

Supporting Information

Cesium-lead-halide Perovskite Triggered Visual Platform: Disposable Paper-based Nano-temperature Sensor for Cold Chain Transport

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Materials and instruments

Lead bromide (PbBr_2 , 99.9% trace metals basis), cesium acetate (CsOAc , $\text{C}_2\text{H}_3\text{CsO}_2$, 99.9% trace metals basis), zinc bromide (ZnBr_2 , 99.9% trace metals basis), Zinc iodide (ZnI_2 , 99% trace metals basis), 1-octadecene (ODE, $\text{C}_{18}\text{H}_{36}$, technical grade, 90%), oleylamine (OLA, $\text{C}_{18}\text{H}_{37}\text{N}$, technical grade, 70%), oleic acid (OA, $\text{C}_{18}\text{H}_{34}\text{O}_2$, technical grade, 90%), and hexane (C_6H_{14} , 98%) were purchased from Aladdin. All chemicals were used without any further purification.

Transmission electron microscopy (TEM, Talos F200S, Thermo Fisher, USA) and X-ray powder diffractometry (XRD, Rigaku-Ultima IV, Japan) and X-ray photoelectron spectroscopy (XPS, Thermo fisher, USA) were used to detect the crystal structures and the elements of materials. A UV-vis spectrophotometer (UV2550, Shimadzu, Japan) was used to record the absorption spectra, while an F-7000 instrument (Hitachi, Japan) was used to record the fluorescence spectra.

Preparation of Cs-OA

CsOAc (0.96 g, 5 mmol) was added to a 25 mL two-neck flask containing OA (10 mL) at room temperature. After that, the mixture was heated at 120°C under N_2 for 120 min to remove residual oxygen and water. The temperature was maintained until the complete dissolution of CsOAc , as evidenced by the mixture becoming transparent. The solution was stored at room temperature, and was heated to 120°C prior to injection in the subsequent reactions.

Synthesis of CsPbBr_3 NCs

PbBr_2 (18.4 mg, 0.05 mmol) and ZnBr_2 (213.9 mg, 0.95 mmol) was added to ODE (20 mL) in a 50 mL three-neck flask, followed by adding OLA (3 mL) and OA (3 mL) at room temperature. The mixture was heated to 120°C under N_2 , then stirred for 120 min in order to remove residual oxygen and water in the solution. The milky solution became transparent upon dissolution of the PbBr_2 and ZnBr_2 . After the temperature was raised to 180°C , the preheated Cs-OA solution (1.0 mL) was then injected swiftly into the reaction solution. Immediately after injection, the solution was quickly cooled to

room temperature in an ice bath. The resulting crude CsPbBr₃ solution was then stored under ambient conditions.

The resulting crude CsPbBr₃ solution was centrifuged at 10 000 rpm for 10 min. The supernatant was discarded after centrifugation. The precipitated CsPbBr₃ NCs were then redispersed in pure 10 mL n-hexane, and then centrifuged at 3500 rpm for 5 min to remove large crystals. The green supernatant was collected to give a solution that was colloidally stable over an extended period.

Anion exchange reaction of CsPbBr₃ NCs

The OLAI precursor was prepared by adding 100 mg ZnI₂ to 10 mL ODE in a 25 mL three-necked round-bottom flask. After drying under vacuum at 120°C for 10 min, 1 mL of the dried OLA mixture was injected to dissolve the salt and held for 12 h. The precursor solution was cooled to room temperature and used. The OLAI in hexane precursor was similar, except that the reaction temperature was 40°C. The anion exchange reaction of CsPbBr₃ NCs was carried out by mixing the solution with 10 μL OLAI precursor solution in hexane at different concentrations.

Preparation of disposable paper-based nano-temperature sensor

The disposable paper-based sensor was prepared by impregnation method. Specifically, a piece of filter paper with a diameter of 1.3 mm was first immersed in 500 μL of CsPbBr₃ NCs solution at room temperature overnight for the evaporation of hexane. These films were stored at 4°C and sealed from light. Then, the disposable paper-based sensor was used to detect different temperatures. The mixed solvent block was placed above the disposable paper-based sensor. When the actual temperature was higher than the corresponding melting point temperature, the melting of the mixed solvent block led to the contact and ion exchange reaction of the OLAI with the CsPbBr₃ NCs, then the fluorescence color change was monitored.

