

Supporting Information

Ligand Assisted Swelling-Deswelling Microencapsulation (LASDM) for Stable, Color Tunable Perovskite-Polymer Composites

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Experimental Section

Materials: Polystyrene substrates were purchased from VWR International, Inc. Acrylonitrile–butadiene–styrene films and cellulose acetate films were purchased from McMaster-Carr. CsCl (99.9%), CsBr (99.999%), CsI (99.999%), PbBr₂ (99.999%), *N,N*-dimethylformamide (extra dry, 99%), octylamine (99%) and oleic acid (90%) were purchased from Sigma-Aldrich. PbCl₂ (99%) and PBI₂ (99%) were purchased from Fisher. CH₃NH₃Br (CH₃NH₃ = MA) and MAI were purchased from Luminescence Technology Corp. MAI was synthesized using the method reported before.^[14] Unless stated otherwise, all materials were used as received.

Perovskite precursor solutions: CsPbX₃ (X stands for Cl, Br or I) perovskite precursor solutions are prepared with concentration of 0.03 mmol mL⁻¹ by mixing CsX and PbX with/without certain ligand(s) [CsX:PbX:octylamine(for one ligand/two ligands):Oleic acid (for two ligands)] = 1:1:0.75:0.75 molar ratio) in DMF while stirring for at least 2 hours before use.

MAPbX₃ perovskite precursor solutions are prepared with a concentration of 0.03 mmol mL⁻¹ by mixing MAX and PbX with/without certain ligand(s) [MAX:PbX:octylamine(for one ligand/two ligands):oleic acid (for two ligands)] = 1.4:1:0.6:3.9 molar ratio) in DMF while stirring for at least 2 hours before use.

Perovskite–polymer composite films: Perovskite precursor solutions were processed onto different polymer film substrates through cotton swab painting or spin-coating at 3000 rpm, followed by baking at 30–75 ° C for 1–8 h inside a glovebox.

Characterizations: HRTEM analyses on the cross-sections of the PPCs were carried out using FEI Tecnai F30 TEM. The cross-sectional samples were prepared using FEI 200 TEM focused-ion-beam instrument. XRD patterns were measured using PANalytical Empyrean system, with Cu K α radiation ($\lambda = 0.154059$ nm) at 45 kV and 40 mA.

PLQY of samples were measured in a FluoroMax Plus (Horiba Jovin Yvon) spectrofluorometer equipped with the Quanta-Phi integrating sphere.

Radiative lifetimes are measured with a home-built sample-scanning confocal microscope described elsewhere.¹ Time correlated single photon counting (TCSPC) excited state lifetime studies were completed by parking an area of interest of the samples over the focused pulsed laser beam with 373 nm wavelength (Picoquant LDH-P-C-375), and collecting photons with a fast single photon counting detector (Picoquant, Micro Photon Devices, PDM series). Photon timing was measured using a pulsed laser driver (PDL 800-D) that provided the timing signal to a PicoHarp 300 TCSPC module in combination with a detector router (PHR 800), all from Picoquant. The time-resolved PL decay curves were fitted with a biexponential function of time and the average recombination lifetime is estimated by averaging both time constants with their weighting factors.

For temperature-dependent PL measurements, the samples were put inside the Linkam LTS350 cryostat, with a heating rate of 5 °C min⁻¹. Laser diode excitation at 405 nm (Thorlabs CPS405) was used and the CsPbBr₃-polymer film was in-situ heated on the stage whose temperature was controlled by a temperature controller (Linkam TMS 94). The PPCs were heated up to a certain temperature, held for 2–3 min to be stable, measured for the spectra (Ocean Optics Spectrometer USB 2000+) and then proceeded to the next temperature point immediately.

To measure the photo-stability, the samples were mounted on a fixed stage. A 457-nm blue laser (Cobolt Twist 200) with an irradiance of 100 mW/cm² was applied as the excitation light source. The PL spectra were in-situ recorded by a spectrometer (Ocean Optics Spectrometer USB 2000+).

To test the stability in both high-temperature and high-humidity environment, the samples were stored in a home-made incubator with 70 °C and 90% RH under normal room lighting, while the references were stored in dark ambient air at room temperature. When conducting relative PL measurements, the samples were taken out from the incubator and cooled down to room temperature. A 457-nm blue laser (Cobolt Twist 200) with an irradiance of 10 mW/cm² was applied as the excitation light source and the PL spectra of both references and samples were recorded by a spectrometer (Ocean Optics Spectrometer USB 2000+). All the stability tests were carried out on as-prepared bare films without any additional barrier protection.

The transparent projection display is enabled by directly exciting PPC film using TransPlay Laser Lineshow Projector developed by Sun Innovations, Inc. The MEMS laser projector has a light wavelength of 405 nm, power output < 300 mW and a scanning speed of 30 kHz.

The viewing angle of transparent display PPC screen film is measured with a 405 nm laser as excitation source (normal incident angle) and Konica Minolta LS-110 luminance meter as the detector.

Reference

[1] D. Tenery, J. G. Worden, Z. J. Hu, and A. J. Gesquiere, *J. Lumin.*, 2009, **129**, 423.

