

Supporting Information:

# Photonic Enhancement in Photoluminescent Metal Halide Perovskite–Photonic Crystal Bead Hybrids

*Victoria Lapointe,<sup>a</sup> Christian J. Imperiale,<sup>b</sup> Sollavi Chengadu,<sup>a</sup> Cristina Pomilio,<sup>a</sup> Meera  
Ganesh,<sup>a</sup> Stéphane Kéna-Cohen,<sup>b</sup> Marek B. Majewski<sup>a\*</sup>*

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

<sup>b</sup> Department of Engineering Physics, Polytechnique Montréal, Montréal, Quebec, Canada

\*E-mail: [marek.majewski@concordia.ca](mailto:marek.majewski@concordia.ca)

## Experimental Methods

### *Materials*

All chemicals were used as received from commercial sources:  $\text{Cs}_2\text{CO}_3$  (Alfa Aesar), oleic acid (OA, 90%, Alfa Aesar), tri-n-octylphosphine (TOP, Alfa Aesar), oleylamine (OLA, 70%, Sigma-Aldrich), 1-octadecene (90%, Sigma-Aldrich), KBr (Sigma-Aldrich),  $\text{Pb}(\text{NO}_3)_2$  (American Chemicals),  $\text{PbCl}_2$  (Baker), hexanes (98%, Sigma-Aldrich), acetone (Thermo Fisher), polystyrene microspheres (with sizes of 190 nm and 370 nm, Polysciences Inc.), and silicone oil (Thermo Fisher).

### *General Synthesis of Photonic Crystal (PC) Polystyrene Microbeads*

To prepare PC microbeads, 3  $\mu\text{L}$  of 3% polystyrene microsphere dispersion with a known diameter (190 nm and 370 nm) was injected into silicone oil contained within a polytetrafluoroethylene (PTFE) evaporating dish (63 or 79 mm in diameter, and 10 or 13 mm in depth) to undergo self-assembly. The PTFE dish is necessary in the synthesis of the PC microbeads for its shallow depth, increased surface area, and its hydrophobic nature where the polystyrene dispersion is also hydrophobic, and this arrangement enables the formation of spherical droplets within the silicone oil during the drying process. This apparatus was placed in an 80 °C oven for 24 – 48 hours to ensure the full evaporation of water to yield photonic microbeads composed of the corresponding polystyrene spheres. The microbeads were then washed with hexanes at least three times to remove all the silicone oil and preserved in a scintillation vial. Microbeads with apparently similar diameters (between 500 – 700  $\mu\text{m}$  from optical light microscopy) were manually isolated and selected for further investigations.

### *General Synthesis of PNCs via Hot Injection*

*Preparation of PbBr<sub>2</sub> Solution* KBr (2.00 g, 16.8 mmol) was dissolved in water (18 MΩ, 4 mL) and stirred for a several minutes. Pb(NO<sub>3</sub>)<sub>2</sub> (3.00 g, 9.10 mmol) was dissolved in water (6 mL) and stirred for 10 minutes. Once both solutions were clear, they were combined and mixed in a separate beaker for 10 minutes. The resulting white precipitate was collected by vacuum filtration. The product was then placed in a vial and dried for a minimum of 2 hours in a 60 °C oven prior to use in the next stage of the synthesis.

### *Preparation of Cs-oleate Solution*

Cs<sub>2</sub>CO<sub>3</sub> (0.814 g, 2.50 mmol), octadecene (40 mL) and OA (2.50 mL, 7.90 mmol) were combined in a 100 mL round-bottom flask. This mixture was heated in a heating mantle to 100 °C while stirring until dissolution, then the temperature was increased to 130 °C for injection while being sparged with nitrogen.

### *Synthesis of CsPbBr<sub>3</sub> PNCs*

A 25 mL round-bottom flask was charged with octadecene (5 mL), PbBr<sub>2</sub> (69.0 mg, 0.200 mmol), OLA (0.50 mL, 1.5 mmol) and OA (0.50 mL, 1.6 mmol). This mixture was heated with stirring while being sparged with nitrogen in a heating mantle to 120 °C until it was fully dissolved. The temperature was then raised to 200 °C. Once the new temperature had been reached and the solution was clear, the Cs-oleate solution (0.40 mL) was quickly injected. This reaction mixture was left to react for 5 seconds and then the flask was placed in an ice water bath; yielding a bright green or bright yellow-green precipitate. Once the solution cooled, the product was placed in a

microcentrifuge tube, and was centrifuged at 13400 RCF for 5 minutes. The supernatant was discarded, and the resulting pellet was dispersed in hexanes and kept in a scintillation vial.

#### *Synthesis of CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub>PNCs*

A 25 mL round-bottom flask was charged with octadecene (5 mL), PbBr<sub>2</sub> (34.5 mg, 0.0950 mmol), PbCl<sub>2</sub> (26.3 mg, 0.0950 mmol), OLA (0.50 mL, 1.5 mmol), OA (0.50 mL, 1.6 mmol), and TOP (0.50 mL, 1.1 mmol). This mixture was heated with stirring while being sparged with nitrogen in a heating mantle to 120 °C until it was fully dissolved. The temperature was then raised to 185 °C. Once the new temperature had been reached and the solution was clear, the Cs-oleate solution (0.50 mL) was quickly injected. This mixture was immediately cooled in an ice water bath, yielding a light yellow-green clear solution. Once cooled, the product was placed in a centrifuge tube, and was centrifuged at 13400 RCF for 5 minutes. The supernatant was discarded, and the resulting pellet was dispersed in hexanes and kept in a scintillation vial.

#### *Formation of PC@PNC Microbead Hybrids*

Polystyrene microbeads were manually separated from the stockpile and placed in a 20 mL scintillation vials. Approximately 1 – 2 mL of PNC colloidal solution was syringe-filtered through a 0.2 μm PTFE filter onto the PC microbeads. The vial containing the two materials was placed in a vacuum oven without heating and left to dry under low vacuum (0.03-0.06 atm) for 48 hours until the PNC appeared dried and absorbed by the PC microbeads. The resulting hybrids were then washed with hexanes to remove any PNCs that were not fully incorporated within the beads.

### *Water Stability Tests for PNC Colloids*

PNC colloids were evaluated in water to compare directly with the water stability of the PC $\subset$ PNC hybrids. By combining three drops of the colloid with distilled water in a cuvette for three seconds, a photoluminescence time-based measurement was observed over a 300 second timeframe measuring the change in intensity at the maximum emission peak.

### *Water Stability Tests for PC $\subset$ PNC Microbead Hybrids*

Hybrids were placed in a 20 mL scintillation vial with ca. 10 mL of water (18 M $\Omega$ ). The reflectance and photoluminescence data of the beads was collected every 4 – 5 days at first and then every week afterwards until they were no longer emissive. After all optical characterization, the beads were first washed with hexanes, left to dry and then put back into the same vial of distilled water until the test was complete. To evaluate any inherent moisture stability increases (owing to the intrinsic hydrophobic nature of the polystyrene microspheres) associated with hybrid formation, once the PC beads underwent vacuum drying with corresponding PNCs, they were first washed several times with hexanes to remove any excess PNCs and then submerged in water (we note that during the evaluation of this process, hybrids were routinely also mounted for optical measurements in silicone oil, and this oil was carefully removed through hexanes washes prior to re-exposure of the hybrids to water).

