Enhancing the Stability of $CsPbBr_3$ Nanocrystals by Sequential Surface Adsorption of S^{2-} and Metal Ions

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Supporting Information

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1. Experimental Procedures

Reagents. Cesium carbonate (Cs_2CO_3, Aladdin, 98%), lead bromide ($PbBr_2$, Aladdin, 98%), indium acetate ($In(Ac)_3$, Alfa Aesar, 99.99%), zinc acetate ($Zn(Ac)_2$, Aladdin, 99%), manganese acetate ($Mn(Ac)_2$, Aladdin, 98%), nickel acetate tetrahydrate ($Ni(Ac)_4 \cdot 4H_2O$, Aladdin, 99.9%), 1-octadecene (ODE, Aladdin, 90%), oleic acid (OA, Sigma-Aldrich, 90%), oleylamine (OAm, Aladdin, 90%), didodecyl dimethylammonium bromide (DDAB, Aladdin, 98%), toluene (Aladdin, 98%), methyl acetate (Aladdin, 98%), $Na_2S \cdot 9H_2O$ (Aladdin, 99.99%), and optical adhesive (Norland 61). All the chemicals were used in this study without further purification.

Preparation of Cs-oleate precursor. In this procedure, 10 mmol of Cs_2CO_3, 20 mL of OA, and 20 mL of ODE was mixed in a 100 mL round-bottom flask equipped with a reflux condenser and a thermocouple probe under standard air free conditions. This mixture was heated to 120 °C and then evacuated for 1 h at 120 °C. Subsequently, the temperature was raised to 150 °C under argon flow the mixed solution formed an optically clear solution. After another 0.5 h, the solution was cooled down to room temperature, and stored as stock solution.

Preparation of $CsPbBr_3$ NCs. 20 mL of ODE, 5 mL of OAm, 5 mL of OA, and 2 mmol $PbBr_2$ were loaded into a 100 mL three-neck flask, degassed at 120 °C for 30 min. Then, the temperature rose to 180 °C under argon atmosphere until $PbBr_2$ salt had completely dissolved. 1 mL of CsOA precursor (0.5 M), which was also pre-heated at 70 °C, was quickly injected into the reaction system. After 5 s, the three-neck flask was placed in an ice-water bath and cooled to room temperature. The crude solution was precipitated by methyl acetate and separated via centrifugation. It should be pointed out that adding methyl acetate of the same volume as that of the crude solution to is helpful for a complete precipitation. The supernatant was discarded and precipitate was dispersed in a toluene solution after centrifugation and stored as stock solution.

Preparation of S^{2-}-DDA^+. 69.395 mg of DDAB and 36.027 mg of $Na_2S \cdot 9H_2O$ were dispersed in 3 mL toluene solution and 3 mL deionized water, respectively. Then, they were mixed together. Subsequently, the mixed solution was treated with sonication for 0.5 h. The S^{2-} anions were gradually transferred from the aqueous phase to the toluene phase, and then it was separated after centrifugation. The S^{2-}-DDA^+ toluene solution (0.05 mol/L) was obtained.

S^{2-}-DDA^+ treatment $CsPbBr_3$ ($CsPbBr_3$·S) NCs. 100 μL S^{2-}-DDA^+ toluene solution (0.05 mol/L) was added into 1 mL of the purified $CsPbBr_3$ NCs (ca. 13 mg/mL), then the mixture solution was stirred for 1 h under room temperature. After that, the $CsPbBr_3$·S NCs were obtained.

Preparation of $CsPbBr_3$·S-In NCs. In this procedure, $CsPbBr_3$·S NCs solution and certain amount of $In(Ac)_3$ was mixed together and stirred for 2 h. Next, the supernatant in the final products mixture solution was collected after centrifugation at 10000 rpm for 2 minutes, the precipitate was discarded. Finally, $CsPbBr_3$·S-In was prepared successfully.

Preparation of other $CsPbBr_3$·S-X NCs. The preparation of other $CsPbBr_3$·S-X NCs was followed the same procedure as $CsPbBr_3$·S-In NCs, wherein the In $(Ac)_3$ was replaced with other metal salt ($Zn(Ac)_2$, $Mn(Ac)_2$, $Ni(Ac)_4 \cdot 4H_2O$).