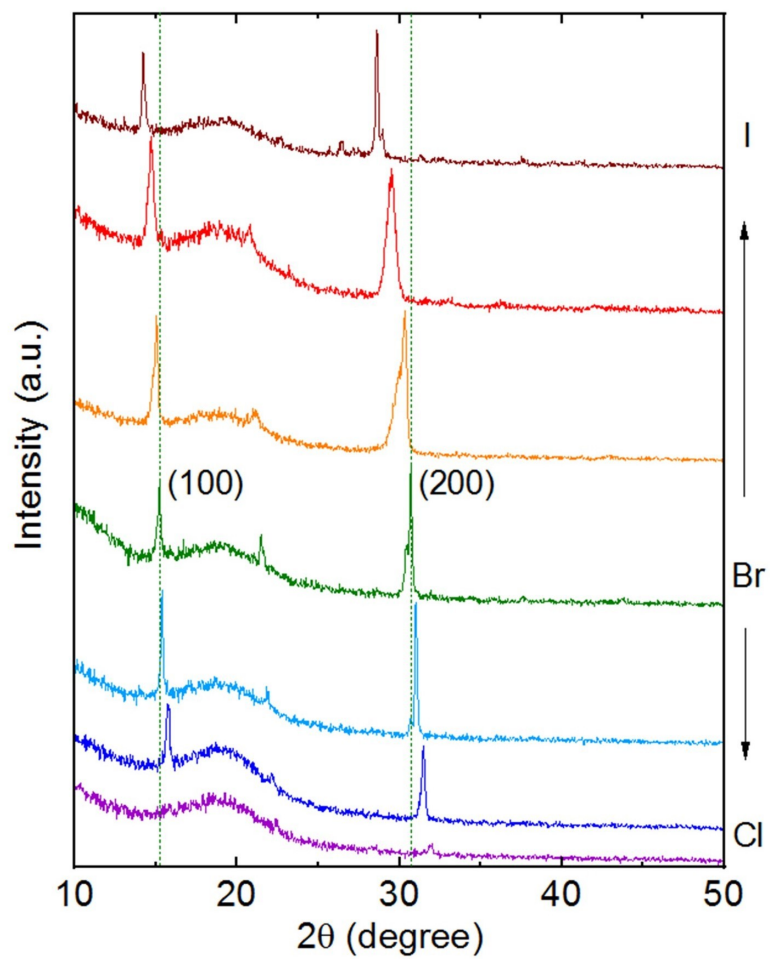


Figure S1. XRD patterns of CsPbX₃-PS composites prepared with single ligand.

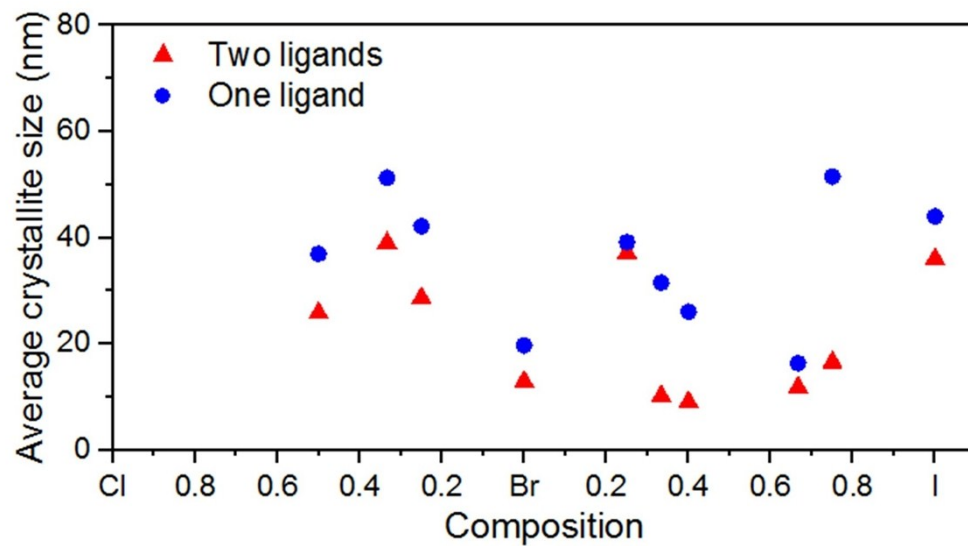


Figure S2. Comparison of the average crystallite size in CsPbX₃-PS composites prepared with two ligands versus single ligand.

Composition	Peak wavelength (nm)	FWHM (nm)
CsPbCl₂Br₁	454.0	19.4
CsPbCl_{1.2}Br_{1.8}	482.1	17.6
CsPbCl₁Br₂	492.0	17.2
CsPbCl_{0.75}Br_{2.25}	501.6	18.5
CsPbCl_{0.45}Br_{2.55}	512.0	17.4
CsPbBr₃	527.3	17.8
CsPbBr_{2.25}I_{0.75}	560.0	24.6
CsPbBr₂I₁	593.7	33.4
CsPbBr_{1.8}I_{1.2}	606.9	35.9
CsPbBr_{1.5}I_{1.5}	640.5	41.5
CsPbBr₁I₂	655.4	30.0
CsPbBr_{0.75}I_{2.25}	665.5	31.2
CsPbI₃	702.5	37.0

Table S1. PL emission peak wavelength and full width at half maximum (FWHM) of CsPbX₃-PS composites of different halide compositions.

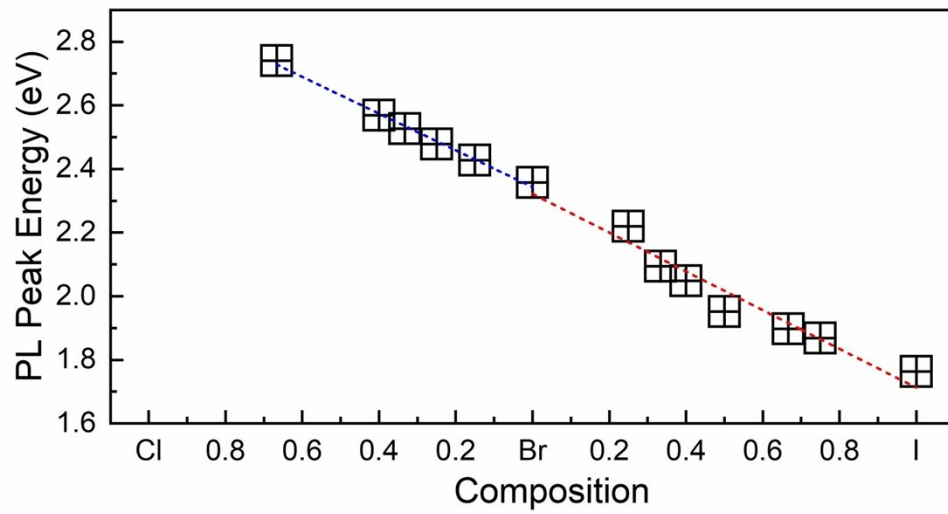


Figure S3. PL peak energy as a function of halide composition in CsPbX₃-PS composites. For CsPb(Cl_{1-x}Br_x)₃, the linear fitting is: Peak Energy = 2.92 - 0.58x; For CsPb(Br_{1-y}I_y)₃, the linear fitting is: Peak Energy = 2.32 - 0.60y.