### *General Characterization Procedures*

All photoluminescence data was collected using a Horiba PTI QuantaMaster 8075 Spectrofluorometer. For solution or colloidal samples, photoluminescence data were collected at an excitation wavelength of 365 nm with an integration time of 0.5 s, step size of 2 nm, slits of 1

nm, with an automatic 5 second dark background collection and were measured in a 1 cm pathlength cuvette with hexanes as a solvent and as a blank. For solid samples, a quartz slide was used as the mounting substrate. Small amounts of vacuum grease were used to keep the solid sample in place followed by addition of one drop of silicone oil. The substrate was oriented vertically in the sample chamber, and its position was adjusted such that light from the excitation monochromator hit directly onto the microbead sample. Photoluminescence data of solid samples was collected at an excitation of 365 nm with an integration time of 0.5 s, a step size of 2 nm, slits of 3 nm, with an automatic 5 second dark background collection. A quartz slide with grease and silicone oil on it was used as a blank for these measurements.

This same instrument equipped with an integrating sphere (Horiba K-Sphere Petit) was used for photoluminescence quantum yield measurements. For solution or colloidal samples, the data was collected at an excitation wavelength of 365 nm with an integration time of 0.5 s, step size of 2 nm, slits of 1 nm, with an automatic 5 second dark background collection and were measured in a 1 cm pathlength cuvette with hexanes as a solvent and as a blank. For solid samples, a single microbead was placed onto the quartz slide with grease and silicone oil and the data was collected at an excitation wavelength of 365 nm with an integration time of 0.5 s and a stepsize of 2 nm, slits of 1 – 3 nm, and with an automatic 5 second dark background collection. A quartz slide, grease, a single unfunctionalized polystyrene microbead which matched as closely as possible by eye the size of the functionalized polystyrene microbead, and silicone oil was used as a blank for these measurements.

Solution UV-Vis absorbance and photoluminescence data were collected using a Horiba PTI QuantaMaster 8075 Spectrofluorometer. Absorbance data were collected with a 0.5 neutral density

filter in the excitation path, an integration time of 0.5 s, step size of 2 nm, 0.5 nm slits, with an automatic 5 second dark background collection.

Reflectance data were collected using a Cary 5000 Series UV-Vis spectrophotometer (Agilent Technologies) with a single beam range between 360 – 800 nm using an EasiDiff reflectance accessory (PIKE Technologies, Inc.). The PC microbeads were placed closely together on a flat stainless-steel stub and held in place with a drop of silicone oil. A baseline measurement was acquired with silicone oil on the same stub.

Optical light microscope data were collected using a Laxco™ LMC-2000 Compound Microscope equipped with a SeBaCam Digital Microscope Camera (with SeBaView Software) using 4X magnification. The polystyrene microbeads were placed on a glass microscope slide with a few drops of silicon oil on top. The microscope images were taken with the microscope light and polarizer or with an external white light diode.

Scanning electron microscopy (SEM) and elemental analysis by energy dispersive X-ray spectroscopy (EDS) were performed on a Phenom ProX G5 scanning electron microscope (Thermo Fisher Scientific). Micrographs were obtained with an acceleration voltage of 5 – 15 keV, and elemental analysis was carried out with an acceleration voltage of 15 keV. The microbead hybrids required 5 nm of gold sputter coating for analysis. Sputter coating carried out using a Cressington, 108 auto/SE sputter coater with MTM – 20 – High – Resolution Film Thickness Controller. Some of the microbeads were cut in half before being put onto carbon tape and sputter coating to get an understanding of the internal structure.

Powder X-ray diffraction (PXRD) data was obtained using a Rigaku Miniflex600/600C benchtop (Applied Rigaku Technologies Inc., Austin, TX, USA) equipped with CuK $\alpha$  X-ray source (wavelength,  $\lambda = 1.54 \text{ \AA}$ , radiation operating at 40 kV and 15 mA), a D/teX Ultra2

high-speed 1D detector or HyPix-400 MF 2D sensitive detector (Applied Rigaku Technologies Inc., Austin, TX, USA) and a nickel filter. Sample data was collected using a continuous coupled  $\theta/2\theta$  scan in the  $2\theta$  – range of  $10 - 50^\circ$  with step size of  $0.01^\circ$ , scan speed of  $1^\circ$  per minute and spin speed of 20 rpm. PNC samples were centrifuged, and the precipitate was dried and placed onto the zero-background silicon wafers, while the PC and hybrid microbeads were finely crushed into a uniform powder using a mortar and pestle and then placed onto the zero-background silicon wafer.

#### *Time-resolved photoluminescence (TRPL) spectroscopy*

Neat PNC films for TRPL spectroscopy were prepared by spin-coating corresponding PNC solutions onto clean glass substrates (acetone + IPA) under inert atmosphere. PC=PNC samples were similarly prepared on clean glass substrates, using a small amount of vacuum grease as an adhesive.

Then, time-resolved photoluminescence data was acquired using a streak camera (Hamamatsu C10910). Optical excitation ( $\lambda$ : 350nm or  $\lambda$ : 390nm; repetition rate: 10kHz) was generated from a commercial optical parametric amplifier (Orpheus-F, Light Conversion) pumped by a Yb:YAG source (Pharos, Light Conversion). Samples were excited at excitation densities of 50, 5 and 0.5  $\mu\text{J}/\text{cm}^2/\text{pulse}$  for excitation at  $\lambda$ : 390nm, and at excitation densities of 5, 0.5 and 0.05  $\mu\text{J}/\text{cm}^2/\text{pulse}$  for excitation at  $\lambda$ : 350nm (high, medium, and low power for each, respectively).

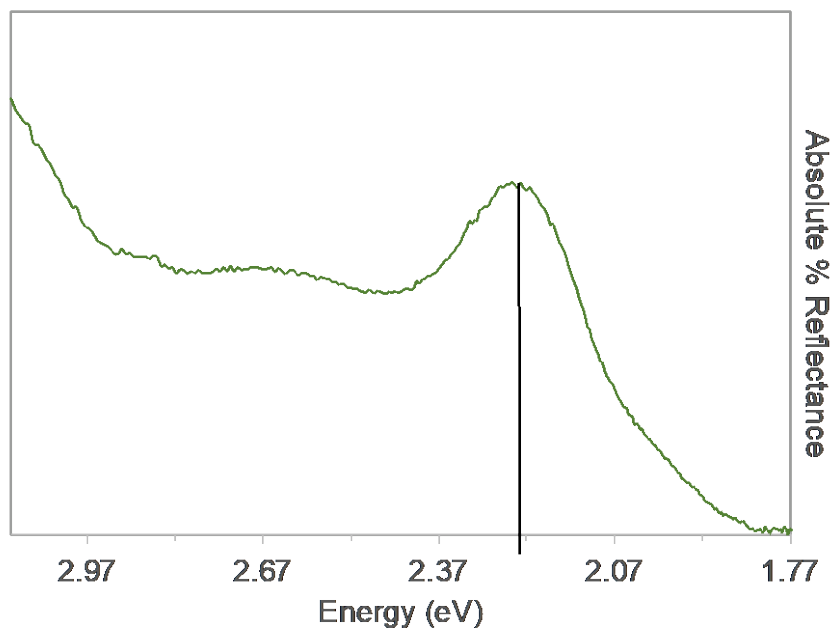
Theoretical PLQY enhancements were calculated as follows:

$PLQY = \frac{k_r}{k_r + k_{nr}}$ ; where  $k_r$  and  $k_{nr}$  represent the rate constants of radiative and non-radiative decay, respectively. Our control system (neat PNC films), possess biexponential dynamics (extracted from biexponential fits to our TRPL data), thereby modifying our equation somewhat:

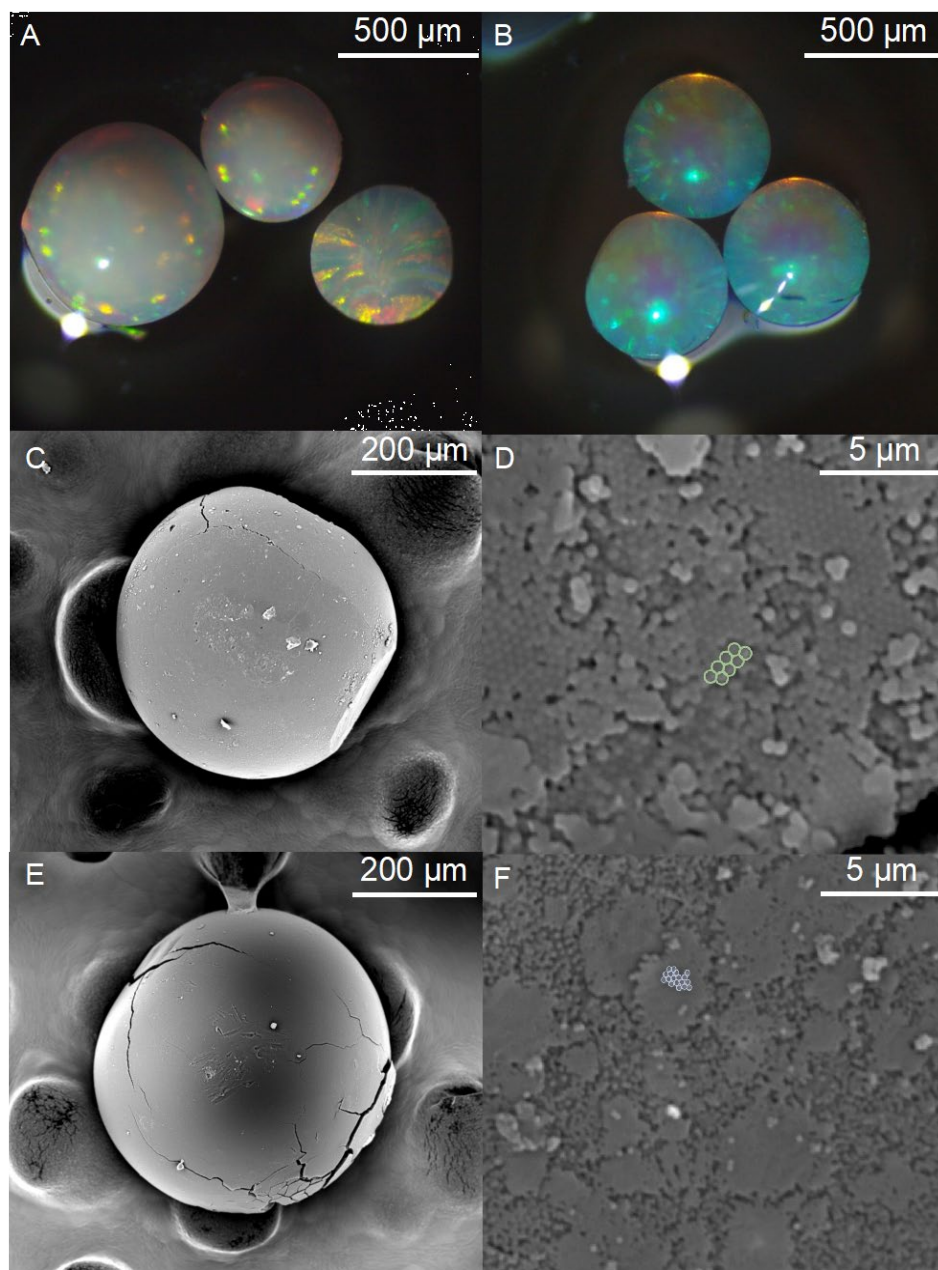


$PLQY = \frac{Ak_1 + (1-A)k_2}{Ak_1 + (1-A)k_2 + k_{nr}}$ ; where  $A$ ,  $k_1$  ( $1/\tau_1$ ) and  $k_2$  ( $1/\tau_2$ ) are extracted from our biexponential fits (see Figure 4 and associated discussion). For example, using our extracted values from neat CsPbBr<sub>3</sub> films ( $A=0.5$ ,  $\tau_1=0.6$  ns,  $\tau_2=2.6$  ns,  $PLQY=0.67$ ), we calculate a  $k_{nr} = 0.5$  ns<sup>-1</sup> ( $\tau_{nr}=2.0$  ns). Assuming a constant  $k_{nr}$  (i.e. all non-radiative decay is intrinsic to PNCs and not associated with the photonic environment), we can then calculate the expected PLQY using the values extracted from a biexponential fit to the PC=PNC samples:

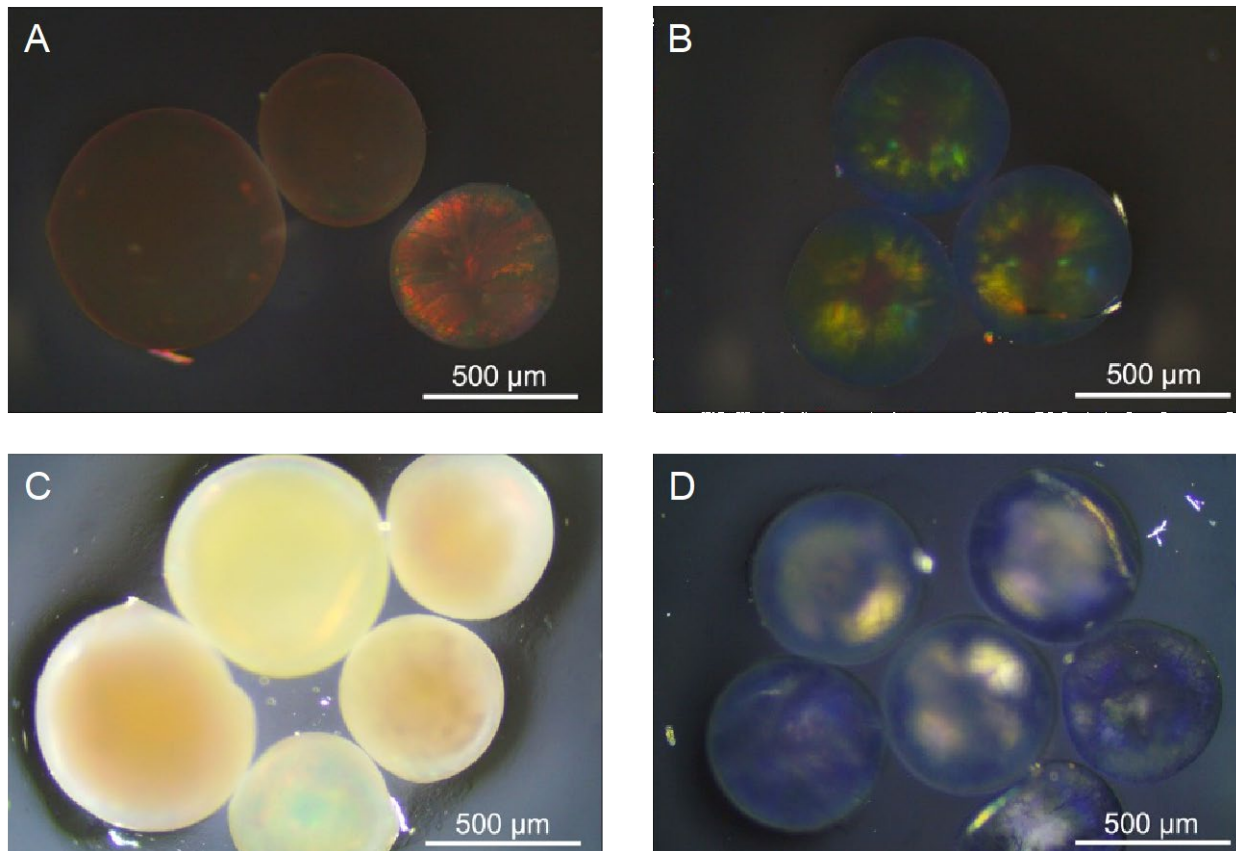
$PLQY = \frac{Ak_1 + (1-A)k_2}{Ak_1 + (1-A)k_2 + k_{nr}}$ ; where  $A=0.6$ ,  $\tau_1=0.2$  ns,  $\tau_2=2.0$  ns,  $\tau_{nr}=2.0$  ns, thereby yielding a theoretical PLQY of 86%. While this approach assumes that all changes to the PNC film lifetime arise from enhancements to the radiative rate, we consider this to be a conservative estimate since we do observe an increase in steady-state PLQY—thus any increases to non-radiative decay rate constants must be offset by the photonic enhancement afforded by the microbeads.



