

Supplementary Materials

A perovskite-based paper microfluidic sensor for haloalkane assays

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Chemicals

Lead(II) iodide (PbI_2 , 99.99%), lead(II) bromide (PbBr_2 , 99.99%), lead(II) chloride (PbCl_2 , 99.99%), Cesium carbonate (Cs_2CO_3 , 99.9%), trioctylphosphine (TOP), cyclohexane (chromatography grade 99.9%), oleic acid (technical grade 90%), oleylamine (technical grade 70%), 1-octadecene (ODE, technical grade 90%), dichloromethane (CH_2Cl_2), and dibromomethane (CH_2Br_2) were obtained from Sigma-Aldrich. Sylgard® 184 silicone elastomer kit for polydimethylsiloxane (PDMS) coating was obtained from Dow Corning. Chromatography paper (100 μm thick) was purchased from Whatman. All chemicals were used without further treatment.

Synthesis of perovskite nanocrystals

Cs-oleate precursor was prepared by adding Cs_2CO_3 (0.4 g), octadecene (ODE; 15 mL) and oleic acid (OA; 1.25 mL) to a 50-ml 2-neck flask. The suspension was heated to 120 °C under stirring in vacuum for 30 min. The reaction was further heated to 150 °C to ensure a complete reaction of Cs_2CO_3 and OA to form the Cs-oleate precursor solution. Perovskite nanocrystals of CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) were synthesized by a previously reported method. PbX_2 (0.36 mmol), oleylamine (1.0 mL), ODE (10 mL), and oleic acid (1.0 mL) were injected to a 50-ml 2-neck flask. The suspension was heated to 120 °C under vigorous stirring in vacuum for 30 min. Subsequently, the reaction was treated by purging with nitrogen and vacuum suction, and then heated to 160 °C for the complete dissolution of the PbX_2 precursors. 1 mL of hot Cs-oleate precursor was injected into the above-mentioned mixture. After 5 s, the reaction was terminated by transferring the flask into an ice bath. The CsPbX_3 nanocrystals were collected by centrifugation at 10000 rpm for 10 min and stored in 4-mL cyclohexane.

Physical characterization

TEM characterization was performed by a Tecnai G2 F20 S-TWIN microscope (FEI Nano Ports), operating at an accelerating voltage of 200 kV. X-ray diffraction analysis was carried out by an X-ray powder diffractometer (DY5261/Xpert3) over an angular range of 5–90°. Luminescent spectra were taken by an Edinburgh Fls980 fluorescence spectrophotometer (Edinburgh Instruments). Absorption spectra were recorded using a UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan). Colorimetric

imaging was performed with a digital camera (Nikon) in an all-manual mode. All spectra were obtained under ambient conditions.

Fabrication of paper microfluidic chips

In a typical procedure, a pattern of six-channel packaging tapes was designed using the Adobe Illustrate software, and printed out by a laser cutting. The patterned tape with six-channels was attached to a chromatography paper. A premixed PDMS prepolymer and its curing agent (10:1 by mass) were degassed, coated on the chromatography paper, and then cured in an 80 °C oven for 10 min. After that, the packaging tape was removed from the chromatography paper, and a six-channel paper microfluidic chip was produced for further experiments.

Haloalkane sensing through anion exchange

A solution (50 mg/mL) of perovskite nanocrystals was dropped into the cyclohexane. Haloalkanes (CH_2Cl_2 , or CH_2Br_2) with various concentrations were added to the perovskite nanocrystals. 50 μL of trioctylphosphine (TOP) was used to accelerate the anion exchange with perovskite nanocrystals. For detection of haloalkanes on the paper microfluidic chip, 200 μL of perovskite nanocrystals containing 20 μL of TOP were dropped onto the microchips. The haloalkanes were dropped onto the microchip, and diffused along with the microchannels for anion exchange reaction. After the color change of perovskite nanocrystals was observed, luminescence spectra of the perovskite nanocrystals were measured by a spectrometer under 365-nm UV excitation.