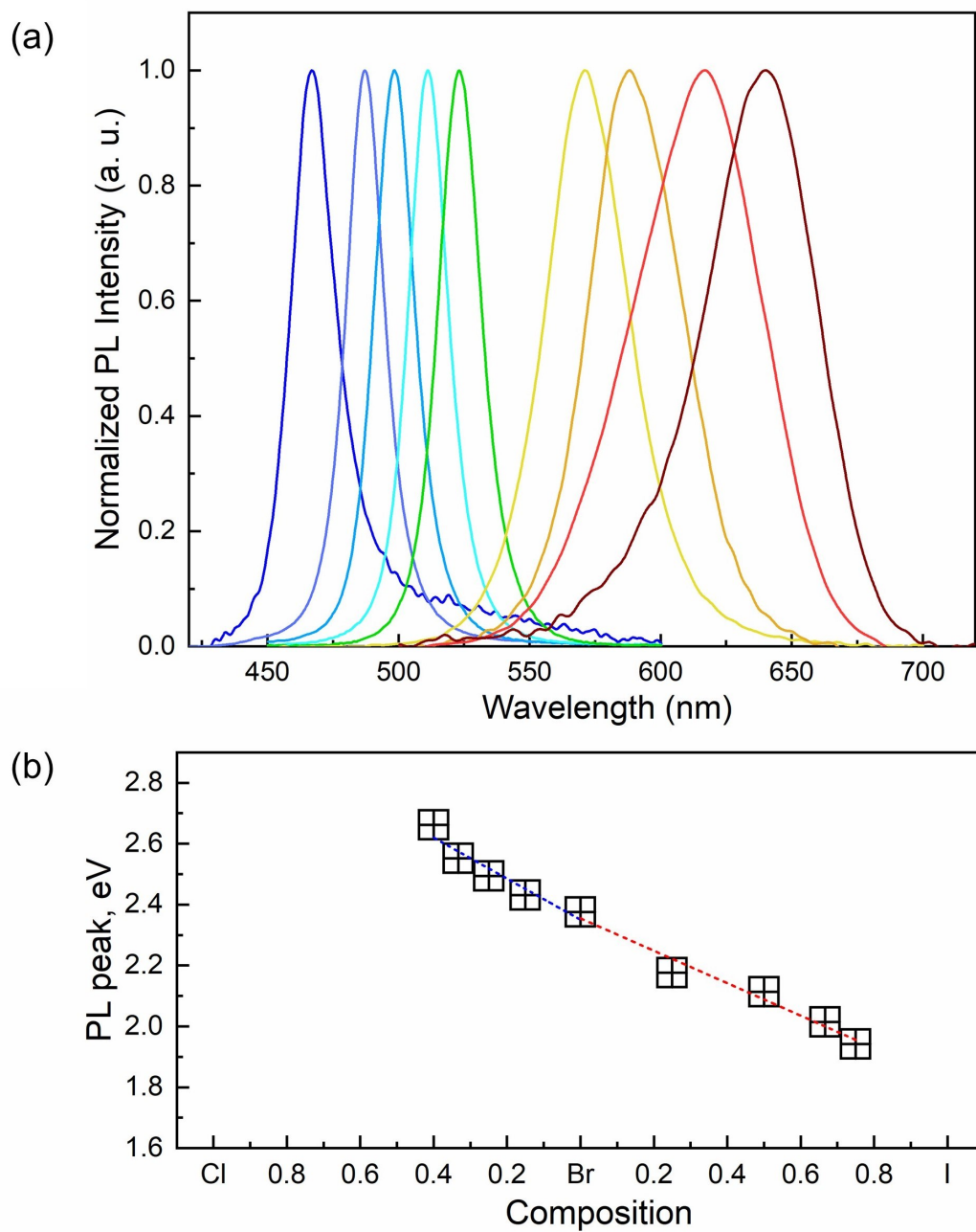


Figure S4. (a) PL emission spectra and (b) PL peak energy as a function of halide composition in CsPbX₃-CA composites. For CsPb(Cl_{1-x}Br_x)₃, the linear fitting is: Peak Energy = 3.03 – 0.68x; For CsPb(Br_{1-y}I_y)₃, the linear fitting is: Peak Energy = 2.35 – 0.53y.