Preparation of metal ions-doped $CsPbBr_3$ NCs. The metal salts ($Mn(Ac)_2$, $Ni(Ac)_4 \cdot 4H_2O$ and In $(Ac)_3$) were added into the pristine $CsPbBr_3$ NCs solution and stirred for 2 h. Next, the supernatant in the final products mixture solutions was collected and precipitate was discarded after centrifugation at 10000 rpm for 2 min. Finally, the $CsPbBr_3$·Mn NCs, $CsPbBr_3$·Ni NCs, and $CsPbBr_3$·In NCs was successfully prepared.

Photostability measurements of solution. Before photostability measurements, all the samples were adjusted to the same optical density (Abs=1.8, 450 nm). 2.5 mL solutions above were transferred into the quartz cuvettes (sealed) and illuminated with the 450 nm LED light (175 mW/cm^2) under 25 °C and 50%-60% RH. The PL emission and UV-vis absorption spectra were recorded at every periodic interval.

LED package. 0.5 mL of $CsPbBr_3$ NCs (ca. 13 mg/mL) in toluene solution was mixed with 300 mg of UV-cured optical adhesive. Then the resulting mixture was vacuumed for o.5 h to remove the toluene and bubbles. 0.5 mL of $CsPbBr_3$·S NCs and $CsPbBr_3$·S-In NCs solution were treated through the same steps. After removing the bubbles, the mixture was dropped onto a blue chip and then UV cured for 15 seconds (365 nm, 80 W/cm^2).

PL quantum yield measurements. The absolute photoluminescence quantum yield (PLQY) of the $CsPbBr_3$, $CsPbBr_3$·S, and $CsPbBr_3$·S-In NCs solution were determined using a fluorescence spectrometer with an integrated sphere excited at the 450 nm LED light source.

2. Figures S1-11

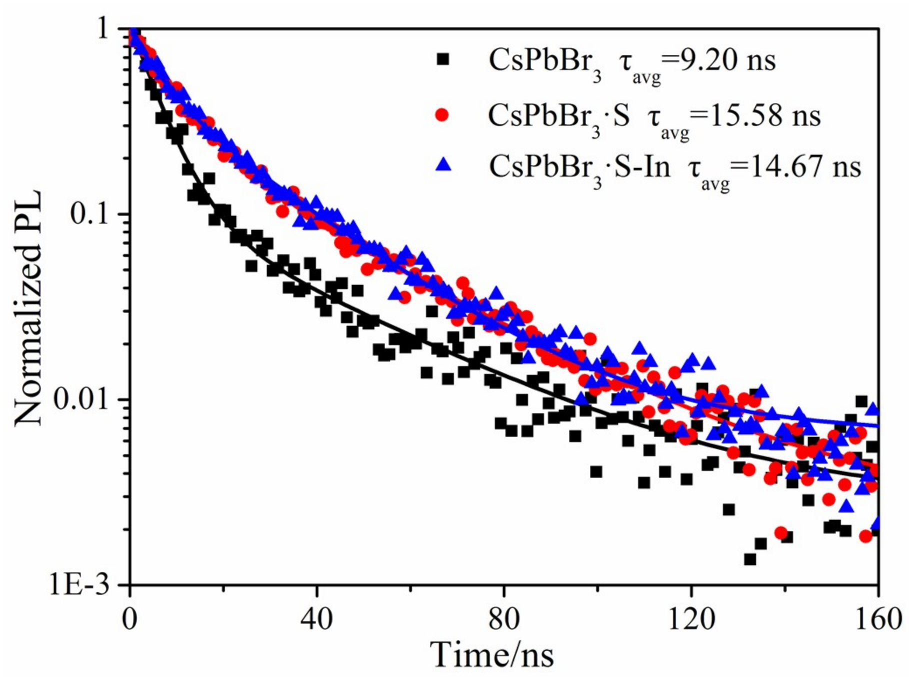

Figure S1. Time-resolved PL (TRPL) decays spectra and the fitted curves of $CsPbBr_3$ NCs, $CsPbBr_3$·S NCs, and $CsPbBr_3$·S-In NCs.