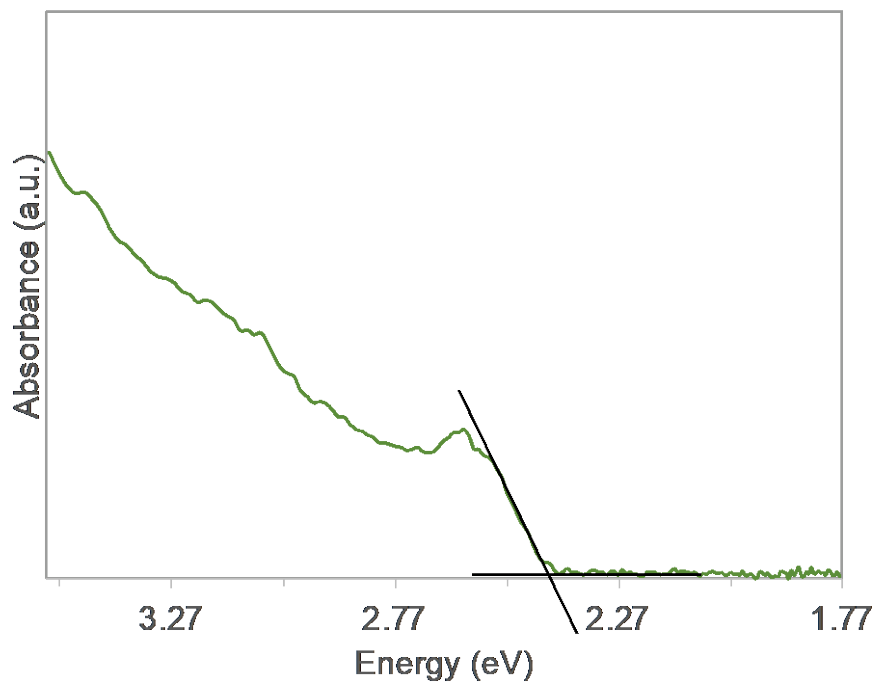
**Figure S1.** Sample calculation for determining the photonic stopband energy using the reflectance spectra of 370PC (the photonic stopband energy is associated to the maximum reflectance peak).



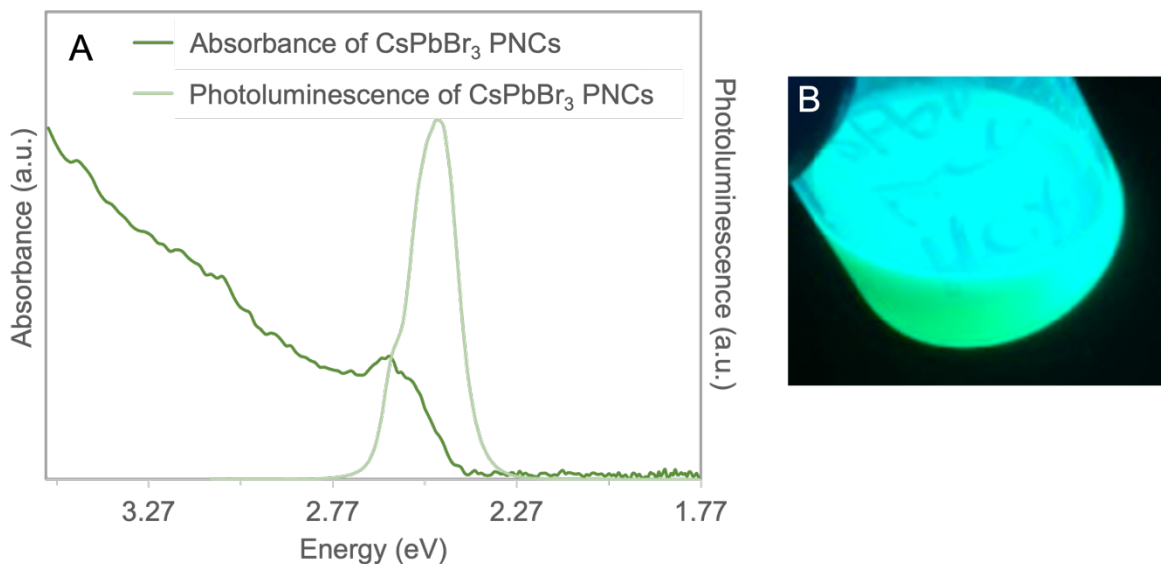
**Figure S2.** Optical light micrographs of (A) 370PC and (B) 190PC microbeads exposed to an external light source from above in silicone oil. Scanning electron micrographs at different magnification of (C) and (D) 370PC; (E) and (F)190PC. Overlaid circles represent individual constituent polystyrene spheres.



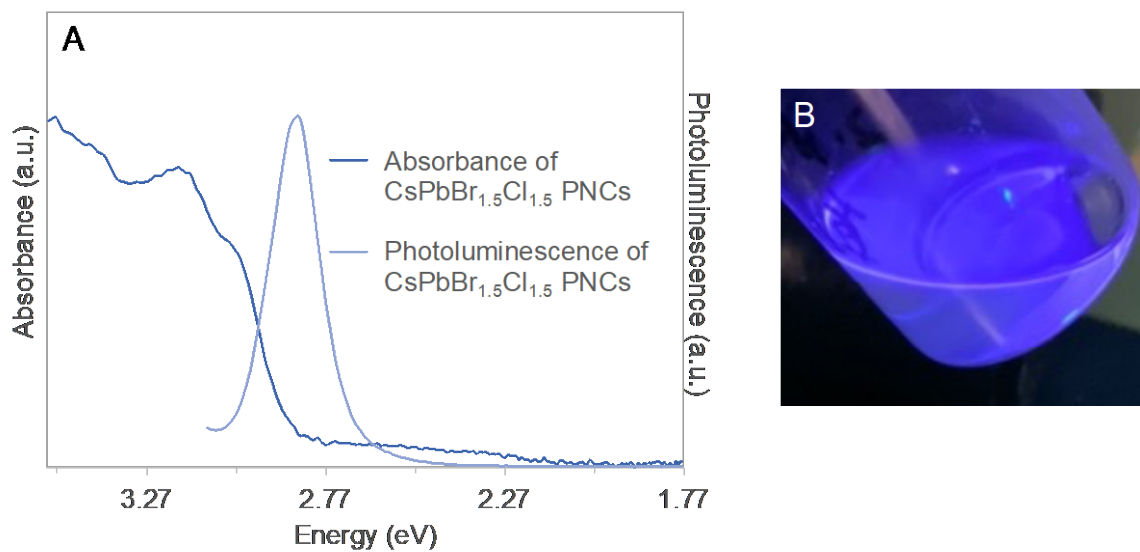
**Figure S3.** Optical micrographs of (A) 370PC and (B) 190PC microbeads and (C) 370PC-CsPbBr<sub>3</sub> and (D) 190PC-CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> microbead hybrids using microscope light and polarizer in silicone oil.



