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Electronic Supporting Information

Interfacial Defect Capture-Induced Abnormal Fluorescence Decay Lifetime of $CsPbBr_3$ /$CsPbBr_3$ Nanodisks

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Experimental section

Materials: Lead(II) oxide (PbO, 99.999%), lead(II) bromide ($PbBr_2$, 99.999%), Cesium carbonate (Cs_2CO_3, 99.9%), Oleylamine (OAm, 80-90%), Oleic acid (OA, 90%), 1-octadecene (ODE, 90%), Manganese acetate tetrahydrate ($Mn(OAc)_2{\cdot}4H_2O$, 99.7%), lead acetate trihydrate ($Pb(OAc)_2{\cdot}3H_2O$, 99.99%), Sulfur powder (S, 99.99%), 1-dodecanethiol (1-DDT, 99.9%), Phenacyl bromide ($C_6H_5COCH_2Br$, 98%), 1,3,5-Trimethylbenzene (AR, 97%), Ethyl acetate (EA, AR, 97%), Hexane (anhydrous, 99.5%) were purchased from Aladdin. All chemicals were used without any further purification.

Preparation of Ce-oleate precursors: Cs_2CO_3 (0.36 g, 1.1 mmoL), octadecene (15 mL) and oleic acid (1.5 mL) were added into 100 mL 3-neck flask, exhausted for half an hour at 120°C, and then heated under Ar to 150°C until all Cs_2CO_3 reacted with OA. The solution was kept at 120°C to avoid solidification before injection.

Preparation of Pb-oleate precursors: $Pb(OAc)_2{\cdot}3H_2O$ (0.76 g, 2 mmoL), octadecene (18.7 mL) and oleic acid (1.3 mL) were added into 100 mL 3-neck flask, exhausted for half an hour at 120 ^oC, and then heated under Ar to 150 ^oC until $Pb(OAc)_2{\cdot}3H_2O$ all reacted with OA. The solution was kept at 120 °C to avoid solidification before injection.

Preparation of S-ODE precursors: S (0.0048 g, 2 mmol) and octadecene (20 mL) were added into 100 mL 3-neck flask and degassed for 5 min. Then, the resulting mixture was sonicated until the complete dissolution of S.

Synthesis of $CsPbBr_3$ QDs: In a typical synthesis, $PbBr_2$ (0.2 g, 0.54 mmoL), ODE (15 mL), OA (1.5 mL) and OAm (1.5 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120^{o}C under Ar flow. After complete dissolution of $PbBr_2$ salt, the temperature was increased to 160^{o}C and then maintained for another 30 min under Ar atmosphere. The preheated Cs-oleate solution was swiftly injected into the transparent precursor solution. After 5 s, the reaction mixture was cooled down using a water bath.

Synthesis of Cs_3MnBr_5 precursors: Mn $(OAc)_2{\cdot}4H_2O$ (0.196 g, 0.8 mmol), phenacyl bromide (0.5572 g,2.8 mmol), OA (1 mL) and ODE (5 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120^{o}C under Ar flow. After that, the temperature was increased to 220°C followed by injection of 1 mL of OLA. Then, the temperature was cooled to 120°C and 0.5 mL of Cs-oleate solution was swiftly injected into the solution and annealed for 3 min. Finally, the reaction mixture was cooled down using a water bath. As synthesized QDs were centrifuged at 6000 rpm for 10 min, and precipitated nanocrystals were redispersed in 1,3,5-Trimethylbenzene (4 mL) for further use.

Synthesis of $CsPbBr_3$/$CsPbBr_3$ NDs: PbO (0.044 g, 0.2 mmol), phenacyl bromide (0.1592 g, 0.8 mmol), OA (2 mL) and ODE (5 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120^{o}C under Ar flow. After that, the temperature was increased to 220°C followed by injection of 0.5 mL of OLA. Then, the temperature was cooled to 110°C and 0.4 mL of Cs_3MnBr_5 precursors was swiftly injected into the solution and annealed for 5 min. Soon after the temperature was increased to 200°C followed by injection of Pb-oleate (0.5 mL), 1-DDT (20 μL) and S-ODE (0.6 mL) and annealed for 1 min.

Finally, the reaction mixture was cooled down using a water bath. Ethyl acetate was added into the crude solution with a volume ratio of 1:3 and the mixture were centrifuged for 1 min at 9000 rpm. The precipitate was dispersed in 2 mL of hexane to obtain a clear solution.

Characterizations: The transmission electron microscopy (TEM) images were taken on a transmission electron microscope (Tecnai 12). The HR-TEM images and EDS elemental mappings were taken on a field emission transmission electron microscope (Tecnai G2 F30 S-TWIN). Steady-state PL spectra were measured by the F-7000 fluorescence spectrometer 2014XHTM158. Ultraviolet-visible (UV-vis) absorption spectra were carried out with LAMBDA 650 spectrometer (PerkinElmer). The X-ray diffraction (XRD) was performed on a D8 ADVANCE diffractometer. The temperature-dependent PL and PLE spectra were measured with the Horiba Jobin Yvon Fluorolog-3 spectrometer. The temperature-dependent time-resolved decay data were performed on an Edinburgh FLS1000 fluorescence spectrometer. The absolute PLQY was determined using a Quantaurus-QY absolute photoluminescence quantum yield spectrometer (C11347-11, Hamamatsu Photonics).