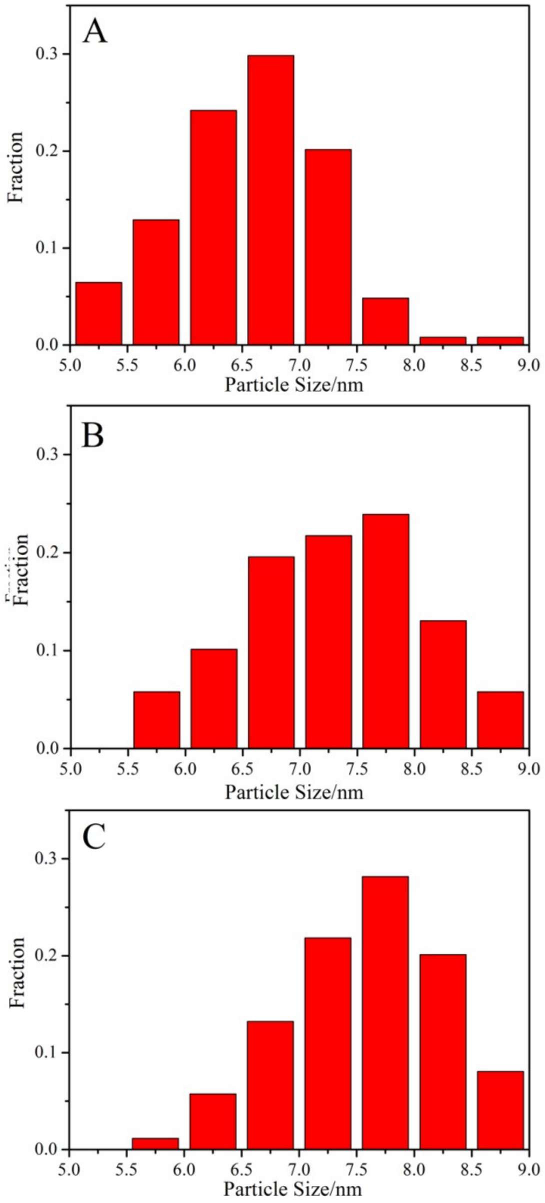

Figure S2. Size distributions of pristine $CsPbBr_3$ NCs (A), $CsPbBr_3{\cdot}S$ NCs (B) and $CsPbBr_3{\cdot}S$-In NCs (C).

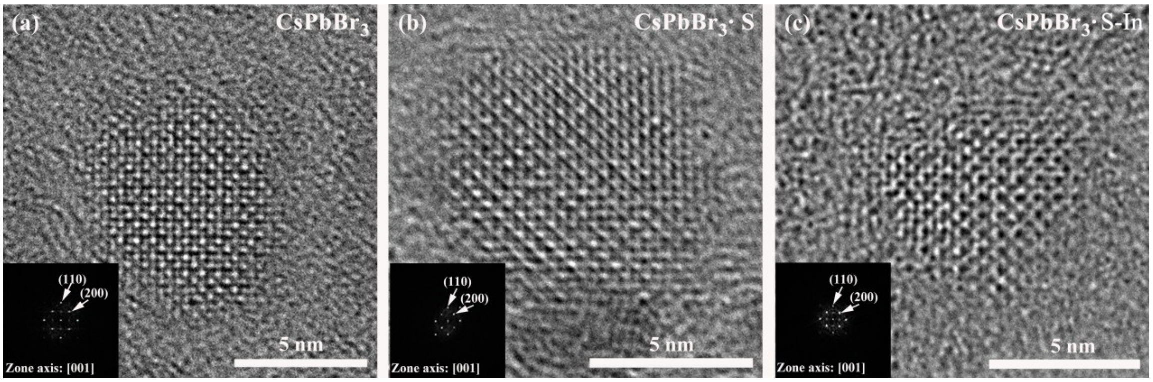

Figure S3. High-resolution TEM (HRTEM) observed from [001] direction and corresponding fast-Fourier transform (FFT) patterns of $CsPbBr_3$ NCs (a), $CsPbBr_3{\cdot}S$ NCs (b), and $CsPbBr_3{\cdot}S$-In NCs (c).