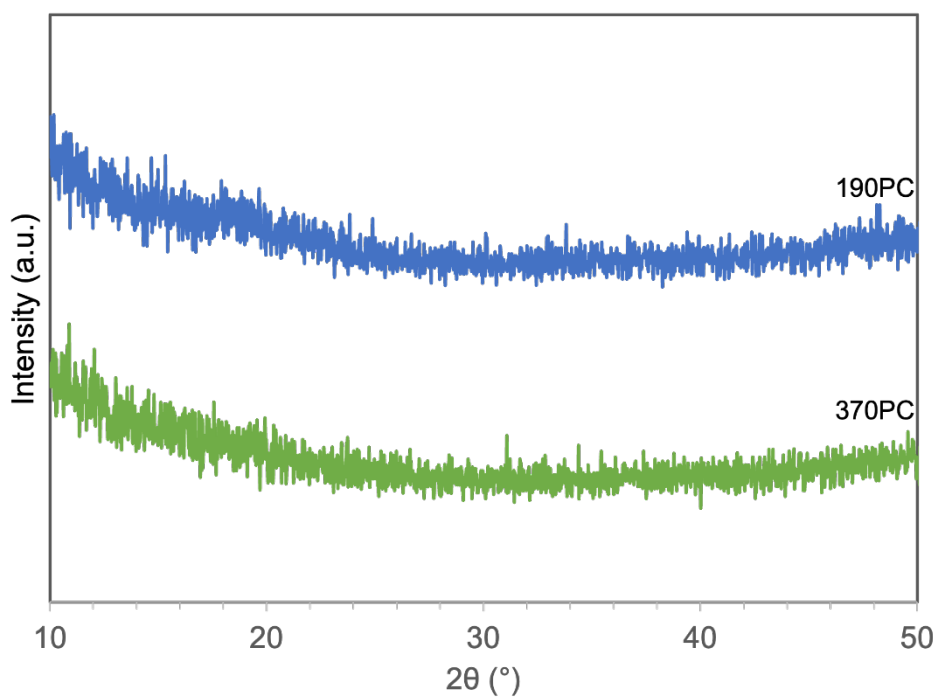
**Figure S4.** Sample calculation for determining the bandgap energy using the absorbance spectrum of CsPbBr<sub>3</sub> PNCs (the bandgap energy is taken as the intersection between the tangent line of the band edge and the tangent line of the baseline).



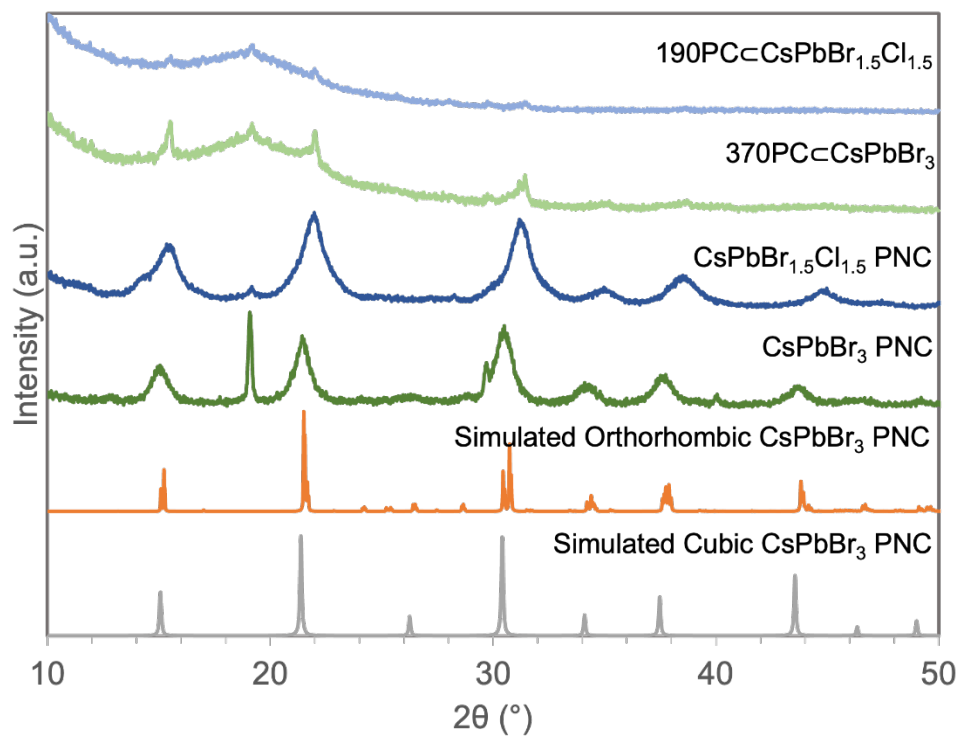
**Figure S5.** (A) Normalized room temperature photoluminescence and absorbance spectra for CsPbBr<sub>3</sub> PNCs in hexanes ( $\lambda_{\text{ex}} = 365$  nm) and (B) image of the respective PNC solution in hexanes under a 365 nm UV lamp.



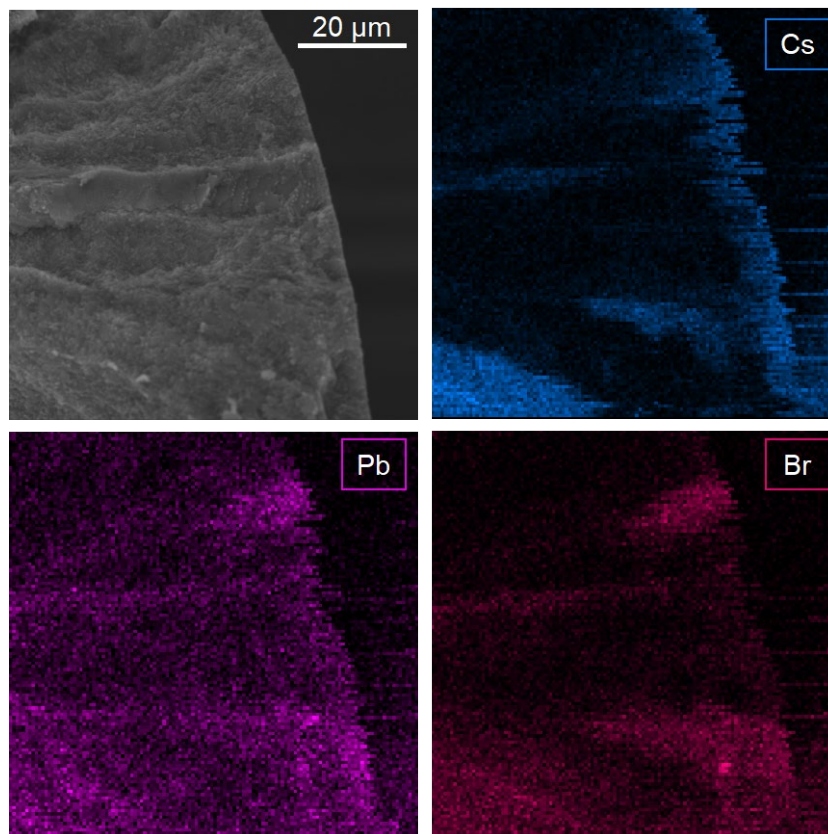
**Figure S6.** (A) Normalized room temperature photoluminescence and absorbance spectra for CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> PNCs in hexanes ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) and (B) photograph of the PNC colloid in hexanes under illumination with a handheld 365 nm UV lamp.