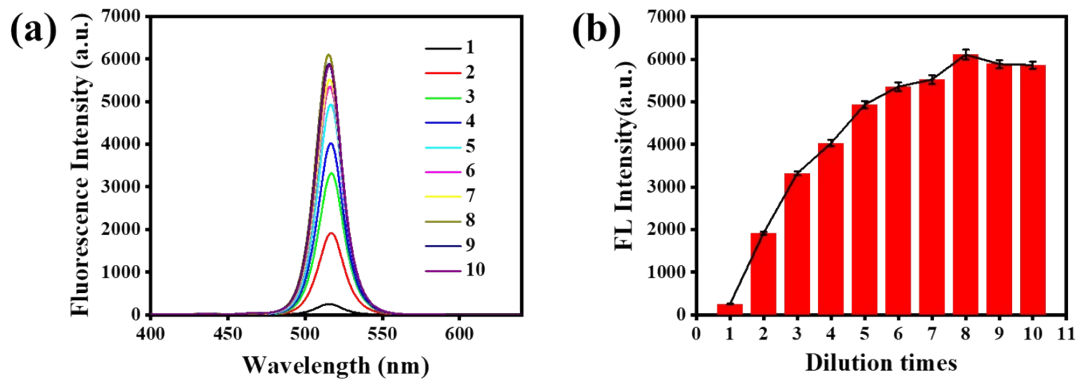


Figure S1. Optimization of fluorescence intensity of CsPbBr₃ NCs, 1 represents stock solution, 2 represents 2-fold dilution, and so on. (a) Fluorescence spectrum of CsPbBr₃ NCs at different dilutions and (b) The corresponding fluorescence intensity of CsPbBr₃ NCs at different dilutions.

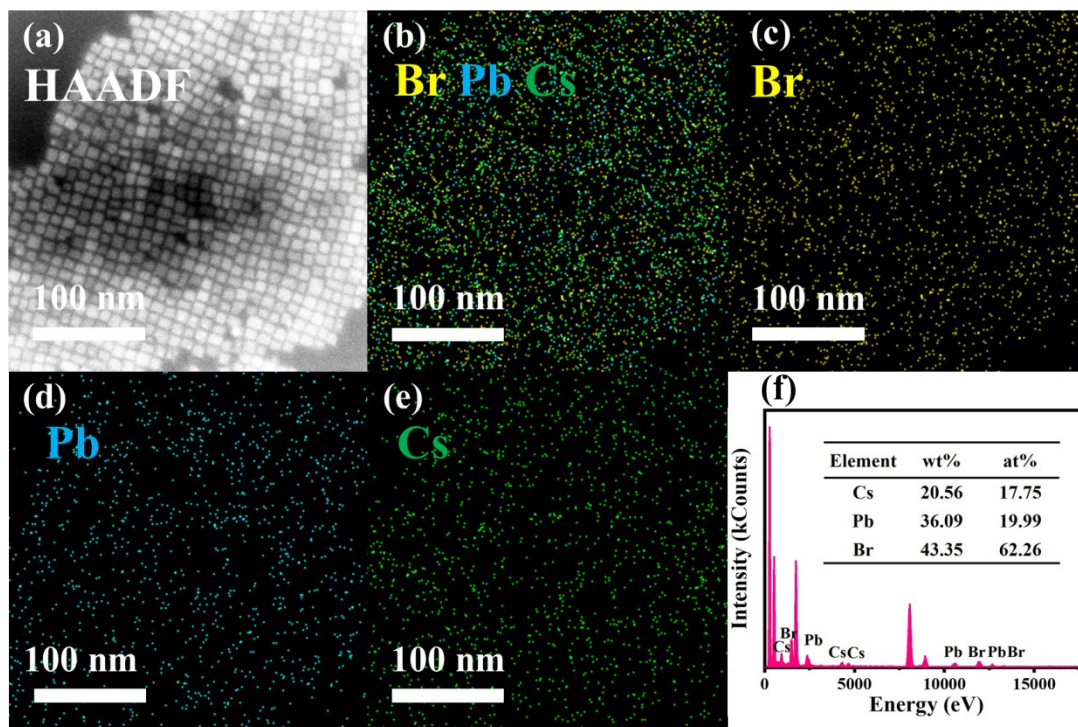


Figure S2. (a-e) elemental mapping, and (f) EDS spectrum of CsPbBr₃ NCs.