Note: The HRTEM results of $CsPbBr_3$ NCs, $CsPbBr_3{\cdot}S$ NCs, and $CsPbBr_3{\cdot}S$-In NCs show they have the same crystal structure. This suggests that S^{2-} and S-In does not affect the crystal structure of $CsPbBr_3$. The NCs in this image were chosen due to their good contrast, and their sizes cannot represent the average sizes of their corresponding samples.

Table S1. The elemental composition of $CsPbBr_3$·S-In NCs according to ICP test.

Element	Content (mg/L)
In	18.07
Pb	614.0

According to the ICP data, the molar ratio of In/Pb was 0.053.

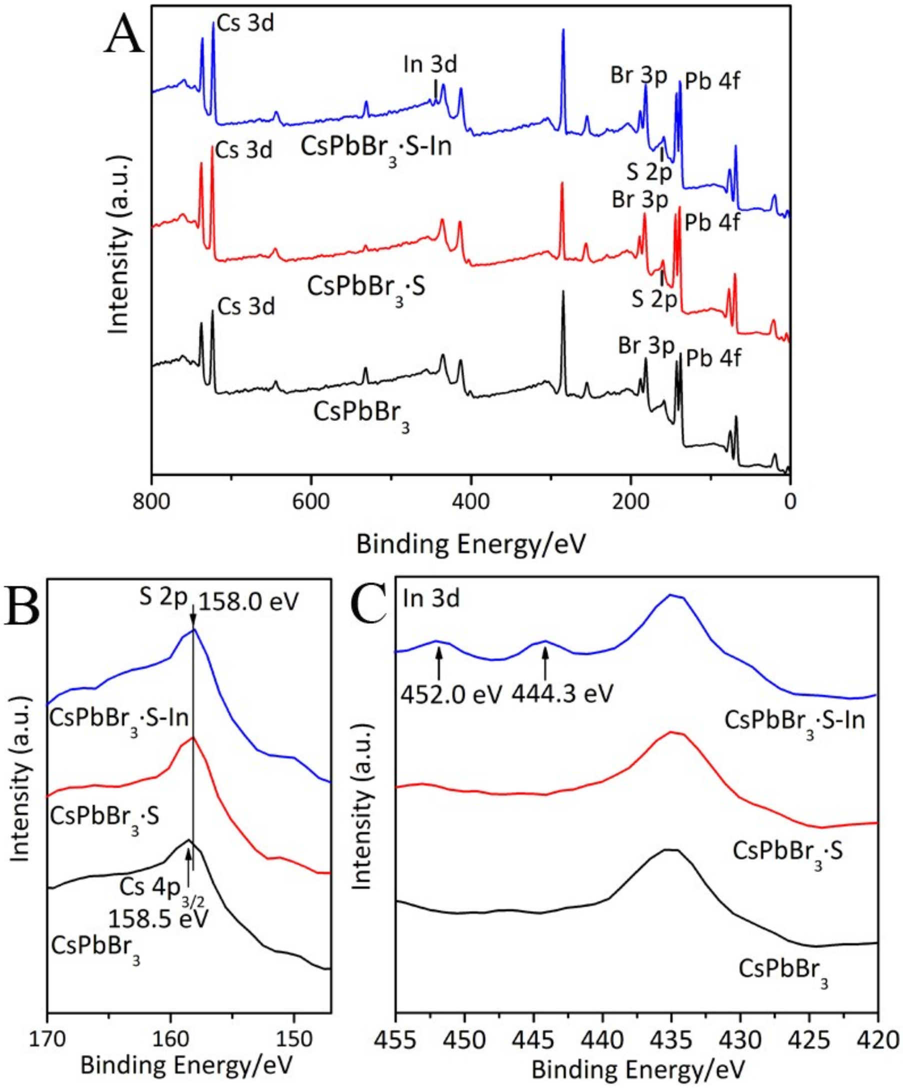

Figure S4. Full range XPS spectra of $CsPbBr_3$ NCs, $CsPbBr_3\cdot S$ NCs, and $CsPbBr_3\cdot S$-In NCs (A), S 2p XPS spectrum (B), and In 3d XPS spectrum (C).