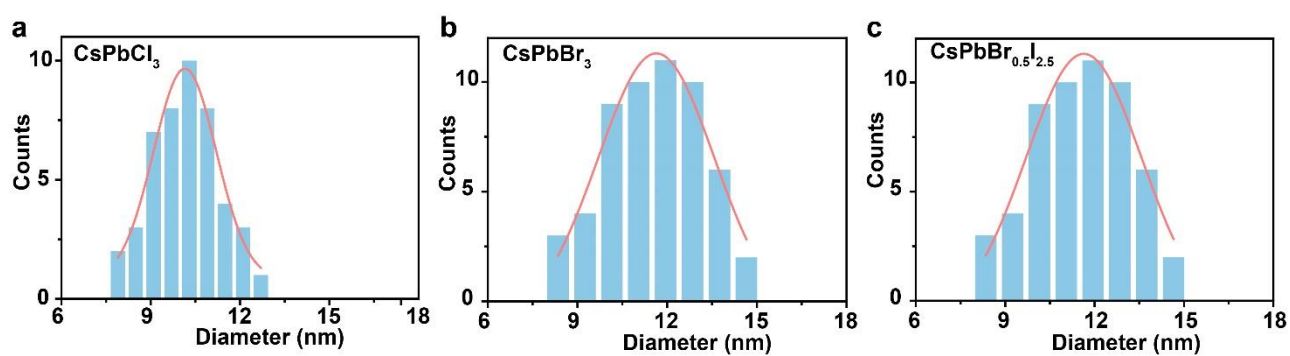


Figure S1. Size distributions of the as-synthesized perovskite nanocrystals. These samples are CsPbCl_3 (a), CsPbBr_3 (b), and $\text{CsPbBr}_{0.5}\text{I}_{2.5}$ (c).