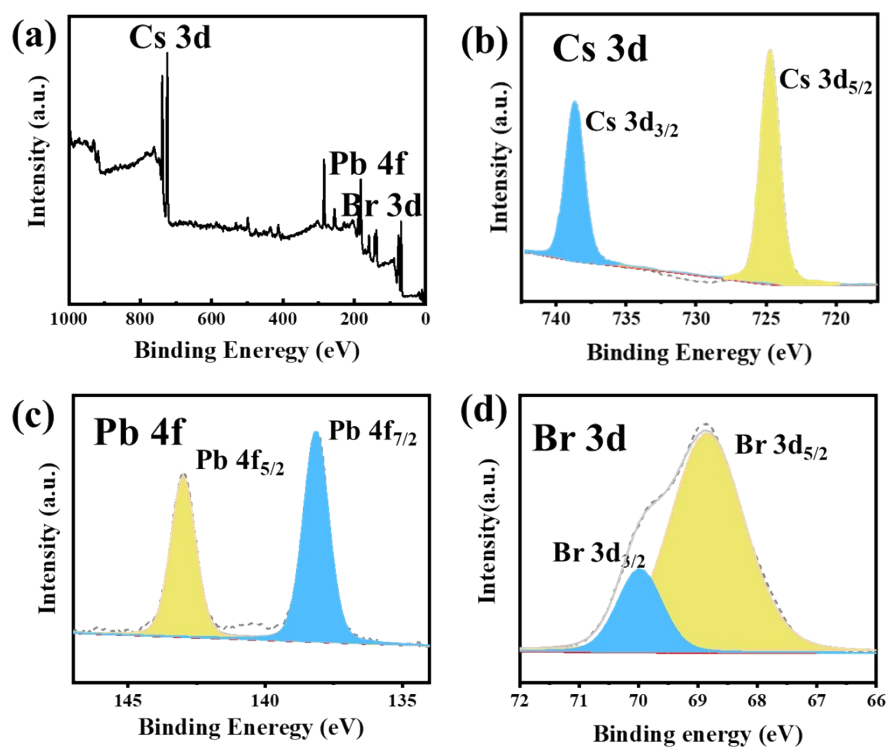


Figure S3. XPS survey of CsPbBr₃ NCs (a), the deconvolution of Cs 3d (b), Pb 4f (c) and Br 3d (d).

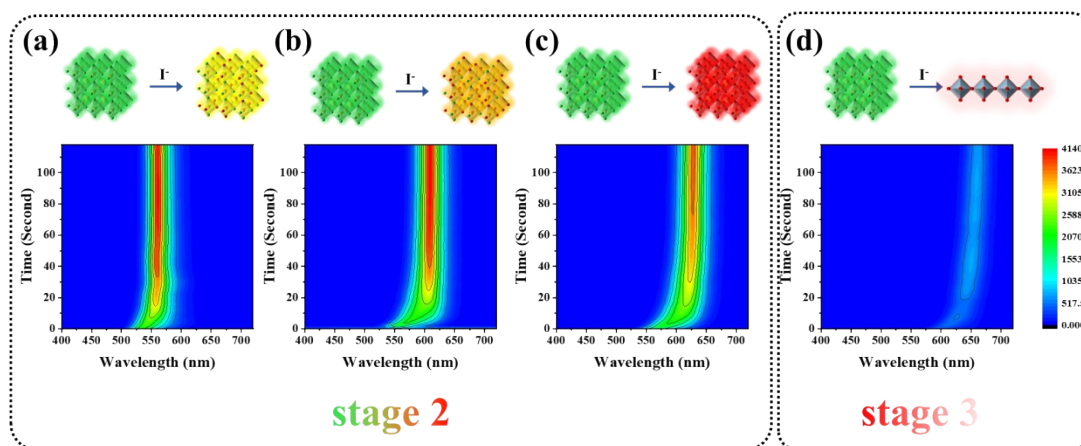


Figure S4. Time-dependent FL emission spectra of CsPbBr₃ NCs after adding 20, 40, 60, 1000 μg/mL OLAI [(a, b, c) correspond to the stage 2, (d) correspond to the stage 3].