As shown in Figure S4B, it is difficult to distinguish from the spectra of S 2p and Cs $4p_{3/2}$, which peaks located at 158.0 eV and 158.5 eV,[1] respectively, because it seems that their spectra are overlapped. Meanwhile, the binding energies at 444.3 eV and 452.0 eV corresponds to In $3d_{5/2}$ and In $3d_{3/2}$ in Figure S4C, respectively.[2]

Table S2. Element content of the $CsPbBr_3 \cdot S$-In NCs sample from the XPS qualitative analysis.

Name	Pos.	FWHM	Area	At%
Cs 3d	723.35	2.735	1352.20	4.62
Pb 4f	137.35	2.619	2639.71	12.70
Br 3p	181.35	3.582	1485.76	46.55
S 2p	157.35	3.954	557.60	33.45
In 3d	442.35	1.530	67.03	2.69

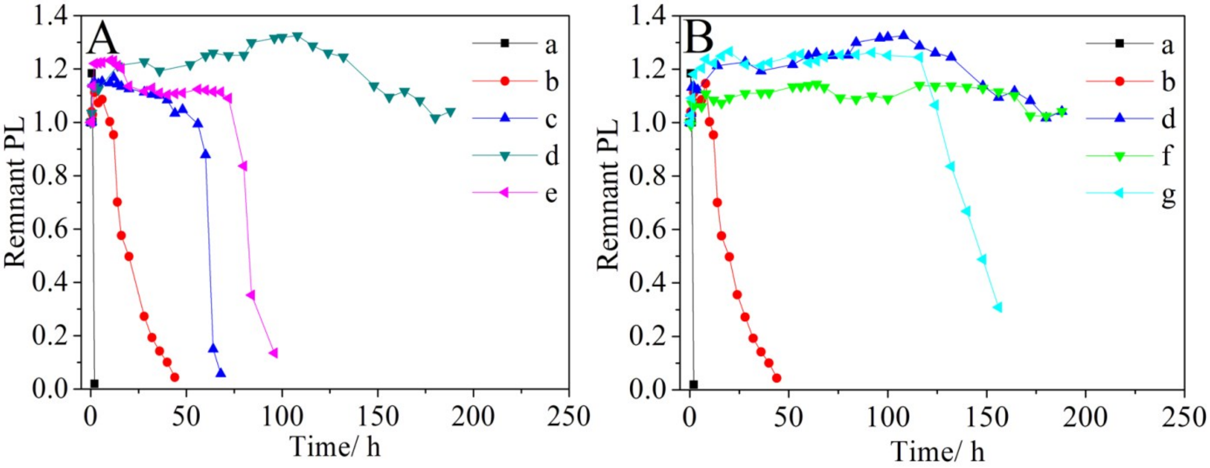

Figure S5. (A) Photostability of the NCs samples respectively treated with different amount of S^{2-}-DDA^{+}: (a) pristine $CsPbBr_3$, (b) 0.005 mmol S^{2-}-DDA^{+}, (c) 0.0025 mmol S^{2-}-DDA^{+} and 0.01 mmol $In(Ac)_3$, (d) 0.005 mmol S^{2-}-DDA^{+} and 0.01 mmol $In(Ac)_3$, (e) 0.0075 mmol S^{2-}-DDA^{+} and 0.01 mmol $In(Ac)_3$. (B) Photostability of $CsPbBr_3{\cdot}S$-In NCs treated with 0.005 mmol S^{2-}-DDA^{+} and different amount of $In(Ac)_3$: (f) 0.02 mmol $In(Ac)_3$ and (g) 0.04 mmol $In(Ac)_3$.