Fitting of temperature-dependent PL

To extract the exciton binding energy, the following simple expression for the dependence of the integrated emission intensity (*I*) versus temperature (*T*) is plotted, and fitted by using an Arrhenius equation. [1, 2]

$$I(T) = \frac{I_0}{1 + Ae^{-Ea/k_B T}} \quad (1)$$

Where I_0 represents the fluorescence intensity at 0 K, A is a pre-exponential factor, denotes the Boltzmann constant, and E_a is the activation energy for exciton dissociation.

Fitting of temperature-dependent FWHM

The temperature-dependent FWHM can be fitted by Boson model:[3]

$$\Gamma(T) = \Gamma_0 + \Gamma_{OP} exp(-E_{OP}/K_B T) \quad (2)$$

In which the first term, Γ_o, is the inhomogeneous broadening and Γ_{op} describe the exciton-phonon contributions to the line width broadening.

Fitting of temperature-dependent bandgap

The temperature-dependent bandgap can be fitted by equation (3).[4]

$$E_g(T) = E_0 + A_{EP} exp(-\hbar\omega/K_B T) \quad (3)$$

Where E_0 is the unrenormalized bandgap, A_{EP} is the electron-phonon coupling coefficient, and $\hbar\omega$ *is* the average energy of optical phonons.

Fitting of temperature-dependent Urbach energy values

To obtain Urbach energy values of $CsPbBr_3$ QDs and $CsPbBr_3$/$CsPbBr_3$ NDs at different temperatures. It can be fitted using the formula provided to elucidate the relationship between Urbach energy and

temperature.

$$E_U(T) = E_U(0) + \frac{2E_U(0)}{exp(\theta_E/T) - 1} \quad (4)$$

In the equation under discussion, E_U (0) represents the static component of Urbach energy (E_U), which is independent of temperature and correlates with the intrinsic disorder within the material. The second term is referred to as the dynamic component of E_U, accounting for the contribution of phonons to the measured value of E_U. Here, T denotes the absolute temperature of the sample, and θ_E represents the Einstein temperature of phonons, which is proportional to the phonon energy.

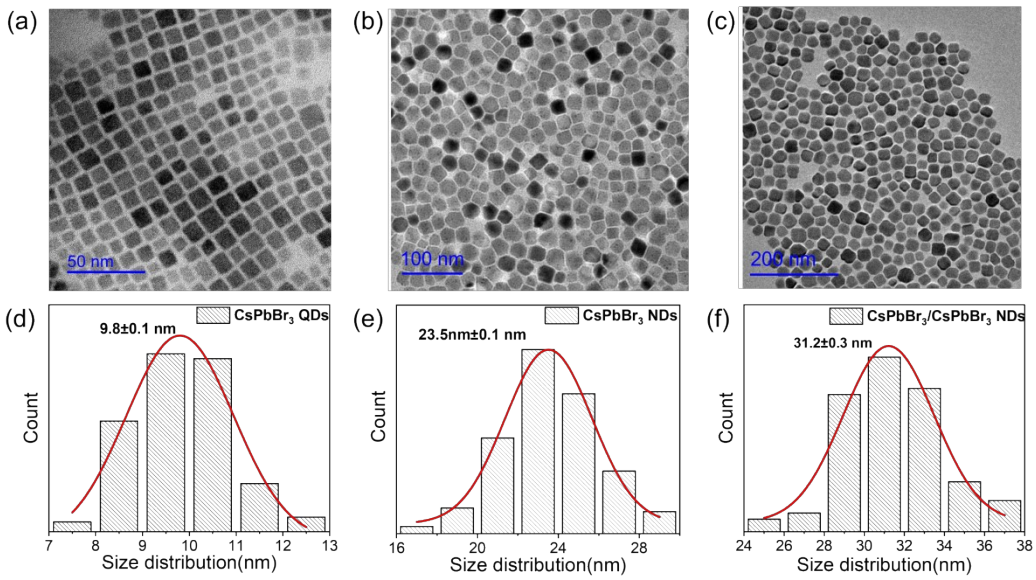

Figure S1. The TEM images of (a) $CsPbBr_3$ QDs, (b) $CsPbBr_3$ NDs, and (c) $CsPbBr_3$/$CsPbBr_3$ NDs and corresponding size distribution of (d) $CsPbBr_3$ QDs, (e) $CsPbBr_3$ NDs, and (f) $CsPbBr_3$/$CsPbBr_3$ NDs.