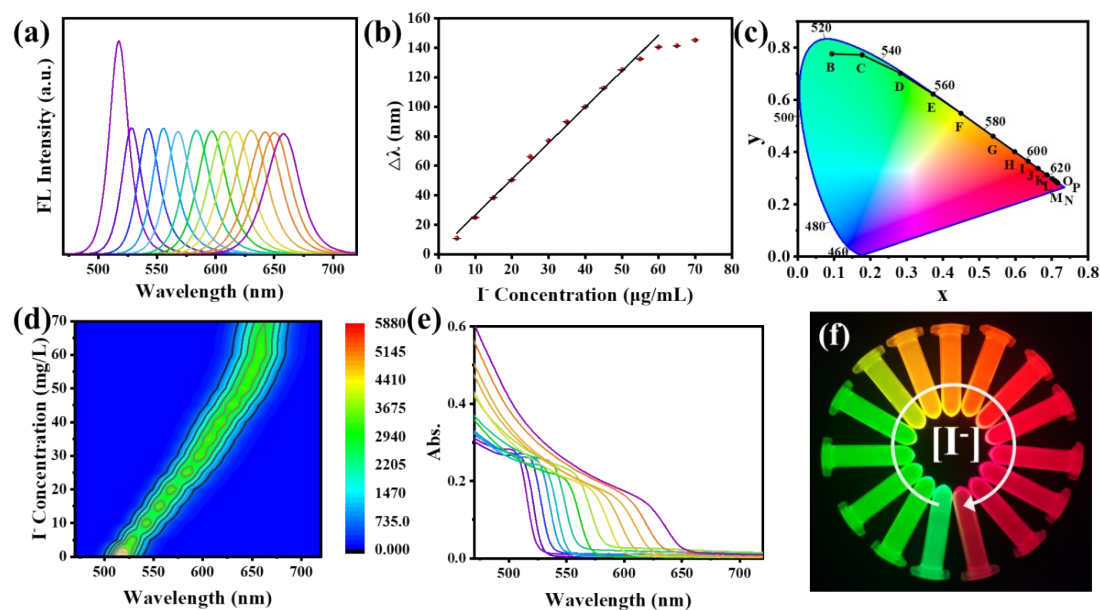


Figure S5. (a) FL emission spectra of CsPbBr₃ NCs after adding different concentrations OLAI in ODE (0 μg/mL, 5 μg/mL, 10 μg/mL, 15 μg/mL, 20 μg/mL, 25 μg/mL, 30 μg/mL, 35 μg/mL, 40 μg/mL, 45 μg/mL, 50 μg/mL, 55 μg/mL, 60 μg/mL, 65 μg/mL, 70 μg/mL). (b) Redshift of CsPbBr₃ FL emission as a function of OLAI concentration in ODE. Linear fitting of results from 5 to 60 μg/mL shown as a black line with $R^2 = 0.99$. (c) CIE chart converted from the FL spectra of CsPbBr₃ exposed to varying amounts of OLAI in ODE. (d) Planar surface spectra of 3D FL emission of CsPbBr₃ NCs after adding different concentrations of OLAI in ODE. (e) UV-vis spectra of CsPbBr₃ NCs after adding different concentrations of OLAI in ODE. (f) Light photos of CsPbBr₃ NCs under 365 nm UV after adding different concentrations of OLAI in ODE.