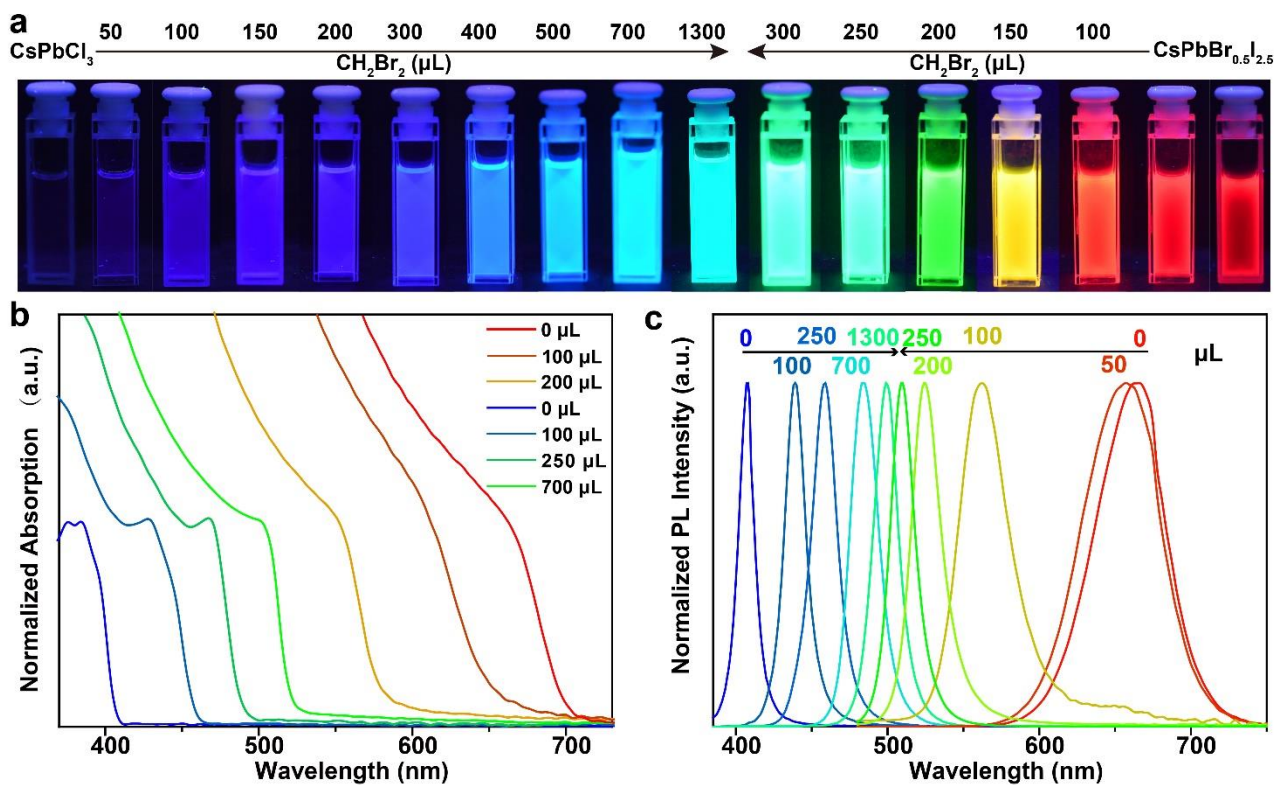


Figure S2 | Optical characterization of perovskite nanocrystals as a function of CH_2Br_2 amounts. (a) Luminescence emission of CsPbCl_3 and $\text{CsPbBr}_{0.5}\text{I}_{2.5}$ in cyclohexane by anion exchanging with varying CH_2Br_2 amounts under 365-nm UV illumination. (b) CH_2Br_2 amount dependence of absorption spectrum for CsPbCl_3 and $\text{CsPbBr}_{0.5}\text{I}_{2.5}$ in cyclohexane. (c) CH_2Br_2 amount dependence of emission spectrum for CsPbCl_3 and $\text{CsPbBr}_{0.5}\text{I}_{2.5}$ in cyclohexane.