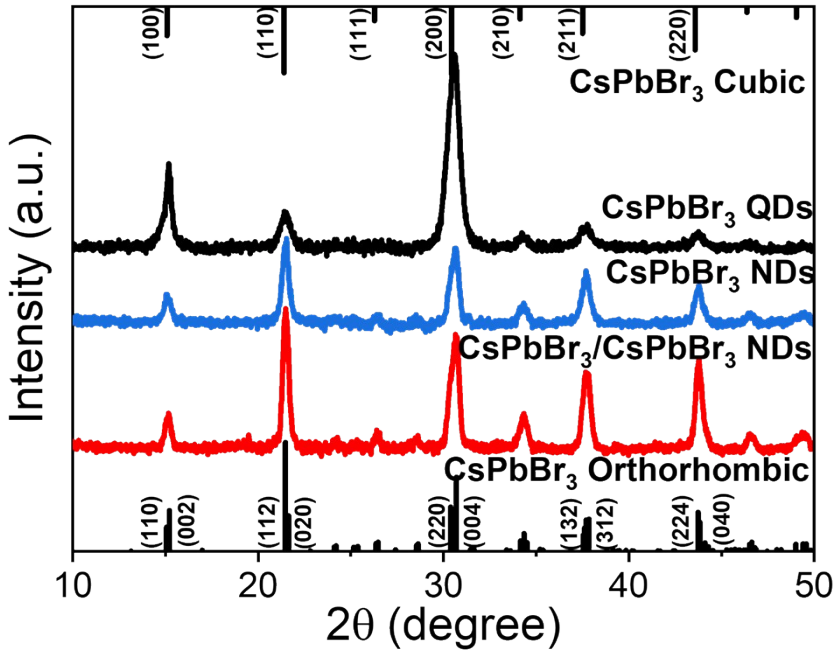

Figure S2. XRD patterns of $CsPbBr_3$ QDs, $CsPbBr_3$ NDs, and $CsPbBr_3$/$CsPbBr_3$ NDs.

Table S1. The content of Cs, Pb, and Mn in $CsPbBr_3$/$CsPbBr_3$ NDs by ICP-MS.

Sample	Cs(mg/L)	Pb(mg/L)	Mn(mg/L)
$CsPbBr_3$/$CsPbBr_3$ NDs	10.249	35.14	0.022

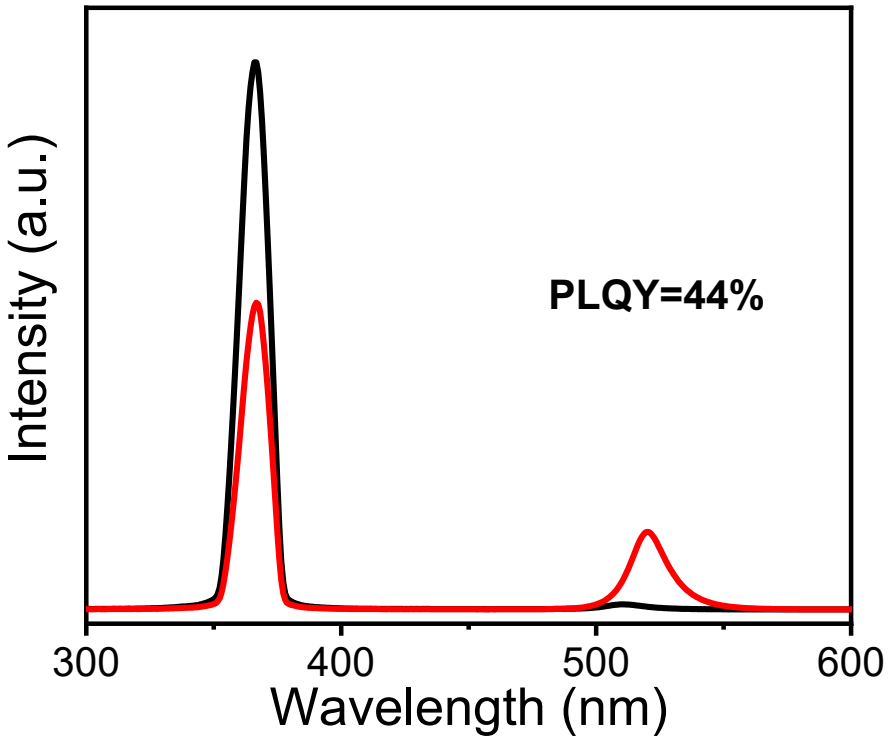

Figure S3. The PLQY value of $CsPbBr_3$ NDs.

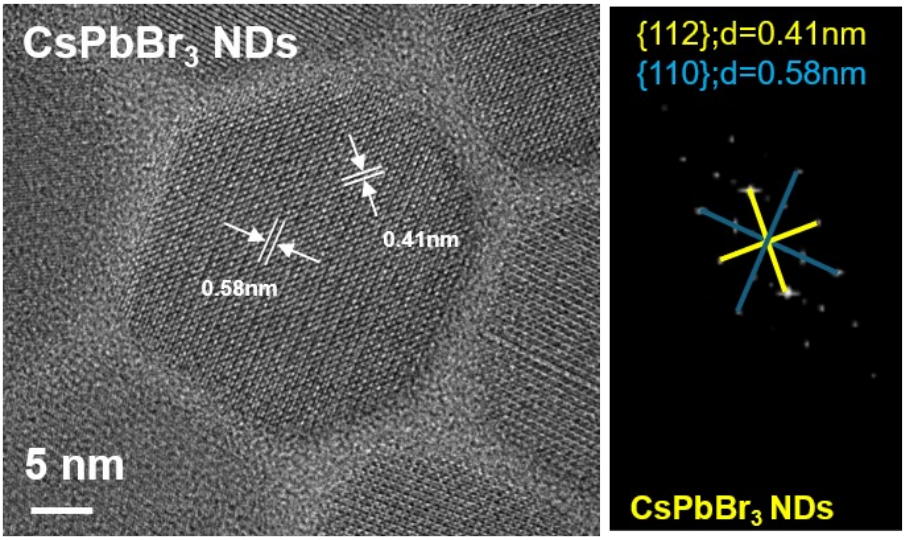

Figure S4. HR-TEM image(left) and FFT (right) of $CsPbBr_3$ NDs.