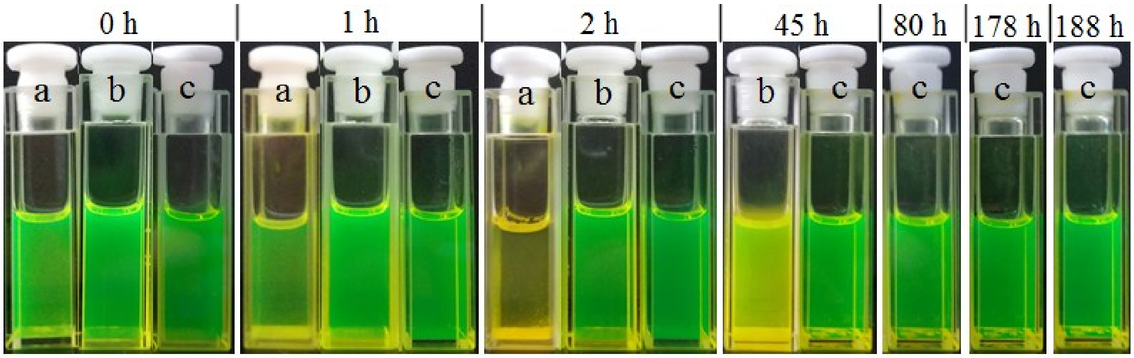

Figure S6. Optical images of $CsPbBr_3$ NCs (a), $CsPbBr_3 \cdot S$ NCs (b), and $CsPbBr_3 \cdot S$-In NCs (c) under illumination with a 450 nm LED light (175 mW/cm^2).

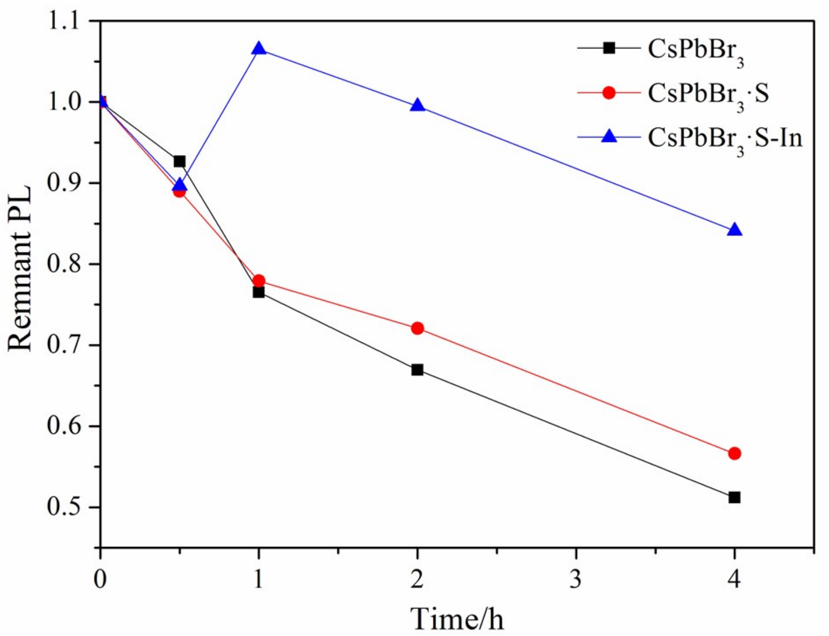

Figure S7. Thermal stability of pristine $CsPbBr_3$, $CsPbBr_3 \cdot S$, and $CsPbBr_3 \cdot S$-In NCs films with heating at 100 °C.