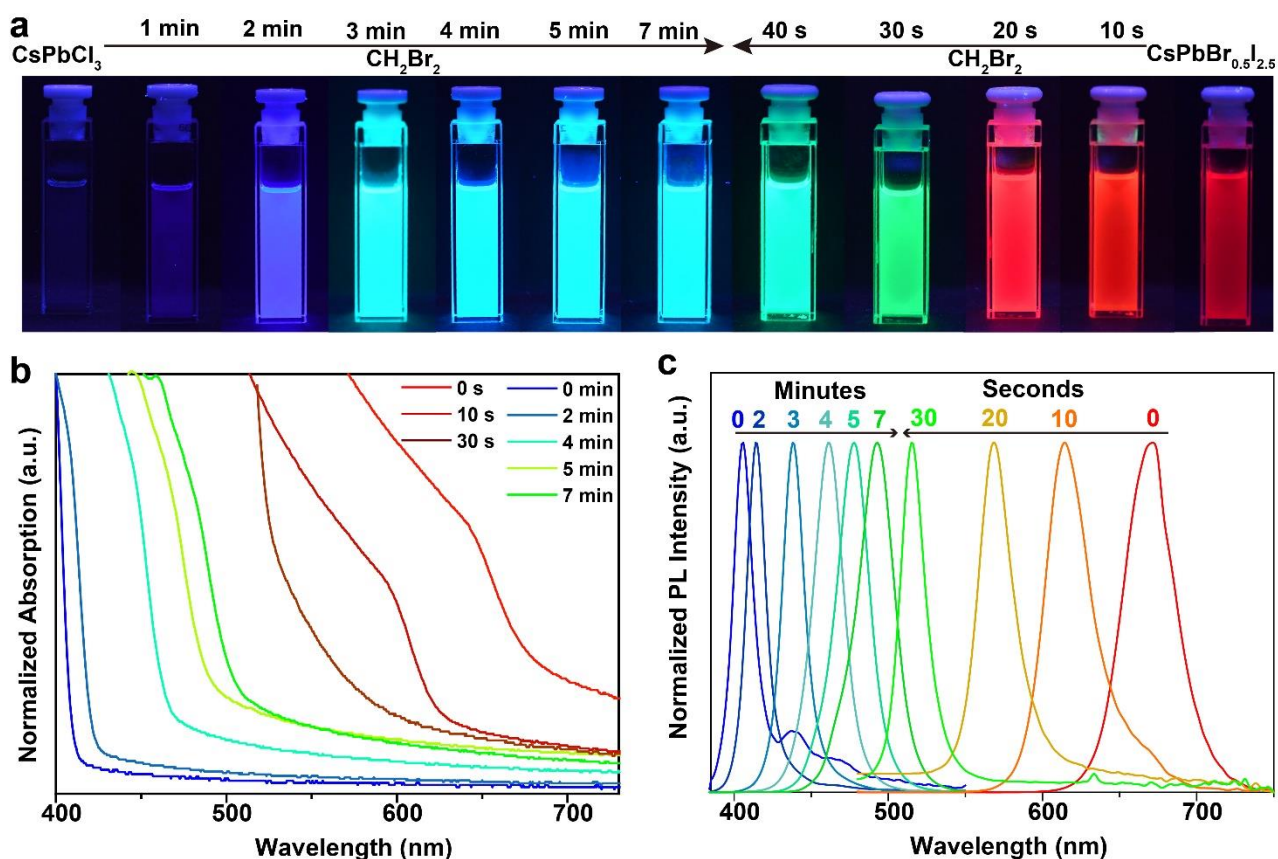


Figure S3 | Optical characterization of perovskite nanocrystals as a function of CH_2Br_2 exchanging time. (a) Luminescence emission of CsPbCl_3 and $\text{CsPbBr}_{0.5}\text{I}_{2.5}$ in cyclohexane by anion exchanging with CH_2Br_2 as a function of exchanging time under an Xe-lamp illumination. (b) Time dependence of absorption spectrum for CsPbCl_3 and $\text{CsPbBr}_{0.5}\text{I}_{2.5}$ in cyclohexane/ CH_2Br_2 . (c) Time dependence of emission spectrum for CsPbCl_3 and $\text{CsPbBr}_{0.5}\text{I}_{2.5}$ in cyclohexane/ CH_2Br_2 .