**Figure S7.** Powder X-ray diffractograms of PC microbeads.

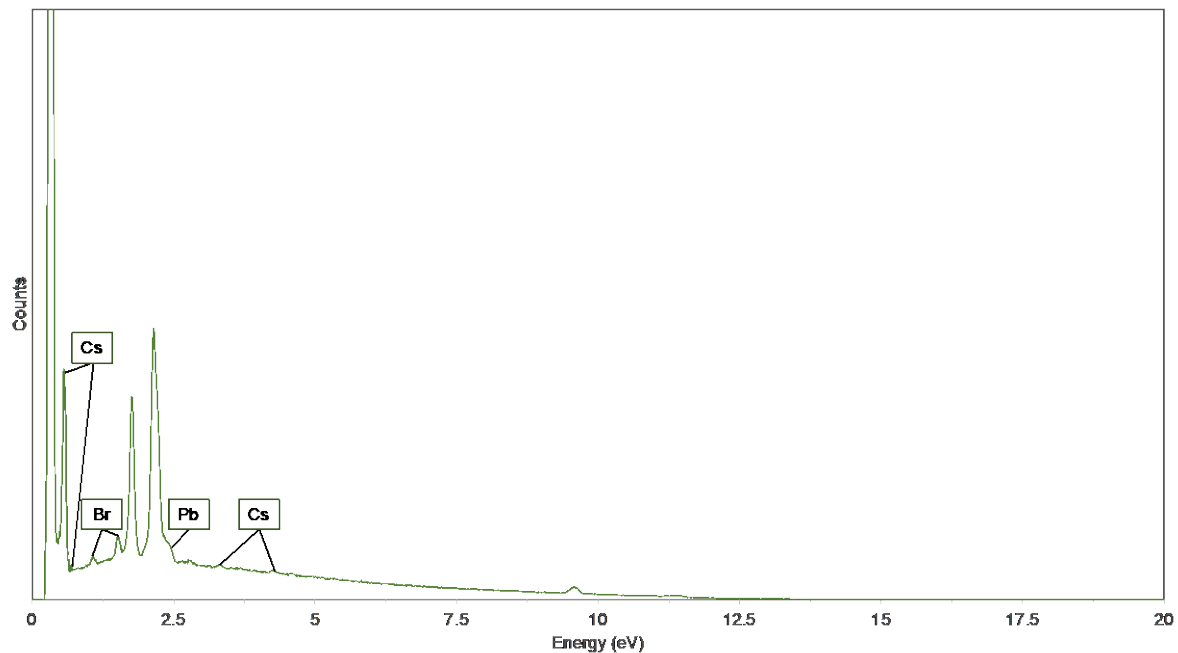


**Figure S8.** Powder X-ray diffractograms of PC@PNC microbead hybrids (light blue and light green) and PNCs (dark blue and dark green) compared to the simulated cubic (grey, ICSD 29073) and orthorhombic (orange, ICSD 9785) PNC patterns.

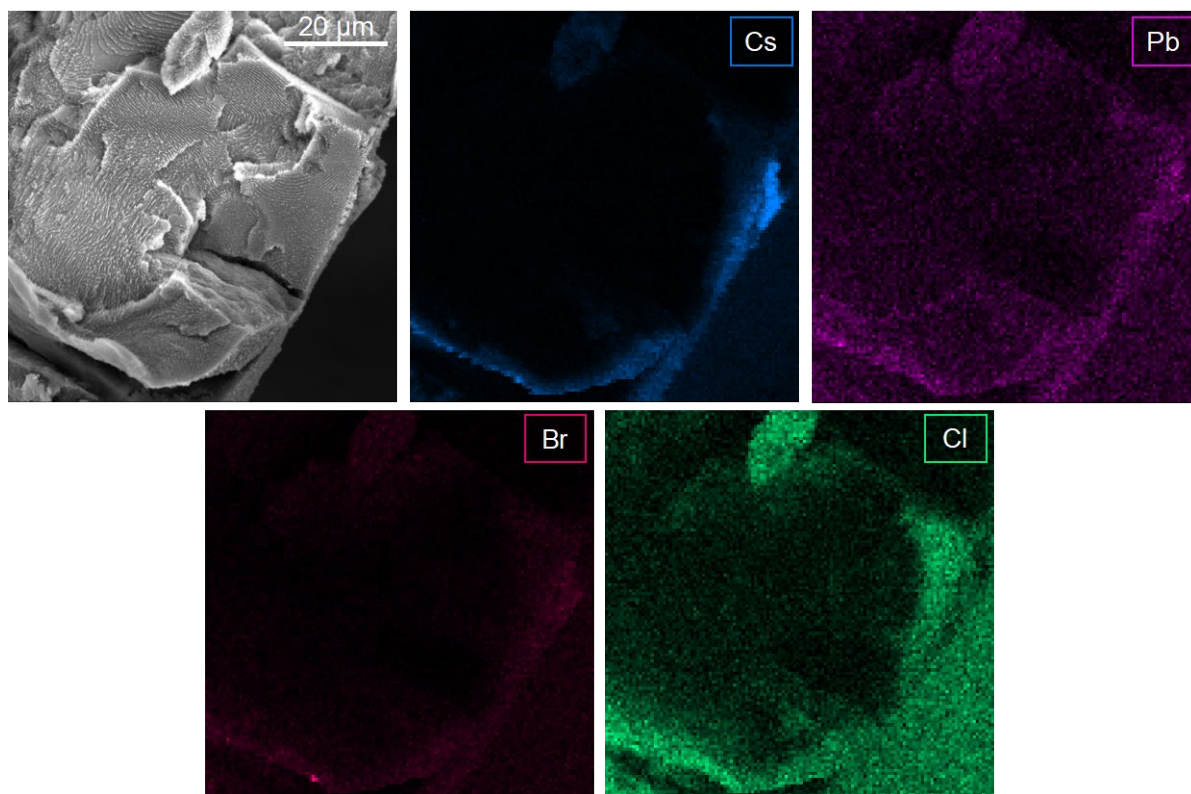


**Figure S9.** Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) mapping of a 370PC-CsPbBr<sub>3</sub> hybrid microbead showing the infiltration of constituent PNC ions into the microbead structure.