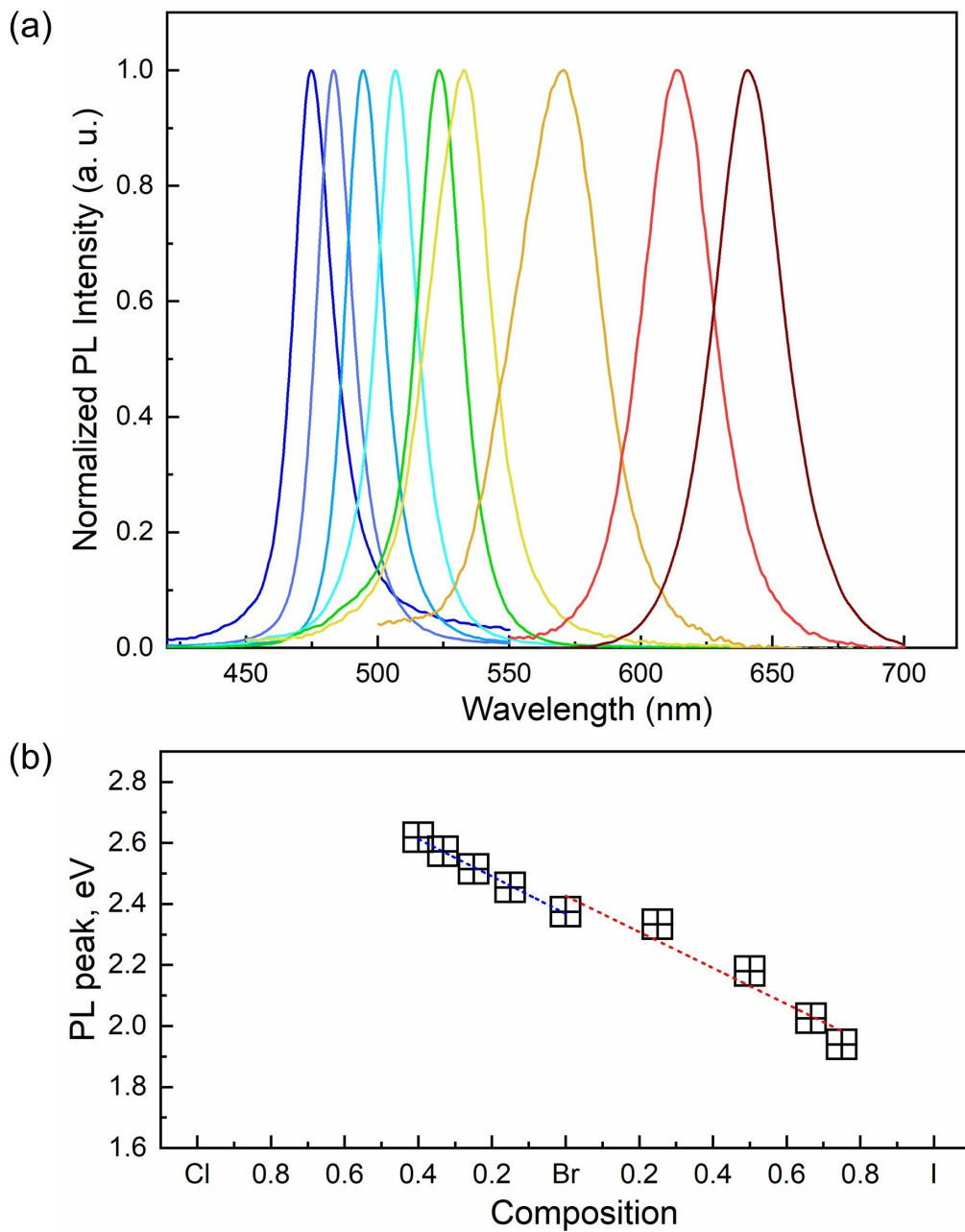


Figure S5. (a) PL emission spectra and (b) PL peak energy as a function of halide composition in CsPbX₃-ABS composites. For CsPb(Cl_{1-x}Br_x)₃, the linear fitting is: Peak Energy = 2.97 – 0.59x; For CsPb(Br_{1-y}I_y)₃, the linear fitting is: Peak Energy = 2.43 – 0.60y.

Polymer	Hildebrand solubility parameter (Mpa^{1/2})
Polystyrene (PS)	19
Cellulose acetate (CA)	25.1
Acrylonitrile butadiene styrene (ABS)	19.2~21.35

Table S2. Hildebrand solubility parameters of different polymers.