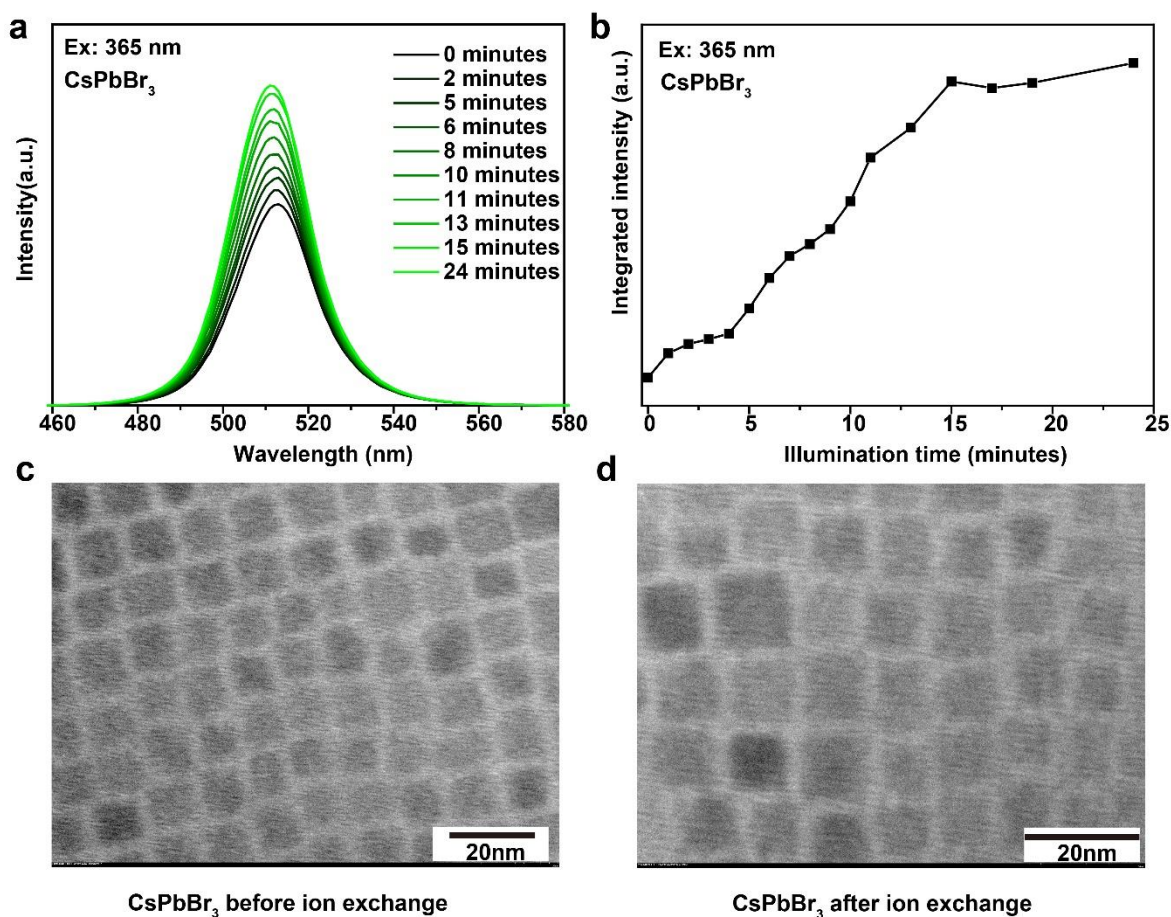


Figure S4 | Changes to the luminescence emission and morphology of CsPbBr₃ nanocrystals exposed to varying amounts of CH₂Br₂. (a) Luminescence emission spectra of CsPbBr₃ nanocrystals in CH₂Br₂/cyclohexane as a function of time. (b) Luminescence emission intensities of CsPbBr₃ nanocrystals in CH₂Br₂/cyclohexane as a function of time. (c) TEM image of pristine CsPbBr₃ nanocrystals, showing a cubic shape. (d) TEM image of CsPbBr₃ nanocrystals after anion exchanging with CH₂Br₂.