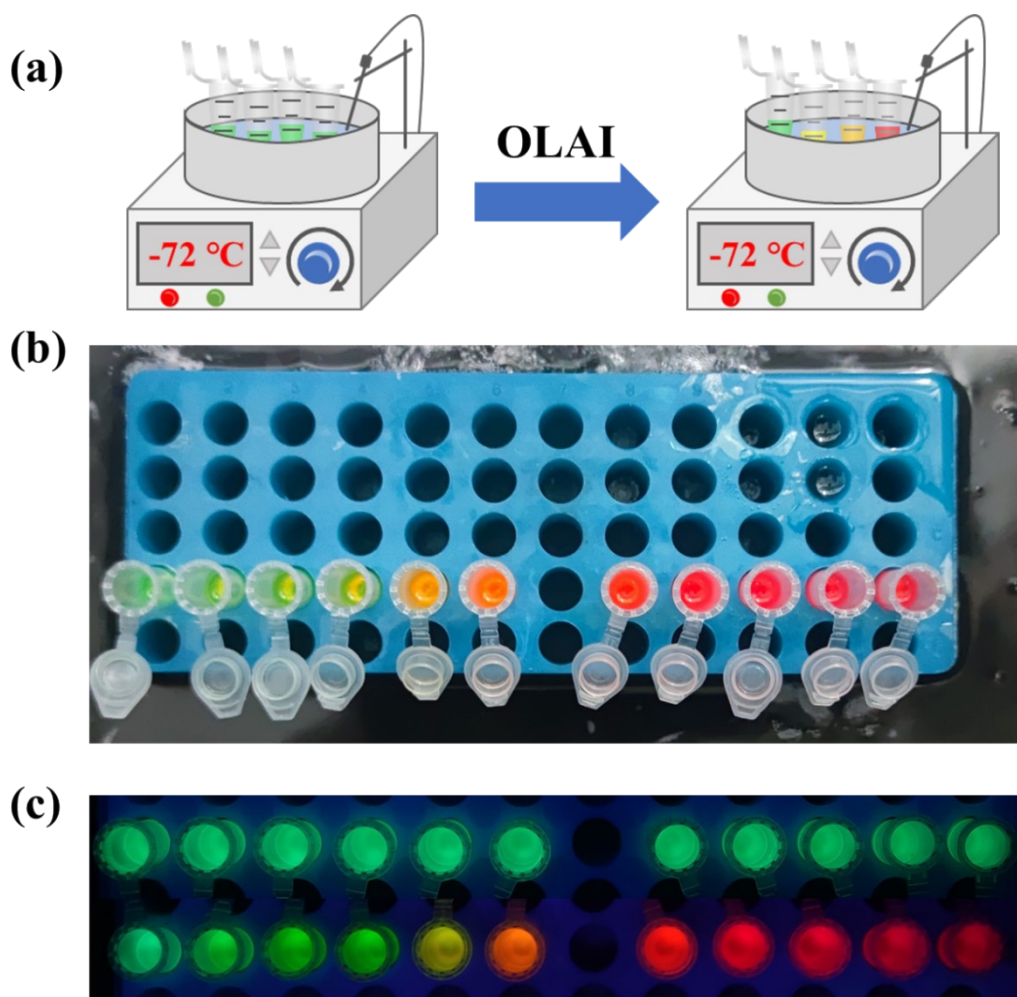


Figure S6. Diagram of the anion exchange reaction of CsPbBr₃ NCs and OLAI in an ethanol-dry ice bath environment (-72°C). (a) Schematic diagram of the reaction apparatus. (b) Photograph of the reaction after daylight irradiation in a cooling bath. (c) Photographs of the reaction before and after 365 nm UV irradiation in a cooling bath (0 µg/mL, 5 µg/mL, 10 µg/mL, 15 µg/mL, 20 µg/mL, 25 µg/mL, 30 µg/mL, 35 µg/mL, 40 µg/mL, 45 µg/mL, 50 µg/mL, 55 µg/mL).

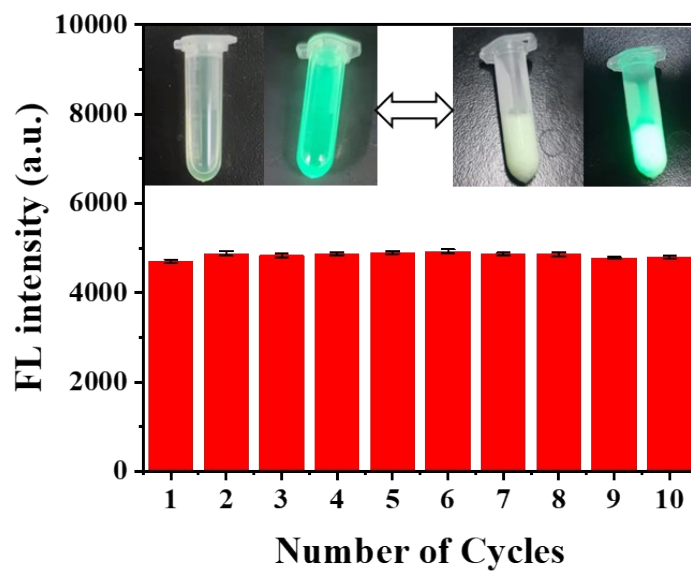


Figure S7. FL emission intensity of CsPbBr₃ NCs with different numbers of freezing cycles, inset: digital photographs of the freezing process in daylight and under a 365 nm UV lamp (left: CsPbBr₃ in the melted state, right: CsPbBr₃ in the solidified state).

Table S1. Summary table of different temperature indicators in recent years

Indicator Type	Materials	The color changes	Indicated temperature	Response	Ref.
Chemical	Gold nanoparticles	Transparent to purple	30°C	6 h	[1]
Chemical	Polydiacetylene/silver nanoparticles	Violet-blue to purple to fuchsia	35°C	24 h	[2]
Enzymatic	Laccase in the electrospun chitosan/poly (vinyl alcohol) fiber	Transparent to deep purple to brown	4 to 40°C	30 min	[3]
Chemical	Xylose-lysine system	Transparent to deep brown	0 to 25°C	2 h	[4]
Flowing	Poly (<i>N</i> -tert-butyl acrylamide- <i>co</i> - <i>N</i> -isopropyl acrylamide- <i>co</i> -acrylamide) and p(NTBAM- <i>co</i> -NIPAM- <i>co</i> -AM) hydrogels	Transparent to pink	2 to 8°C	80 min	[5]
Diffusional	A dyed noneutectic ethylene glycol/water mixture	Transparent to blue	-70 to -60°C	2 min	[6]
Flowing	Carbon dots and water/dimethyl sulfoxide solvent	Green to yellow	-68 to 4°C	Less than 1 min	[7]
Flowing-Chemical	CsPbBr ₃ and n-Hexane/1-Octadecene	Green to yellow to orange to red	-68 to 4°C	Less than 1 min	This work

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