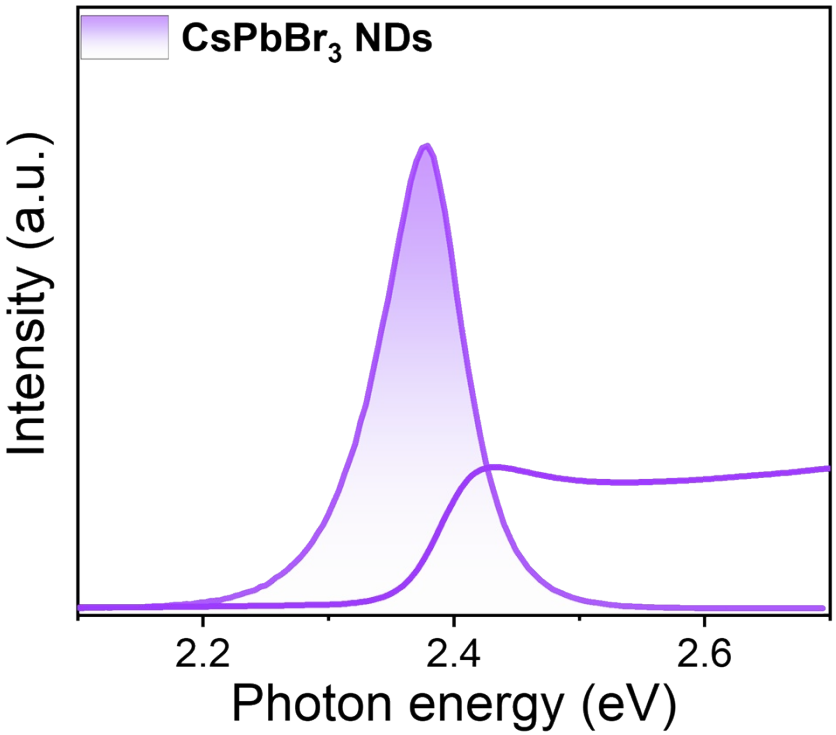

Figure S5. The PL and UV spectra of $CsPbBr_3$ NDs.

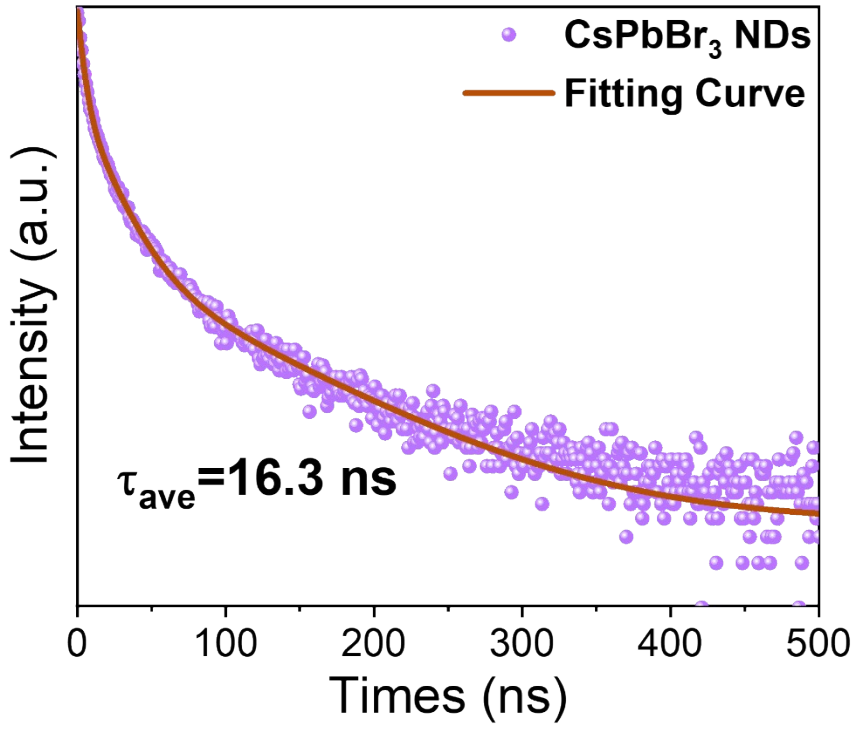

Figure S6. The fluorescence decay lifetime of $CsPbBr_3$ NDs.