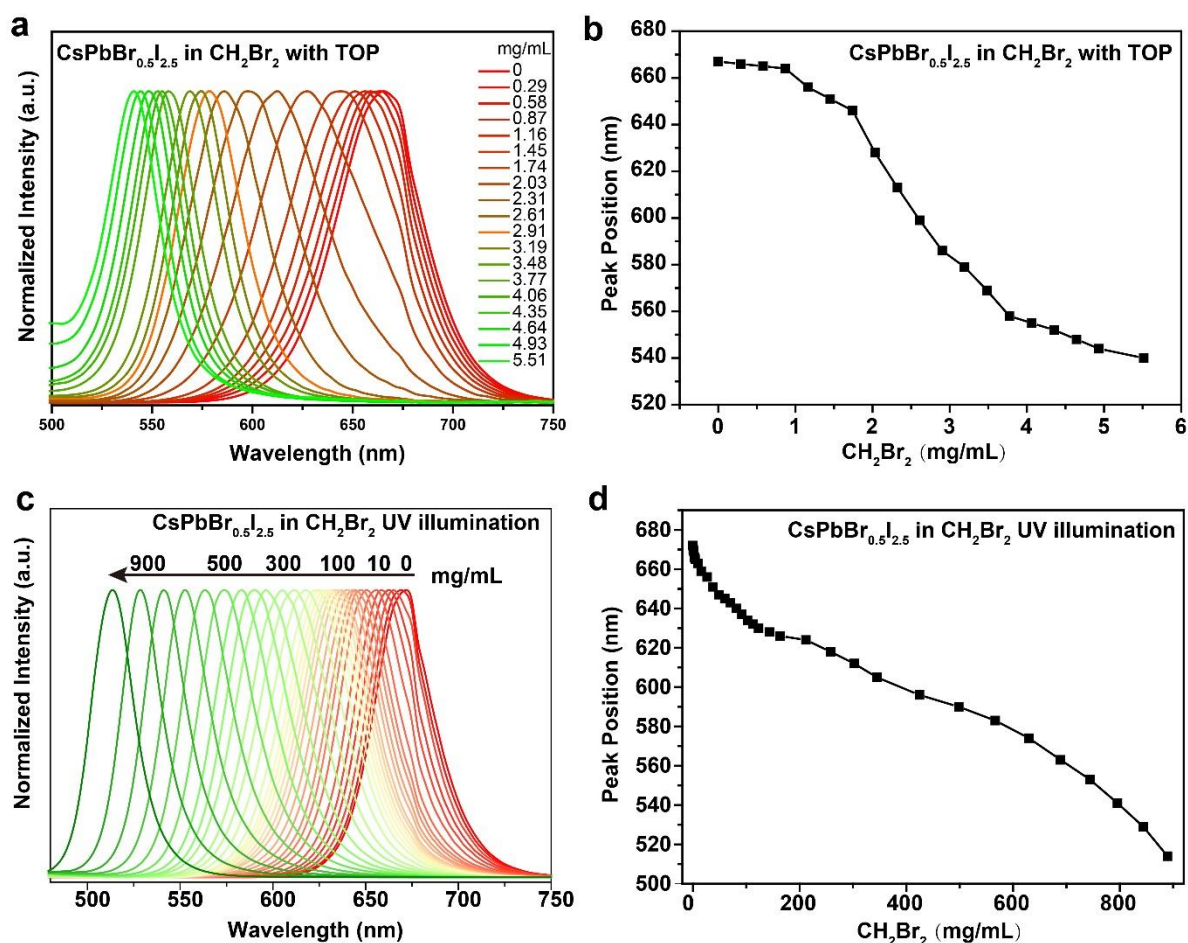


Figure S5 | Detection of CH₂Br₂ using CsPbBr_{0.5}I_{2.5} nanocrystals with the addition of TOP and under UV illumination. (a) Luminescence emission spectra of CsPbBr₃ nanocrystals as a function of the amount of the added CH₂Br₂ with TOP. (b) Emission wavelength shift of CsPbBr_{0.5}I_{2.5} nanocrystals as a function of the amount of the added CH₂Br₂ with TOP. (c) Luminescence emission spectra of CsPbBr_{0.5}I_{2.5} nanocrystals upon UV illumination, as a function of the amount of CH₂Br₂ added. (d) Emission wavelength shift of CsPbBr_{0.5}I_{2.5} nanocrystals upon UV illumination, as a function of the amount of CH₂Br₂ added.