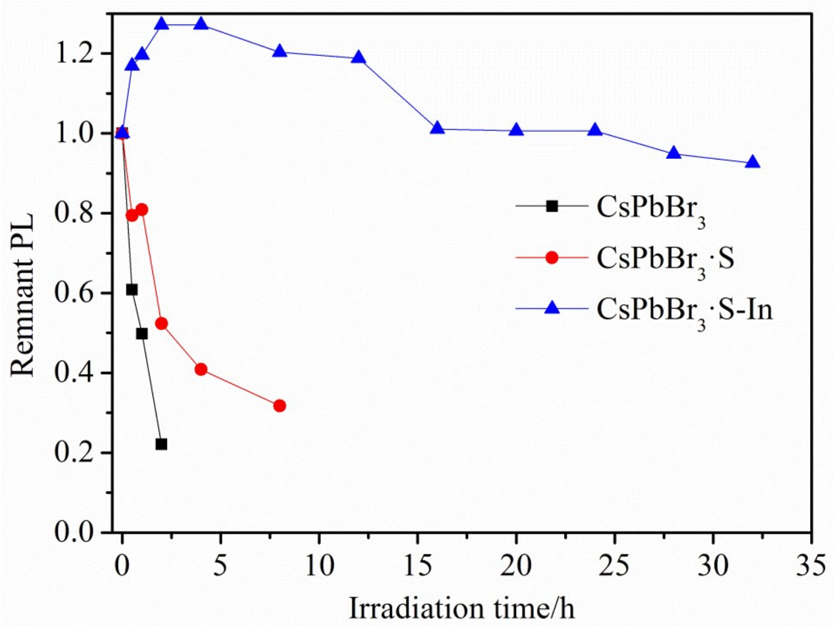

Figure S8. Photostability of pristine $CsPbBr_3$ NCs, $CsPbBr_3{\cdot}S$ NCs, and $CsPbBr_3{\cdot}S$-In NCs sealed with optical adhesive on LED chip (5 mA, 2.7V).

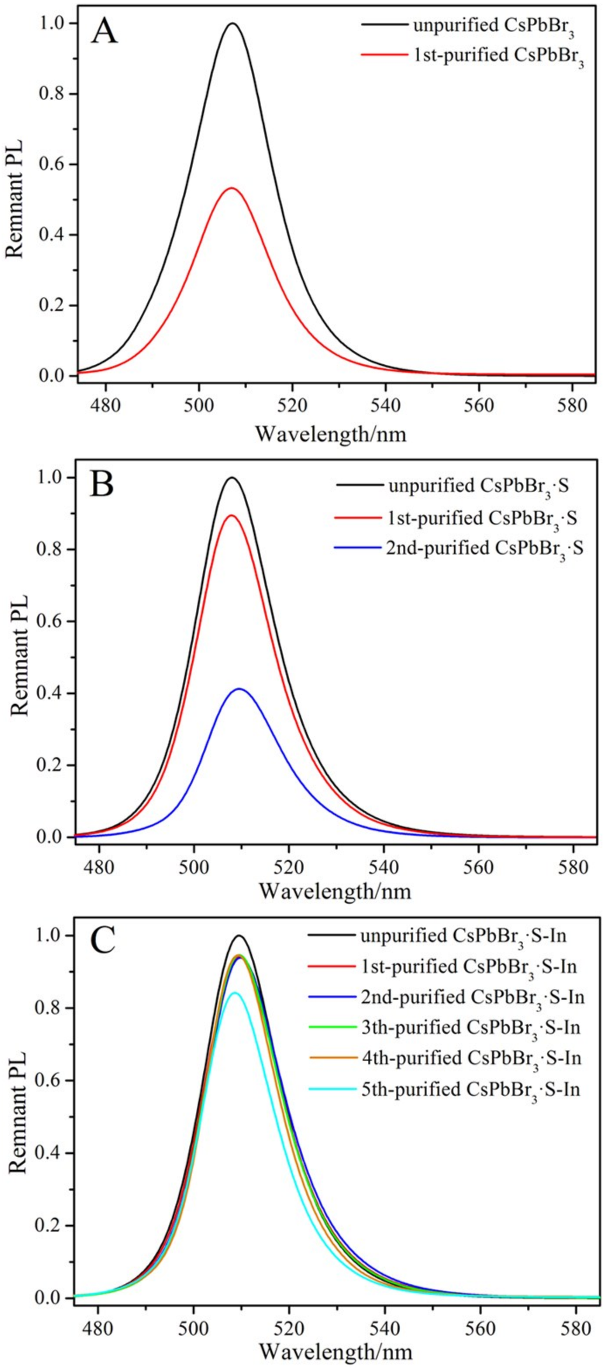

Figure S9. PL spectra of CsPbBr$_3$ NCs (A), CsPbBr$_3$·S NCs (B), and CsPbBr$_3$·S-In NCs (C) solutions after washing with different times.