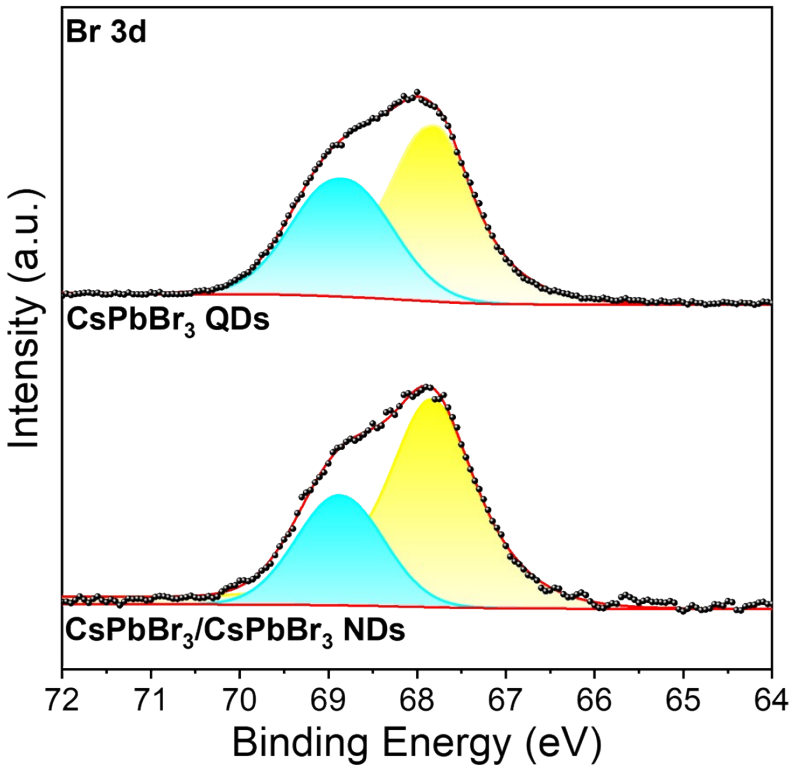

Figure S7. Br 3d XPS spectra of $CsPbBr_3$ QDs and $CsPbBr_3$/$CsPbBr_3$ NDs.

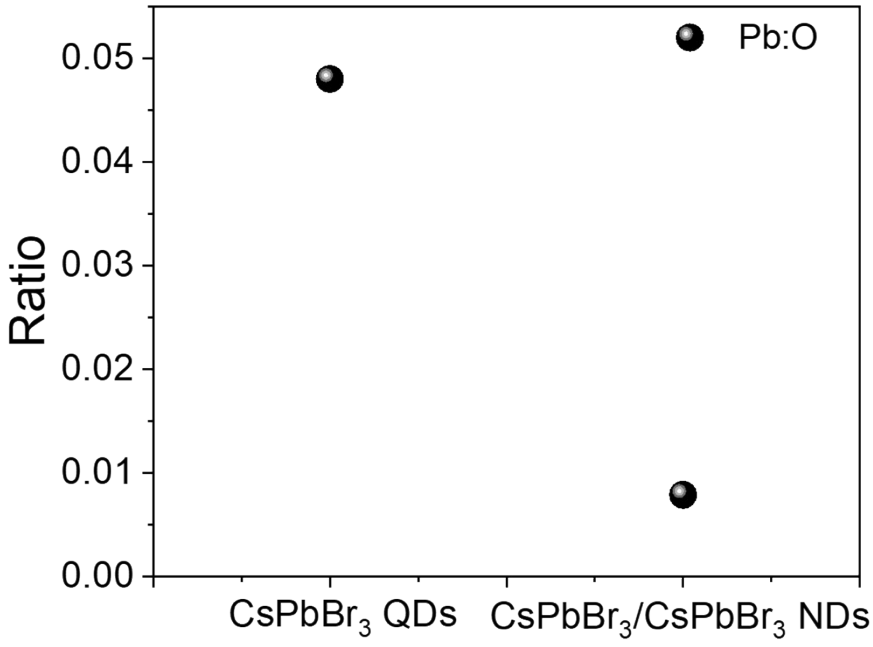

Figure S8. The elemental ratio of Pb to O on the surface of $CsPbBr_3$ QDs and $CsPbBr_3$/$CsPbBr_3$ NDs.