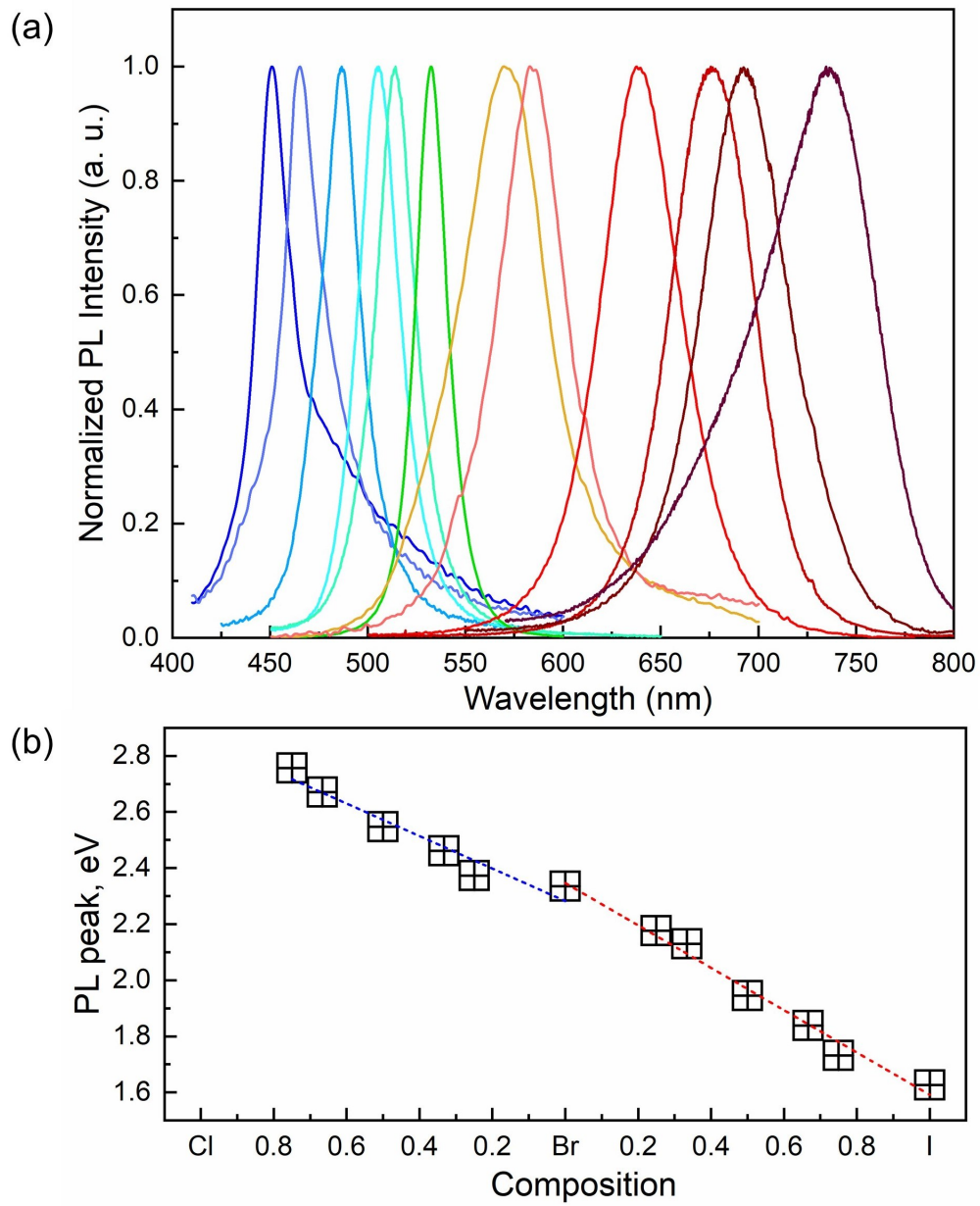


Figure S6. (a) PL emission spectra and (b) PL peak energy as a function of halide composition in MAPbX₃-PS composites. For MAPb(Cl_{1-x}Br_x)₃, the linear fitting is: Peak Energy = 2.86 – 0.56x; For MAPb(Br_{1-y}I_y)₃, the linear fitting is: Peak Energy = 2.35 – 0.75y.

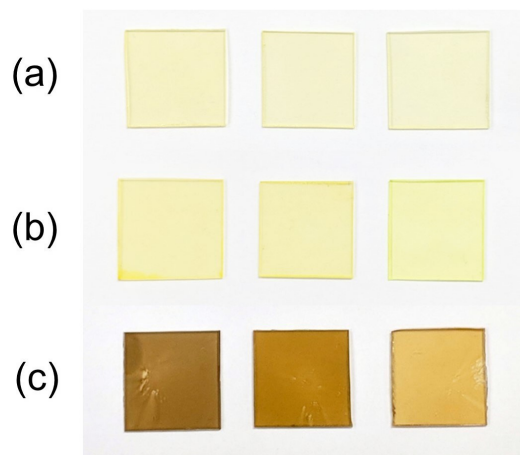


Figure S7. Photographs of (a) blue ($\text{CsPbClBr}_2\text{-PS}$), (b) green ($\text{CsPbBr}_3\text{-PS}$) and (c) red ($\text{CsPbBrI}_2\text{-PS}$) composites prepared with (left) no ligand, (middle) one ligand or (right) two ligands under ambient light.

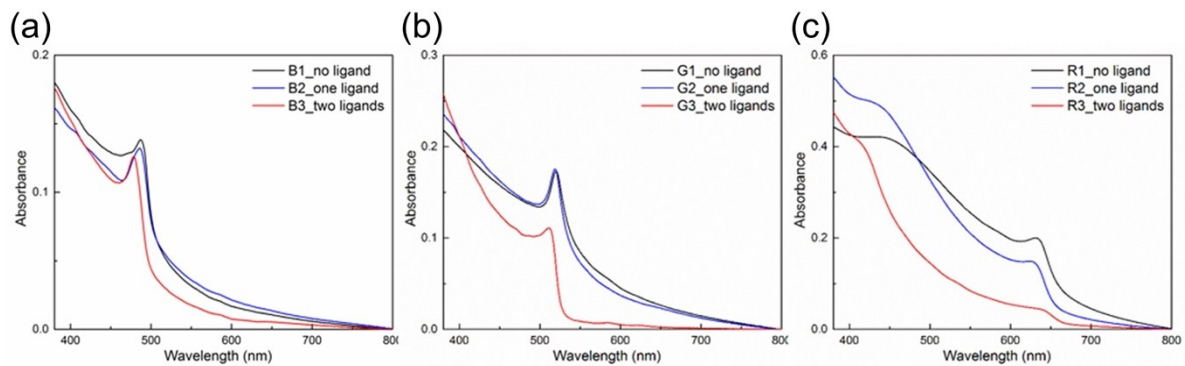


Figure S8. UV-vis absorption spectra demonstrating scattering effect of the (a) blue (CsPbClBr₂-PS), (b) green (CsPbBr₃-PS) and (c) red (CsPbBrI₂-PS) composites prepared with no ligand (black line), one ligand (blue line), or two ligands (red line).

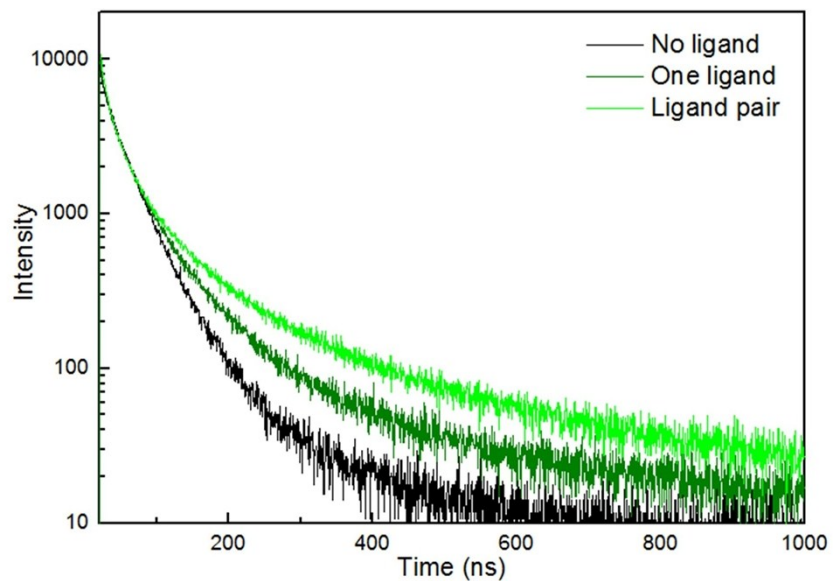


Figure S9. PL decay curves for CsPbBr₃-PS composites prepared with no ligand (black line), one ligand (dark green line), or two ligands (green line). Red lines are the fitting curves for each condition.

Table S3: PL decay lifetimes of CsPbBr₃-PS composites prepared with different ligand conditions. τ_1 : slow PL lifetime, τ_2 : fast PL lifetime, τ_{avg} : average PL lifetime.