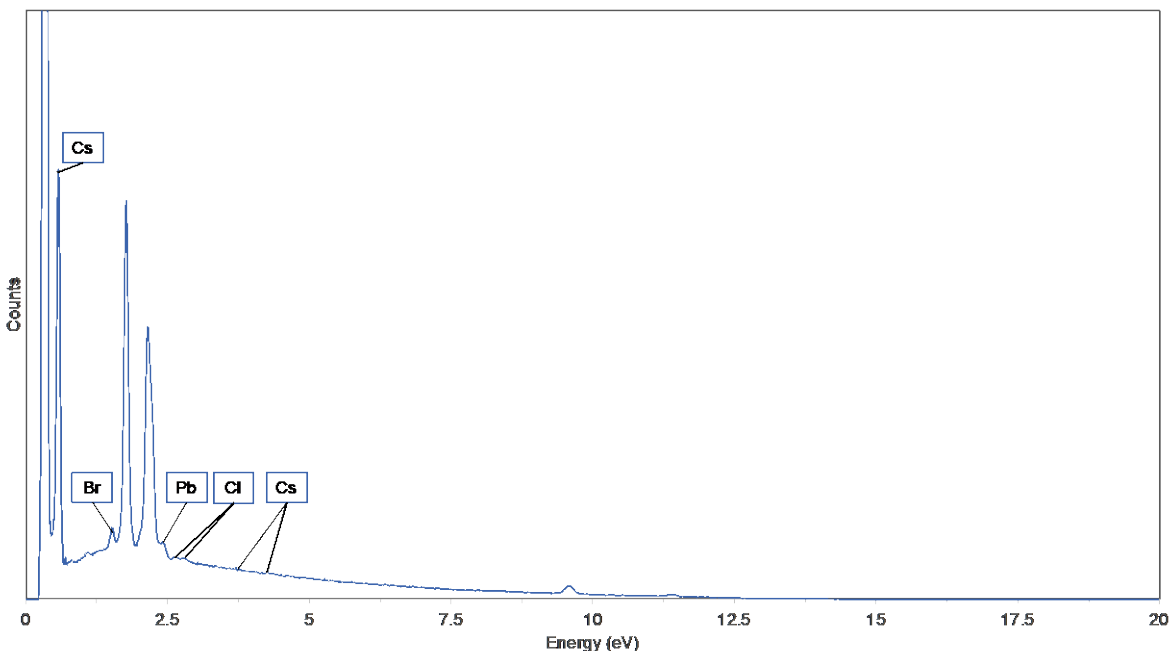




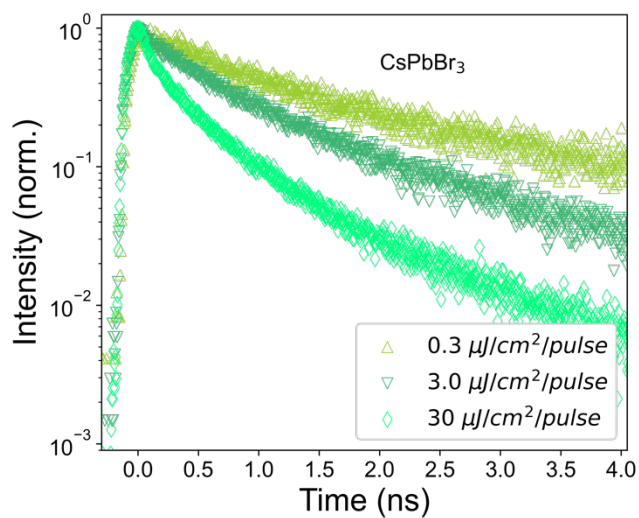
**Figure S10.** EDS mapping spectrum of 370PC=CspbBr<sub>3</sub> hybrid microbead.



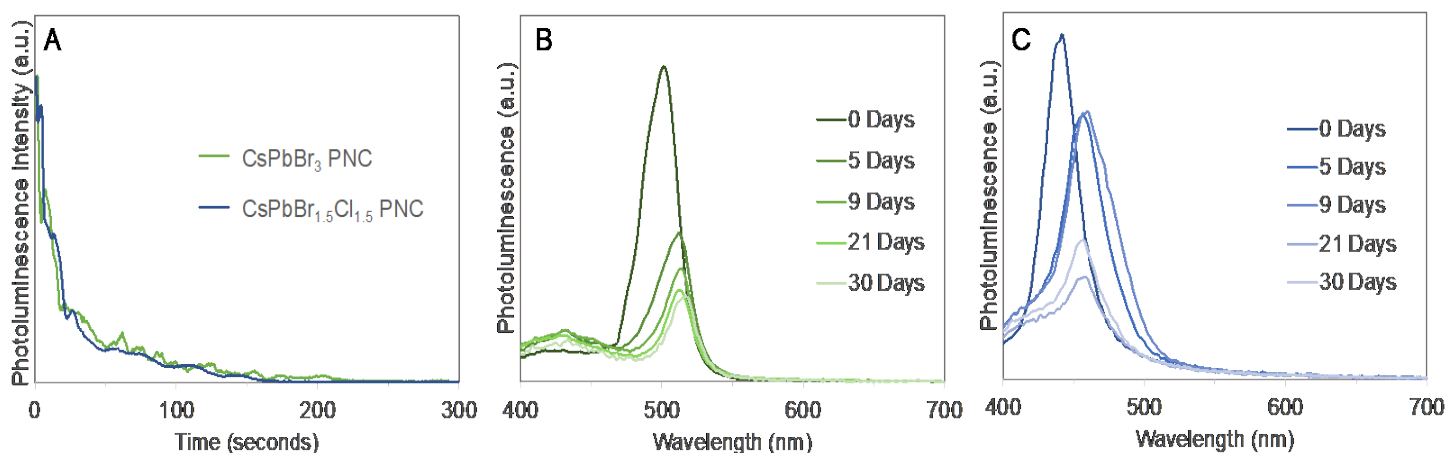
**Figure S11.** Scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) mapping of a 190PC=CspbBr<sub>1.5</sub>Cl<sub>1.5</sub> hybrid microbead showing the infiltration of constituent PNC ions into the microbead structure.



**Figure S12.** EDS mapping spectrum of 190PC-CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> hybrid microbead.



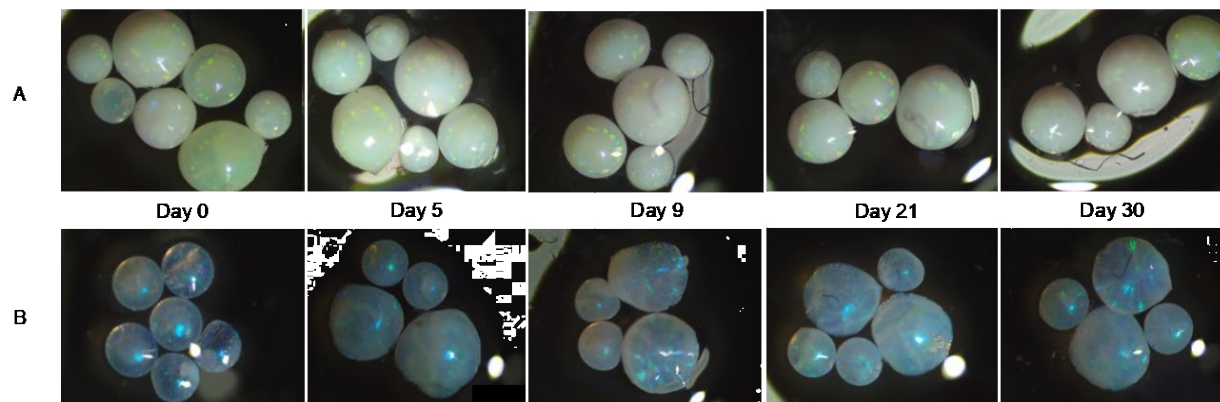
**Figure S13.** Excitation-density-dependent time-resolved photoluminescence dynamics of CsPbBr<sub>3</sub> films. Since the measured dynamics are highly dependent on the incident excitation density, all time-resolved measurements presented in the main text are conducted at 0.3 μJ/cm<sup>2</sup>/pulse ( $\lambda_{\text{ex}} = 390$  nm).