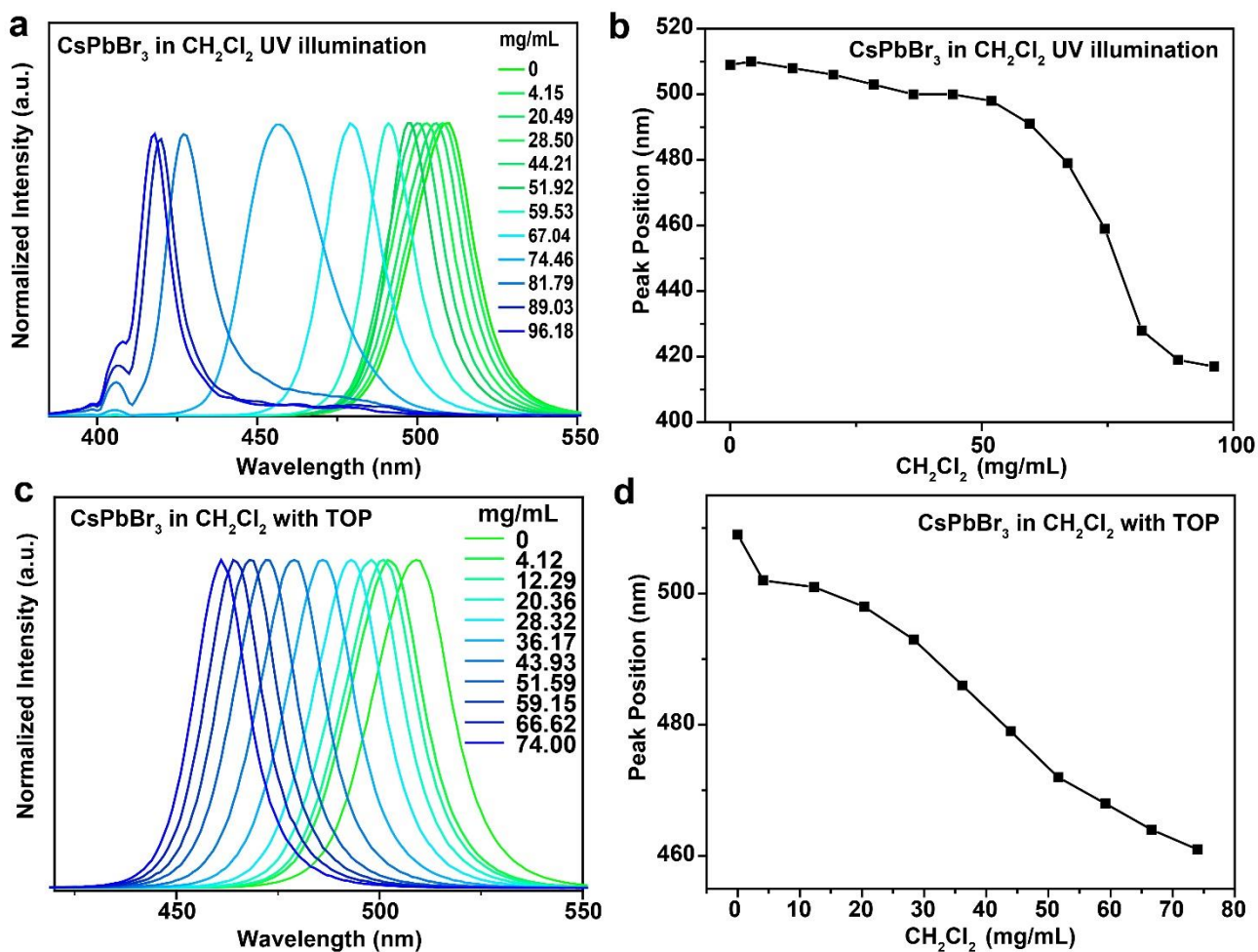


Figure S6 | Detection of CH₂Cl₂ using CsPbBr₃ nanocrystals with the addition of TOP and under UV illumination. (a) Luminescence emission spectra of CsPbBr₃ nanocrystals under UV illumination, as a function of the amount of CH₂Cl₂ added. (b) Emission wavelength shift of CsPbBr₃ nanocrystals under UV illumination, as a function of the amount of CH₂Br₂ added. (c) Luminescence emission spectra of CsPbBr₃ nanocrystals as a function of the amount of the added CH₂Cl₂ with TOP. (d) Emission wavelength shift of CsPbBr₃ nanocrystals as a function of the amount of the added CH₂Cl₂ with TOP.

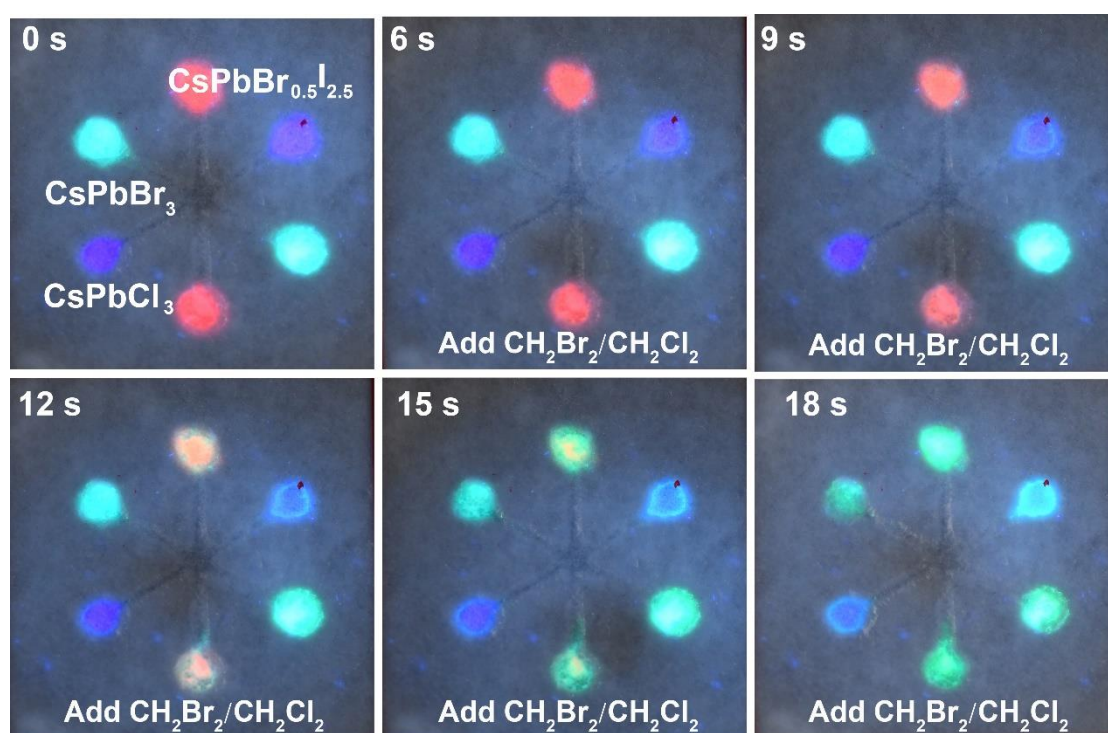


Figure S7 | Luminescence images of perovskite nanocrystals exchanged with $\text{CH}_2\text{Cl}_2/\text{CH}_2\text{Br}_2$ on a paper-based microfluidic device as a function of reaction time.