Condition	τ_1 (ns)	f_1 (%)	τ_2 (ns)	f_2 (%)	τ_{avg} (ns)
No ligand	26.77	72.4	64.2	27.6	37.1
One ligand	27.4	72.6	97.1	27.4	46.5
Ligand pair	25.5	73.8	137.7	26.2	55.0

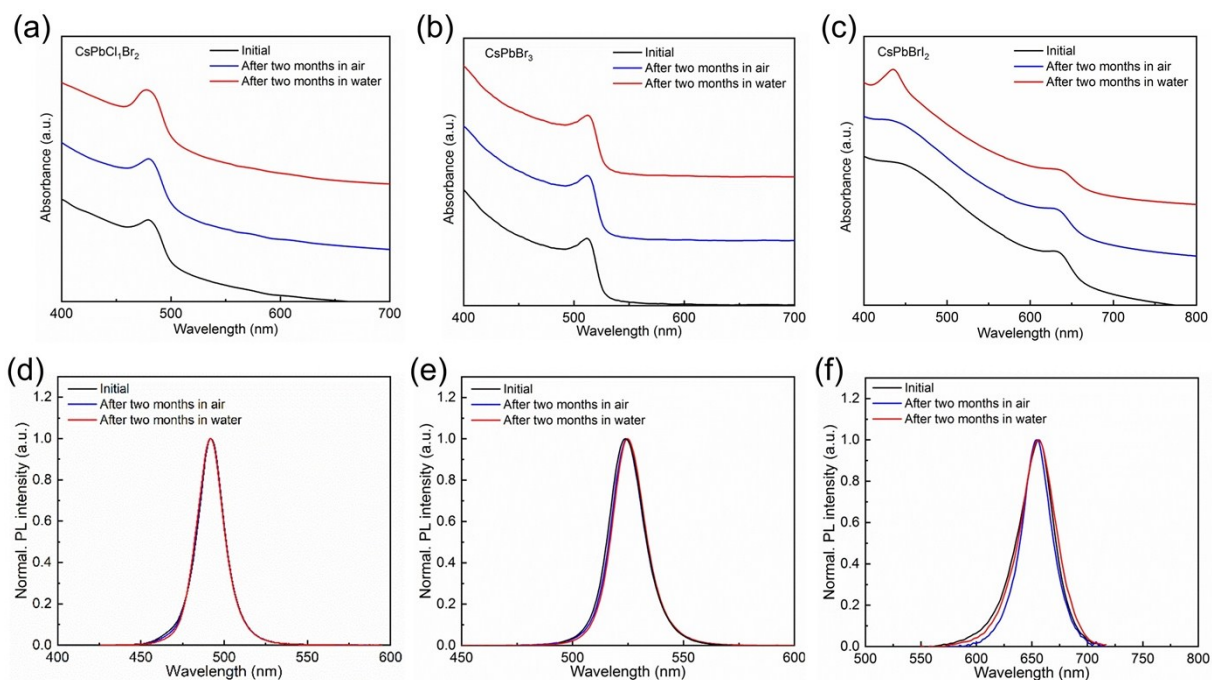


Figure S10. (a-c) UV-vis absorption spectra and (d-f) normalized PL emission spectra of samples at initial state, after two months in air, or after two months in water. (a, d) blue CsPbClBr₂-PS composites. (b, e) green CsPbBr₃-PS composites. (c, f) red CsPbBrI₂-PS composites.

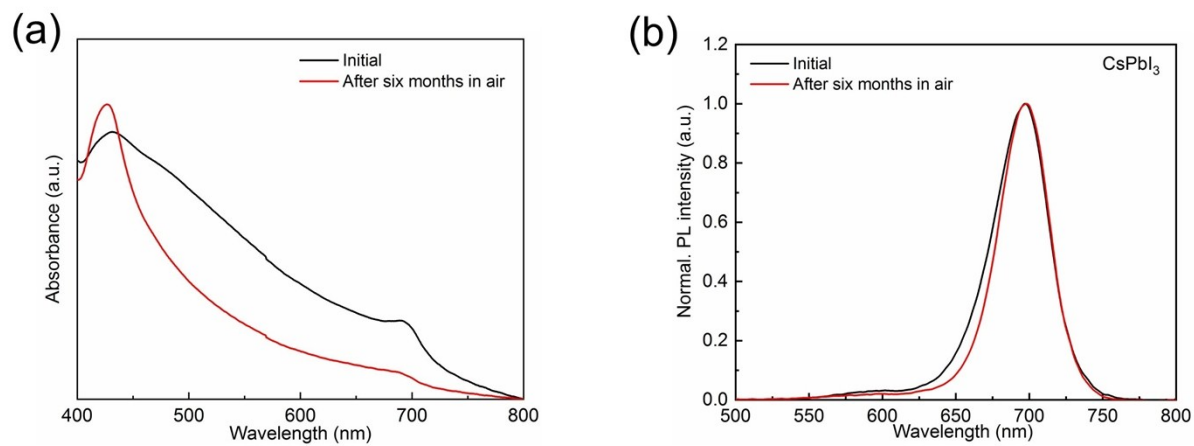


Figure S11. (a) UV-vis absorption spectra and (b) PL emission spectra of CsPbI₃-PS composites before and after six months storage in air.