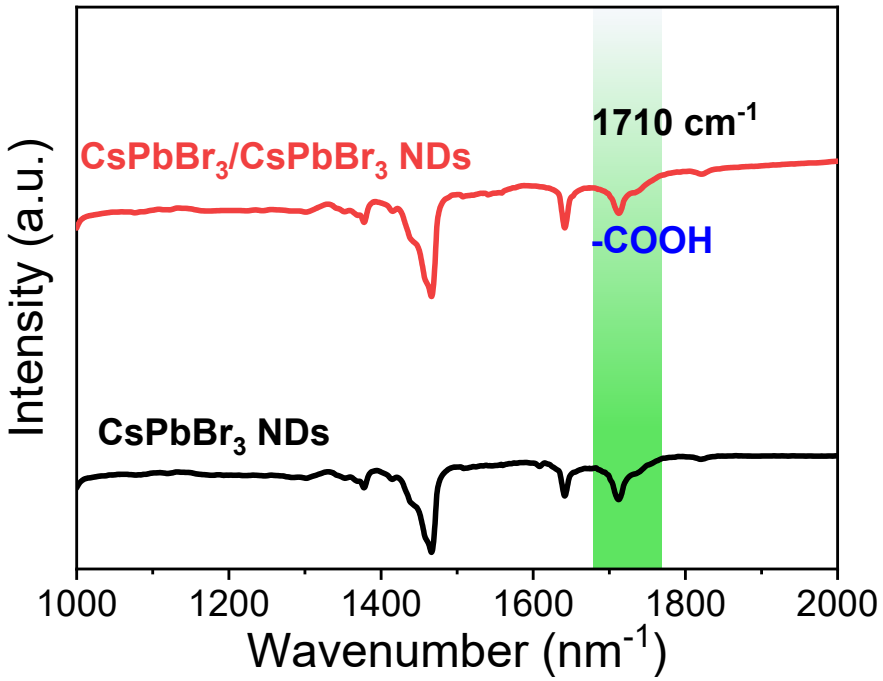

Figure S9. The FTIR data of $CsPbBr_3$ NDs and $CsPbBr_3$/$CsPbBr_3$ NDs.

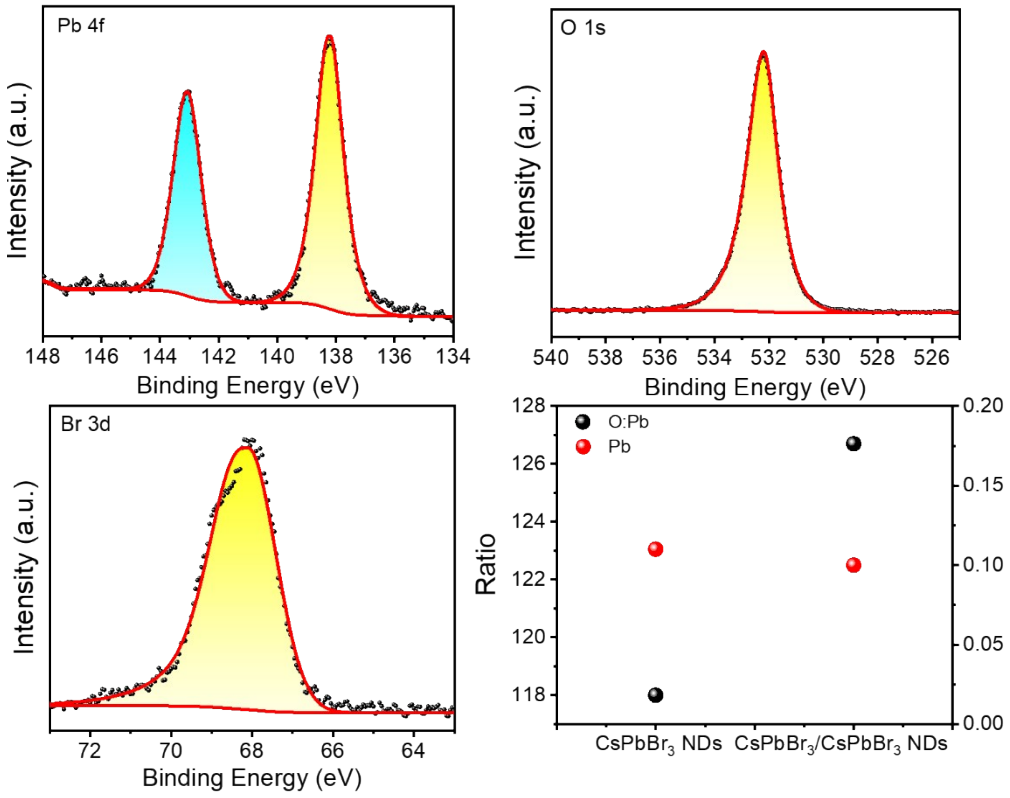

Figure S10. The Pb4f, O1s, and Br 3d XPS of $CsPbBr_3$ NDs and the atomic content of Pb and ratio of O/Pb on the surface of $CsPbBr_3$ NDs and $CsPbBr_3$/$CsPbBr_3$ NDs.

Table S2. The average lifetime, radiative and non-radiative rate of $CsPbBr_3$ QDs, $CsPbBr_3$ NDs, and $CsPbBr_3$/$CsPbBr_3$ NDs.

Samples	τ (ns)	QY (%)	K_r (ns^{-1})	K_{nr} (ns^{-1})
$CsPbBr_3$ QDs	11.6	49	0.042	0.0440
$CsPbBr_3$ NDs	16.3	44	0.027	0.0340
$CsPbBr_3$/$CsPbBr_3$ NDs	102.6	51	0.005	0.0048

Calculation of them is quoted from the article of Shen et.al.[5]