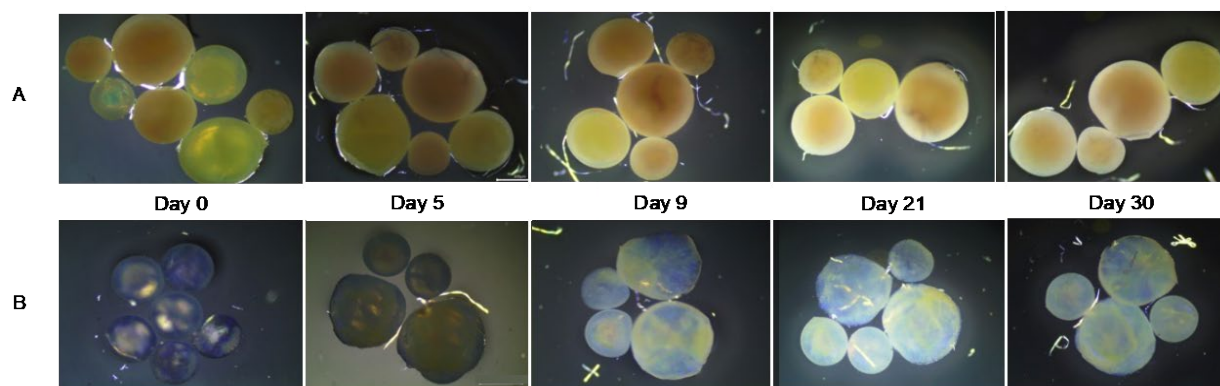
**Figure S14.** Solution time-based photoluminescence of (A) CsPbBr<sub>3</sub> PNCs measured at the 500 nm emission peak (green) and CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> PNCs measured at the 438 nm emission peak (blue) in water ( $\lambda_{\text{ex}} = 365$  nm). Solid-state photoluminescence of (B) 370PC@CsPbBr<sub>3</sub> microbead hybrids and (C) 190PC@CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> microbead hybrids over the course of 30 days of water immersion.



**Figure S15.** Photographs of (A) 370PC@CsPbBr<sub>3</sub> and (B) 190PC@CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> microbead hybrids after being submerged in water under a UV lamp (365 nm).

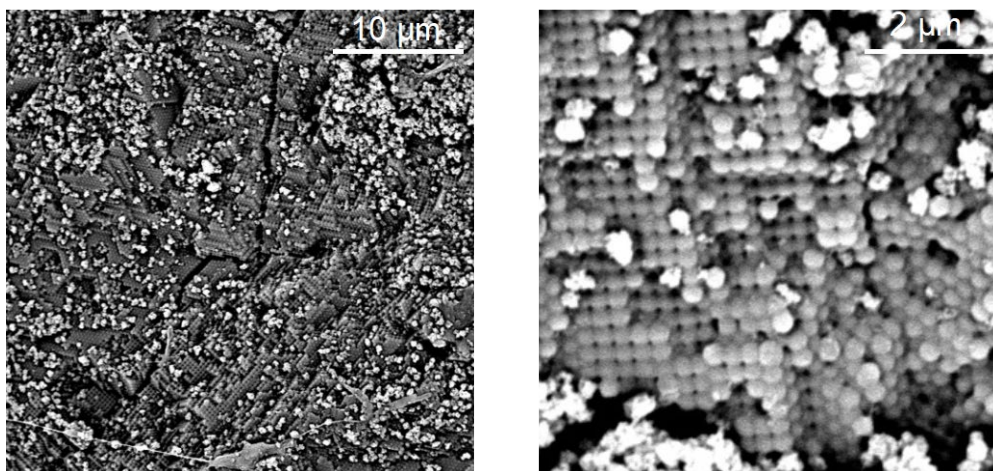


**Figure S16.** Optical micrographs of (A) 370PC⊂CsPbBr<sub>3</sub> and (B) 190PC⊂CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> microbead hybrids during water stability test illuminated with an external light in silicone oil.

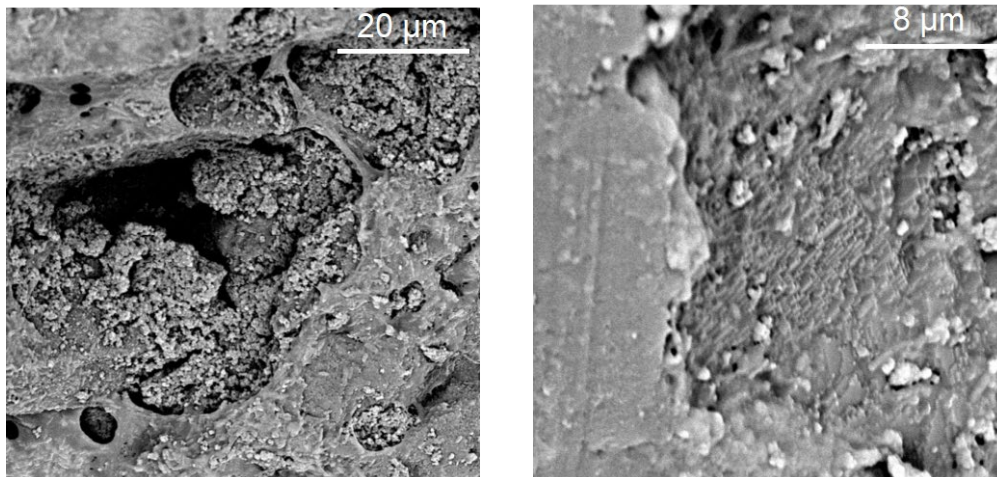


**Figure S17.** Optical micrographs of (A) 370PC⊂CsPbBr<sub>3</sub> and (B) 190PC⊂CsPbBr<sub>1.5</sub>Cl<sub>1.5</sub> microbead hybrids during water stability test under microscope light and polarizer.

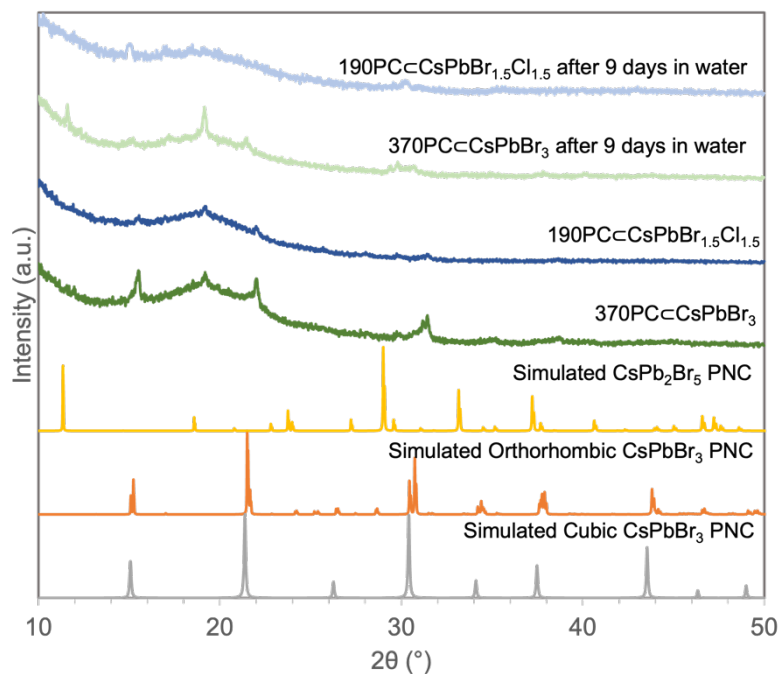




**Figure S18.** Scanning electron micrographs at different magnification of 370PC=CspbBr<sub>3</sub> microbead hybrids after the 30-day water stability test.



**Figure S19.** Scanning electron micrographs at different magnification of 190PC=CspbBr<sub>1.5</sub>Cl<sub>1.5</sub> microbead hybrids after the 30-day water stability test.



**Figure S20.** Powder X-ray diffractograms of PC⊂PNC microbead hybrids (light blue and light green) and PNCs (dark blue and dark green) compared to the simulated cubic CsPbBr<sub>3</sub> (grey, ICSD 29073), orthorhombic CsPbBr<sub>3</sub> (orange, ICSD 9785), and CsPb<sub>3</sub>Br<sub>5</sub> (yellow, mp-1238811).