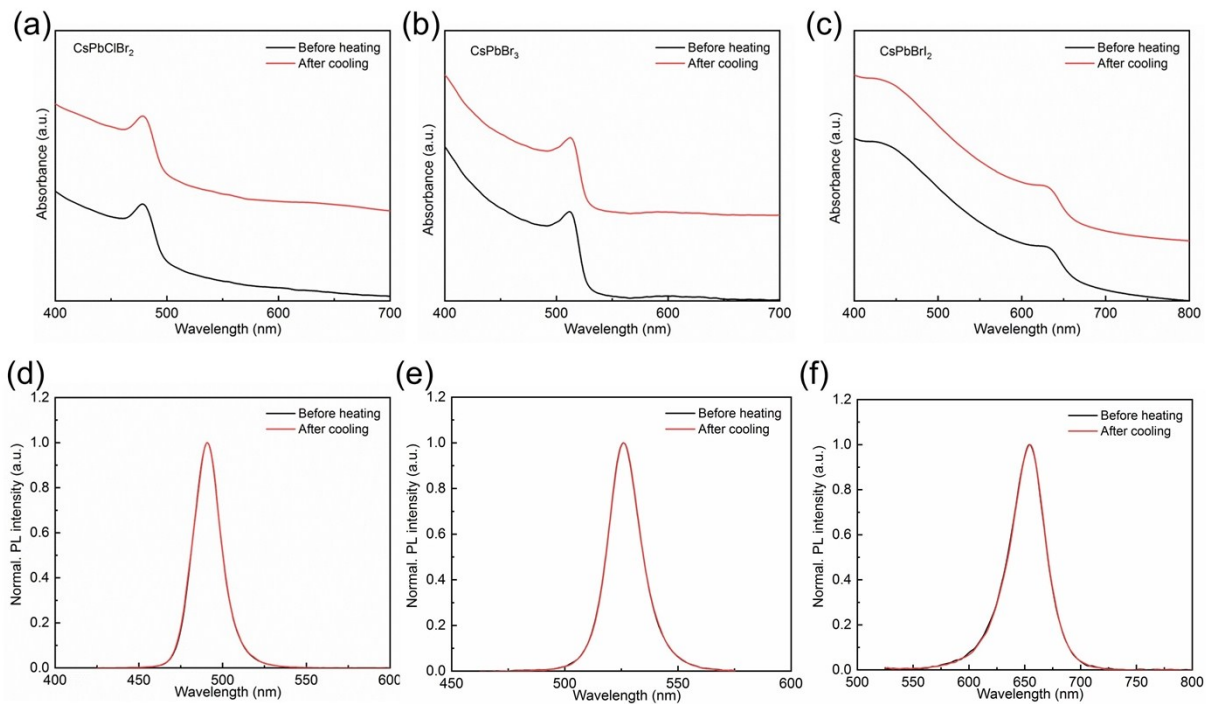


Figure S12. (a-c) UV-vis spectra and (d-f) normalized PL emission spectra of samples before and after heating treatment. (a, d) blue CsPbClBr₂-PS composites; (b, e) green CsPbBr₃-PS composites; (c, f) red CsPbBrI₂-PS composites.

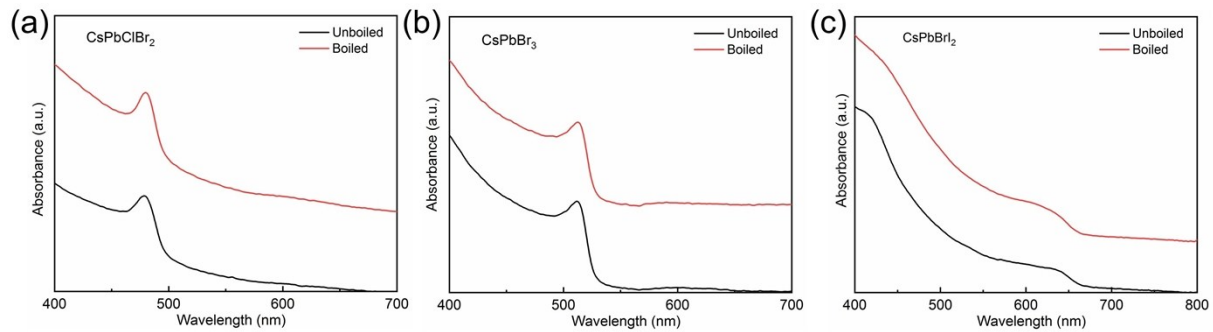


Figure S13. UV-vis spectra of samples before and after boiling treatment. (a) blue CsPbClBr₂-PS composites; (b) green CsPbBr₃-PS composites; (c) red CsPbBrI₂-PS composites.

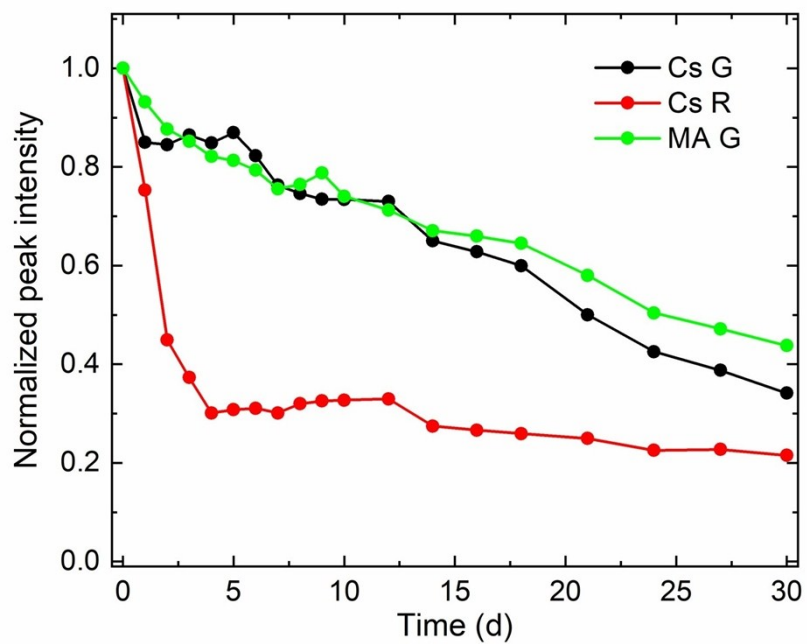


Figure S14. The PL evolution of different PPCs over time under constant temperature (70 °C) and humidity (90% RH).