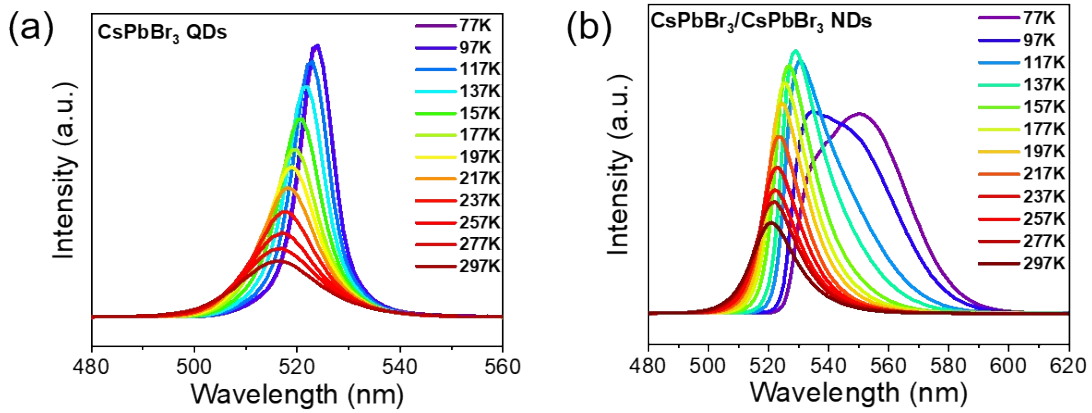

Figure S11. The temperature-dependent PL spectra of (a) $CsPbBr_3$ QDs and (b) $CsPbBr_3$/$CsPbBr_3$ NDs measured from 77K to 297K.

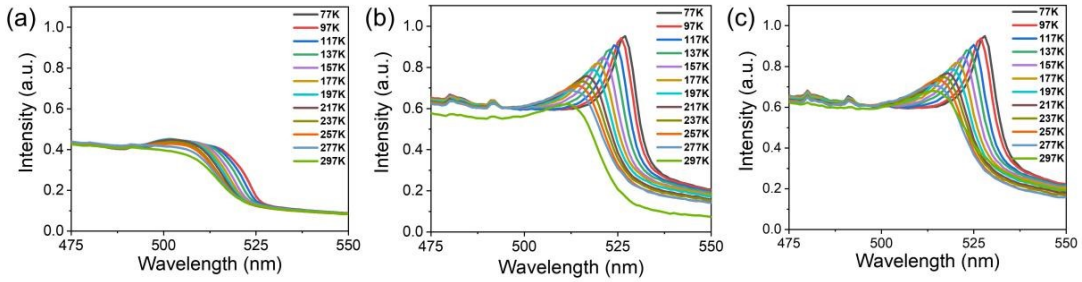

Figure S12. the temperature-dependent absorption spectra (a) $CsPbBr_3$ QDs, (b) $CsPbBr_3$ NDs, and (c) $CsPbBr_3$/$CsPbBr_3$ NDs measured from 77K to 297K.

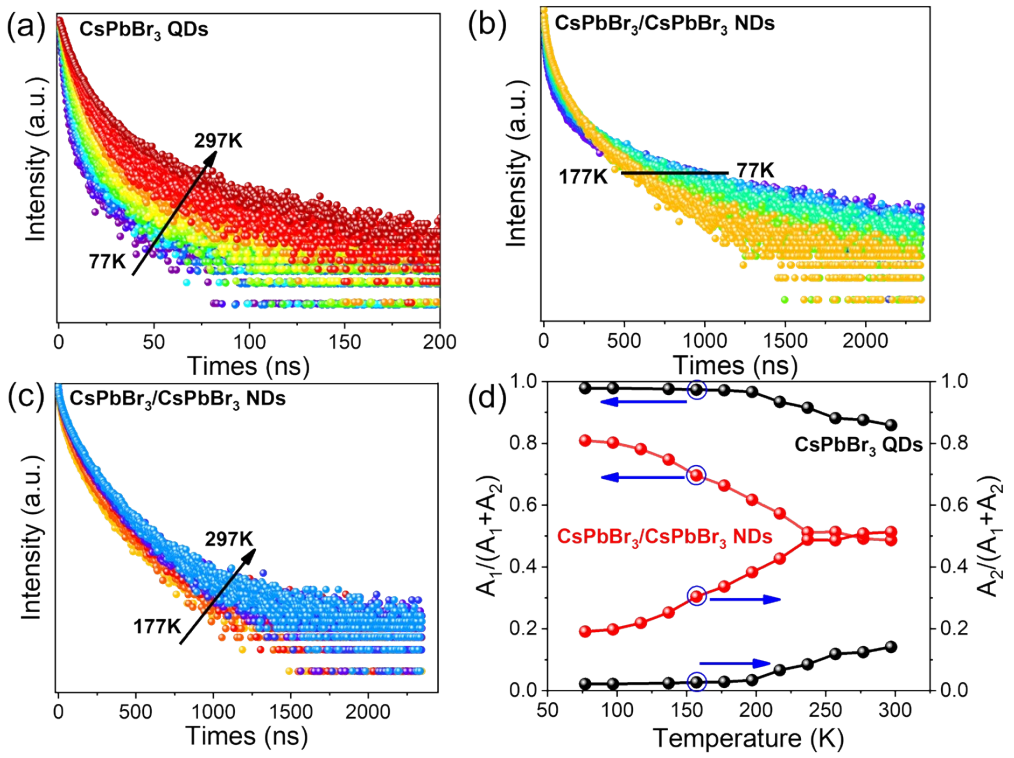

Figure S13. (a) The time-resolved fluorescence decay lifetime of QDs from 77K to 297K. The time-resolved fluorescence decay lifetime of $CsPbBr_3/CsPbBr_3$ NDs in the temperature range of (b) 77K ~ 177K and (c) 177K ~ 297K. (d) Temperature-dependent ratios of the amplitude components $A_1/(A_1+A_2)$ and $A_2/(A_1+A_2)$.

