.40	1.60
L1	0.67	1.88	3.39	0.33	1.04	1.96
L2	0.79	2.41	3.25	0.21	0.88	2.12
L3	0.68	1.74	2.91	0.32	1.09	1.91
L4	0.81	1.68	2.92	0.19	1.13	1.87
L5	0.93	1.89	3.08	0.07	1.04	1.96

[a] The values were determined according to the crystal structure $Cs_{1-x}FA_xPbBr_yI_{3-y}$.

Table S3. Relative quantum yields of PeNC in octane calculated with DCM dye in ethanol as reference

Sample	Integrated photoluminescence /10^6	Absorbance	Relative Quantum Yield (QY)[a]
DCM	1.9	0.31	0.44
L0	3.9	0.48	0.72
L1	3.7	0.38	0.79
L2	4.4	0.58	0.74
L3	3.9	0.45	0.76
L4	4.3	0.62	0.70
L5	4.3	0.64	0.69

[a] The relative quantum yield was determined with equation $\Phi s = \Phi r \left(\frac{Fs\,(1-10^{-Ar})}{Fr\,(1-10^{-As})}\right)\frac{n_s^2}{n_r^2}$,

in which Φs and Φr are PLQY of PeNC and reference, respectively, *Fs* and *Fr* are integrated fluorescence intensities of PeNC and reference, respectively, *As* and *Ar* are absorbances at the excitation wavelength of PeNC and reference, respectively, n_s and n_r are refractive indices of the solvents used for PeNC and reference, respectively.

Table S4. TCSPC fitted parameters of corresponding PeNC solutions obtained from fitting PL transients (Figure 3) with excitation at 375 nm.

Sample	τ/ns	β	τ_{PL}/ns[a]	$k_r/10^{-7}$ s^{-1}	$k_{nr}/10^{-7}$ s^{-1}
L0	10.6	0.91	11.1	6.49	2.52
L1	13.3	0.93	13.8	5.72	1.52
L2	13.8	0.93	14.3	5.18	1.82
L3	15.3	0.92	15.8	4.78	1.51
L4	13.8	0.94	14.2	4.92	2.11
L5	13.9	0.93	14.4	4.77	2.14

[a] Average PL lifetimes were calculated with equation $\tau_{PL} = \frac{\tau}{\beta}\Gamma(\frac{1}{\beta})$; here Γ is Gamma function.