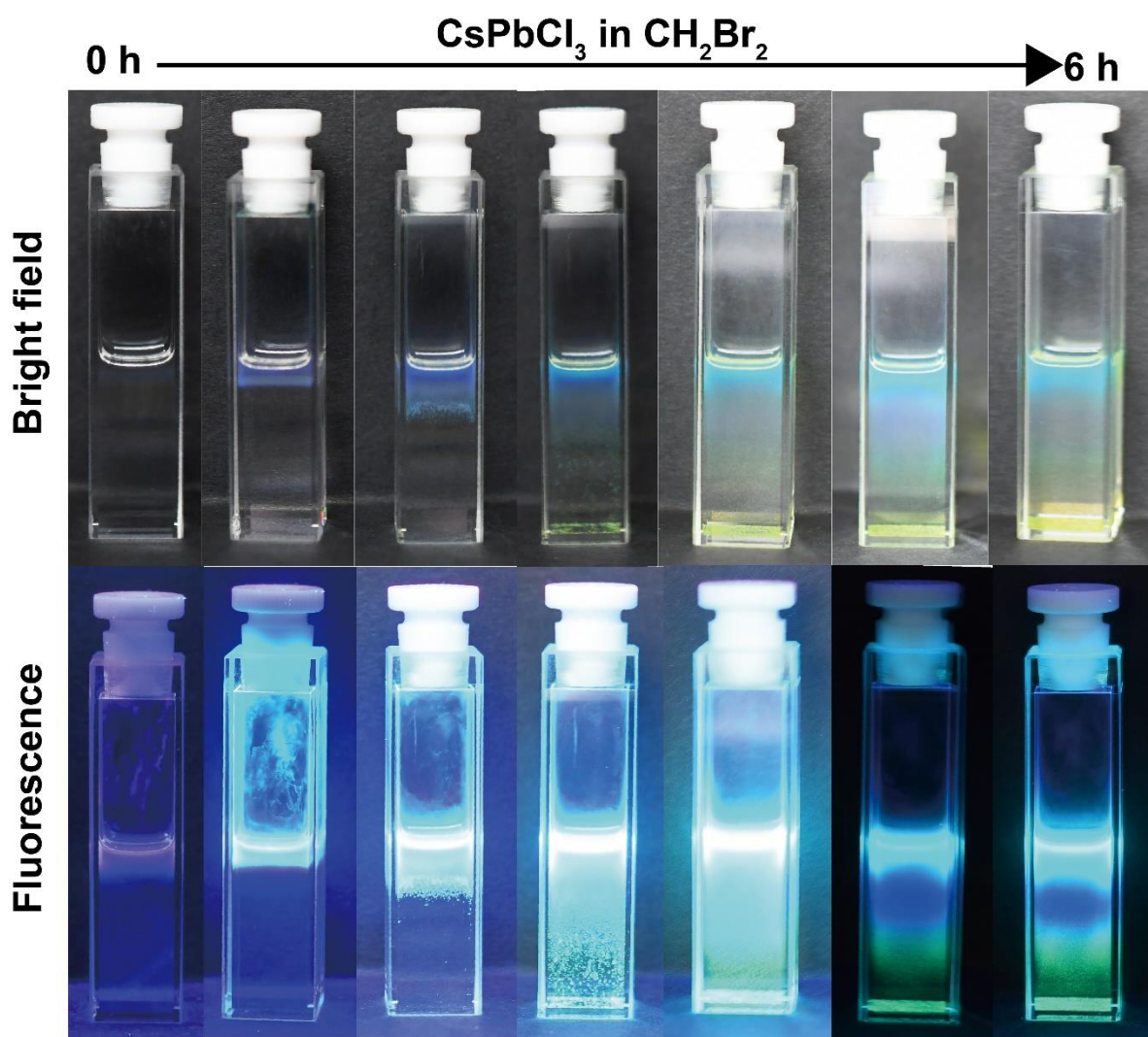


Figure S8 | Bright field and luminescence images of CsPbCl_3 nanocrystals exchanged with CH_2Br_2 as a function of reaction time.