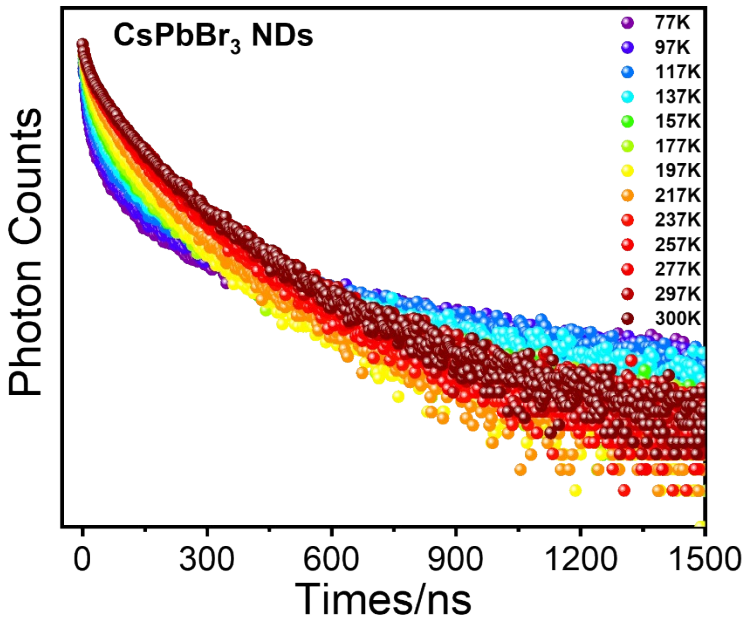

Figure S14. The time-resolved fluorescence decay lifetime of $CsPbBr_3$ NDs from 77K to 297K.

Table S3. Temperature-dependent Fluorescence lifetime data for $CsPbBr_3$ QDs via double exponential fitting.

Temperature(K)	τ_1(ns)	A_1	τ_2(ns)	A_2	τ_{av}(ns)
77	1.34	1.00	12.10	0.022	3.12
97	1.49	1.00	13.18	0.022	3.39
117	1.78	1.09	14.58	0.023	3.67
137	2.15	1.02	16.38	0.025	4.39
157	2.52	1.03	16.91	0.028	4.74
177	3.00	1.03	17.69	0.030	5.28
197	3.47	1.03	18.29	0.036	5.78
217	3.74	0.99	14.94	0.007	6.21
237	3.97	0.97	15.26	0.090	6.94
257	4.09	0.93	15.79	0.125	8.09
277	4.37	0.93	18.31	0.132	9.57
297	4.72	0.90	20.10	0.148	11.05

Table S4. Temperature-dependent fluorescence lifetime data for $CsPbBr_3/CsPbBr_3$ NDs via double exponential fitting.

Temperature(K)	τ_1(ns)	A_1	τ_2(ns)	A_2	τ_{av}(ns)
77	4.80	0.78	79.30	0.18	64.1
97	5.50	0.77	88.20	0.19	71.5
117	7.30	0.75	97.40	0.21	78.4
137	9.35	0.71	100.50	0.24	80.8
157	11.06	0.66	93.95	0.29	76.4
177	11.80	0.63	90.60	0.32	74.5
197	12.94	0.59	90.40	0.37	75.9
217	15.84	0.55	96.10	0.41	81.6
237	17.35	0.49	104.50	0.47	91.6
257	17.22	0.49	108.90	0.46	95.8
277	17.20	0.47	110.50	0.49	98.3
297	17.84	0.46	115.80	0.49	103.3

References

1. B. Chon, J. Bang, J. Park, C. Jeong, J. H. Choi, J. B. Lee, T. Joo and S. Kim, *J. Phys. Chem. C*, 2011, **115**, 436-442.
2. J. Li, X. Yuan, P. Jing, J. Li, M. Wei, J. Hua, J. Zhao and L. Tian, *RSC Adv.*, 2016, **6**, 78311-78316.
3. B. Ai, C. Liu, Z. Deng, J. Wang, J. Han and X. Zhao, *Phys. Chem. Chem. Phys.*, 2017, **19**, 17349-17355.
4. K. Wei, Z. Xu, R. Chen, X. Zheng, X. Cheng and T. Jiang, *Opt. Lett.*, 2016, **41**, 3821.
5. X. Shen, Y. Zhang, S. V. Kershaw, T. Li, C. Wang, X. Zhang, W. Wang, D. Li, Y. Wang, M. Lu, L. Zhang, C. Sun, D. Zhao, G. Qin, X. Bai, W. W. Yu and A. L. Rogach, *Nano Lett.*, 2019, **19**, 1552-1559.