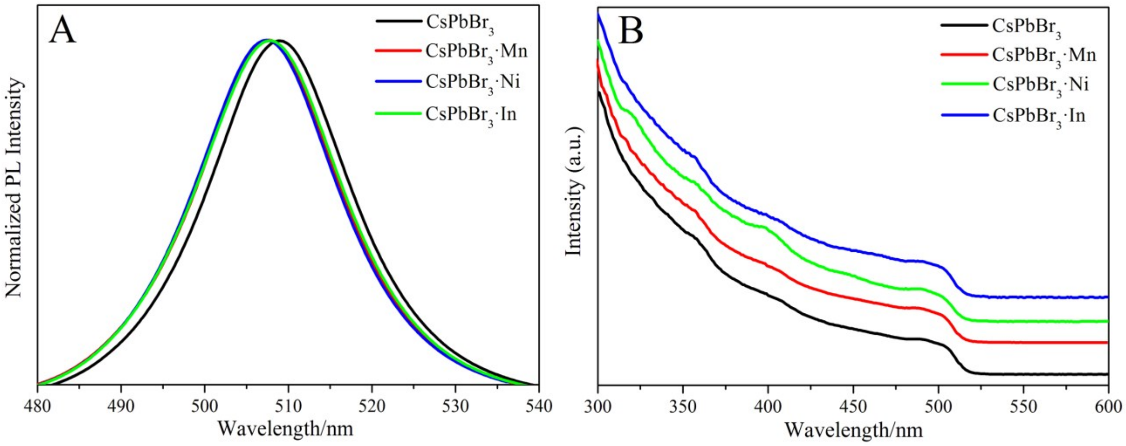

Figure S10. PL spectra (A) and UV-vis absorption spectra (B) of the $CsPbBr_3$, $CsPbBr_3$·Mn, $CsPbBr_3$·Ni, and $CsPbBr_3$·In NCs.

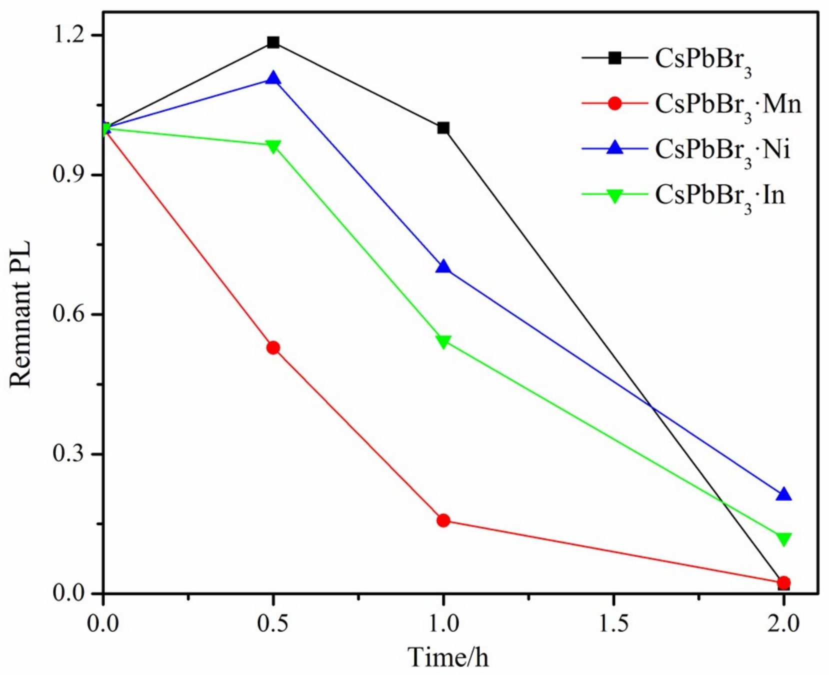

Figure S11. Photostability of the $CsPbBr_3$, $CsPbBr_3$·Mn, $CsPbBr_3$·Ni, and $CsPbBr_3$·In NCs under illumination with a 450 nm LED light (175 mW/cm^2)

References:

1. M V Elizarov, O V Lozkina, D I Yeletz, A V Emeline , V K Ryabchuk and A A Murashkina, *Journal of Physics: Conference Series,*2018, **993**, 1-5.
2. Teny Theresa John, C. Sudha Kartha, K.P. Vijayakumar, T. Abe, Y. Kashiwaba, *Applied Surface Science*, 2005, **252**, 1360-1367.