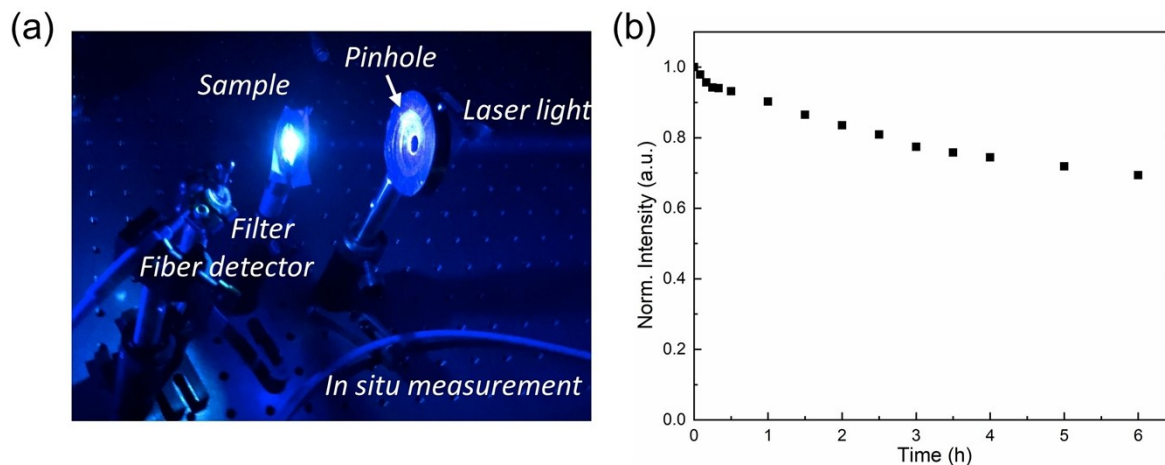


Figure S15. Photostability of green PPCs. (a) In situ photostability measurement setup with a collimated laser beam excitation. Laser flux density: $I(457\text{ nm}) = 100\text{ mW/cm}^2$; (b) Relative PL intensity under excitation of a 457-nm laser at different time. It should be noted that normally the composite film can recover its PL intensity after the excitation is turned off. But here a more rigorous condition, in situ measurement, is applied.

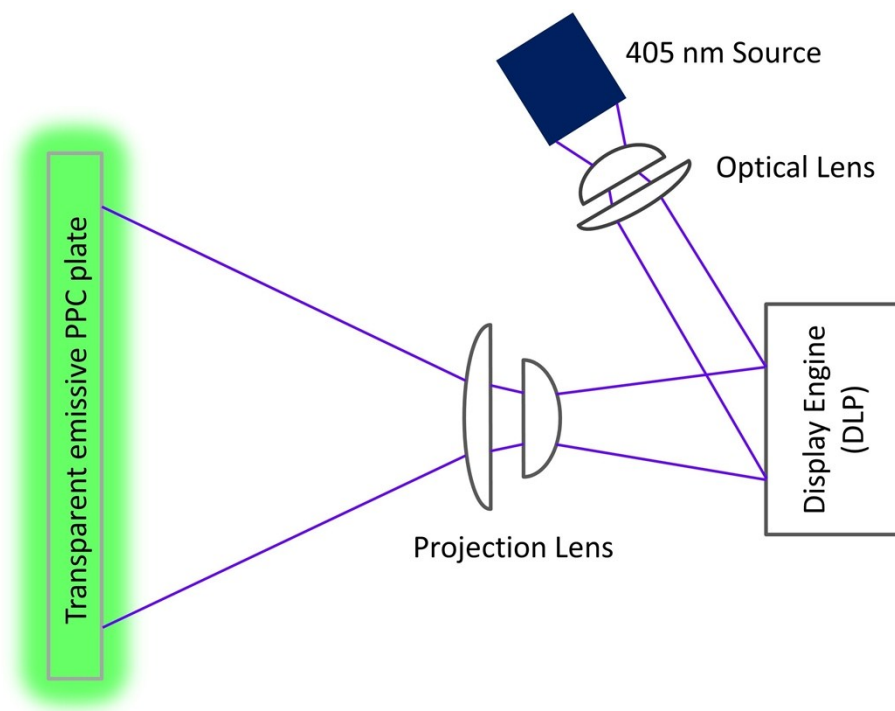


Figure S16. Schematic plot of the transparent emissive projection display. A 405 nm UV light source is manipulated by a display engine to form images and the images are projected onto the large-size PPC plate. Abbreviation: DLP (digital light processing).

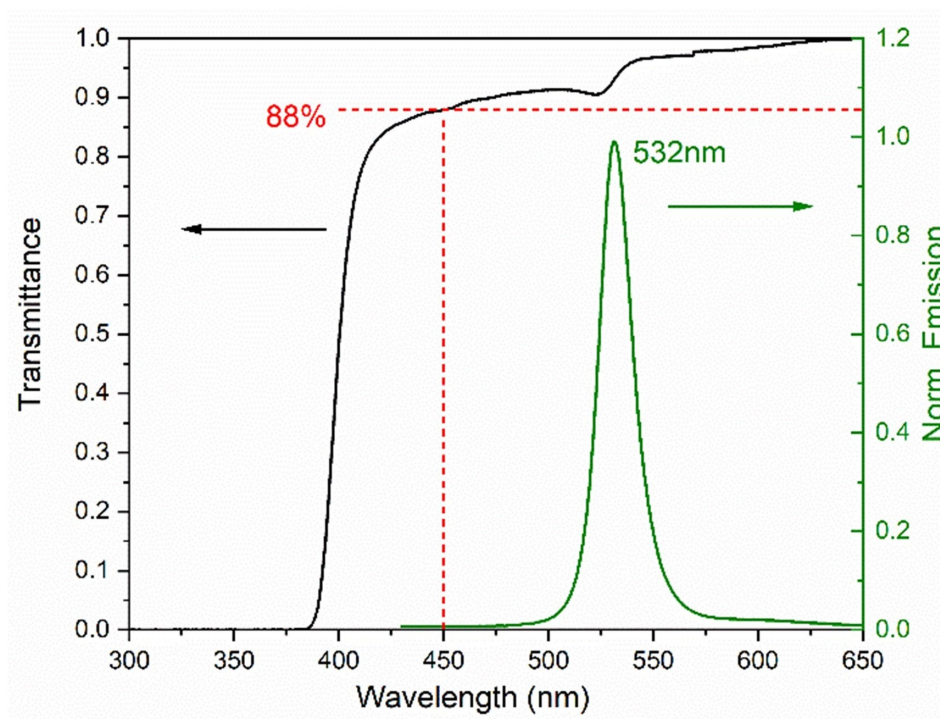


Figure S17. Transmittance and PL emission of the PPC plate for transparent projection displays.