Supporting Information

Upconversion Perovskite Nanocrystal Heterostructures with Enhanced Luminescence and Stability by Lattice Matching

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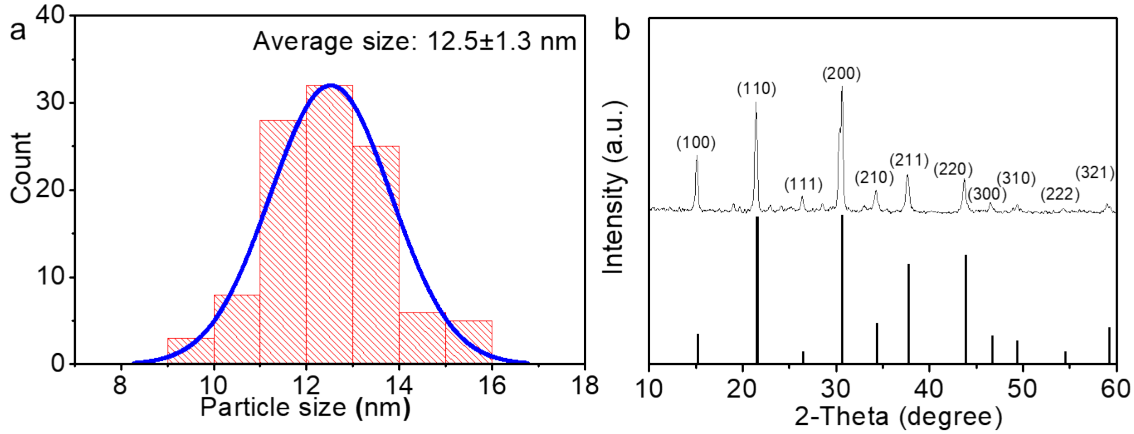

Figure S1. $CsPbBr_3$ PQD. (a) Statistical distribution histogram of $CsPbBr_3$ PQD (average size:12.5±1.3 nm), (b) XRD pattern of $CsPbBr_3$ PQD and standard PXRD pattern of cubic phase $CsPbBr_3$ (JCPDF NO. 54-0752).

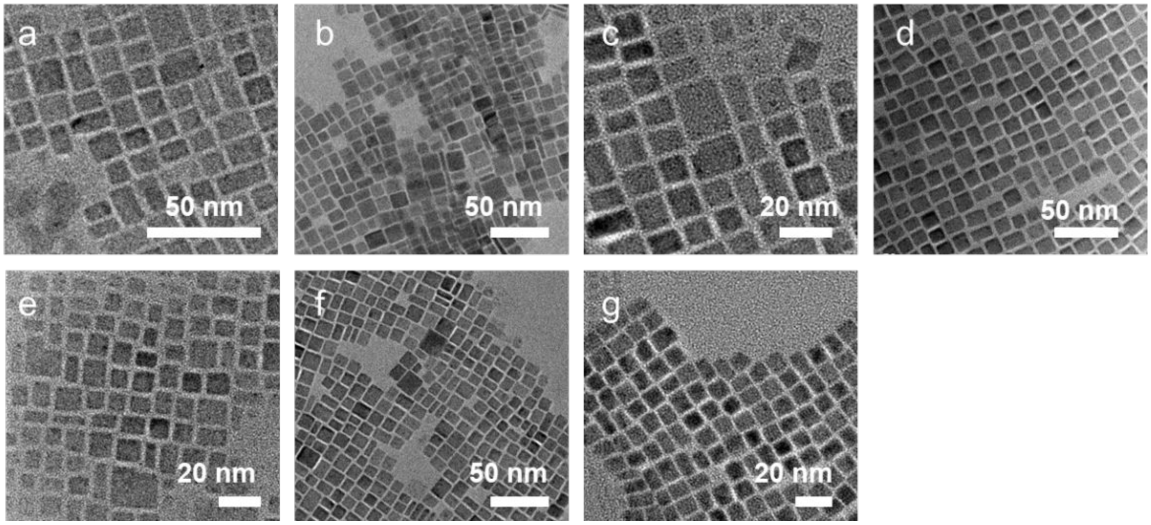

Figure S2. TEM images of $CsPbX_3$ (X = Cl, Br or I) PQD with different halide ratios. (a) Cl/Br = 2/1, (b) Cl/Br = 1/1, (c) Cl/Br = 1/2, (d) Cl or I/Br = 0/1, (e) I/Br = 1/2, (f) I/Br = 1/1, (g): I/Br = 2/1.

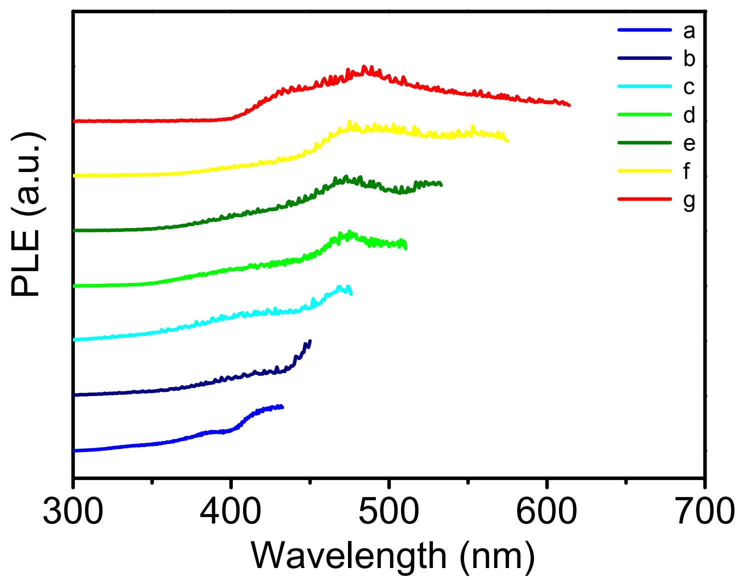

Figure S3. Excitation spectra of $CsPbX_3$ (X = Cl, Br or I) PQD with different halide ratios. (a) Cl/Br = 2/1, (b) Cl/Br = 1/1, (c) Cl/Br = 1/2, (d) Cl or I/Br = 0/1, (e) I/Br = 1/2, (f) I/Br = 1/1, (g) I/Br = 2/1.

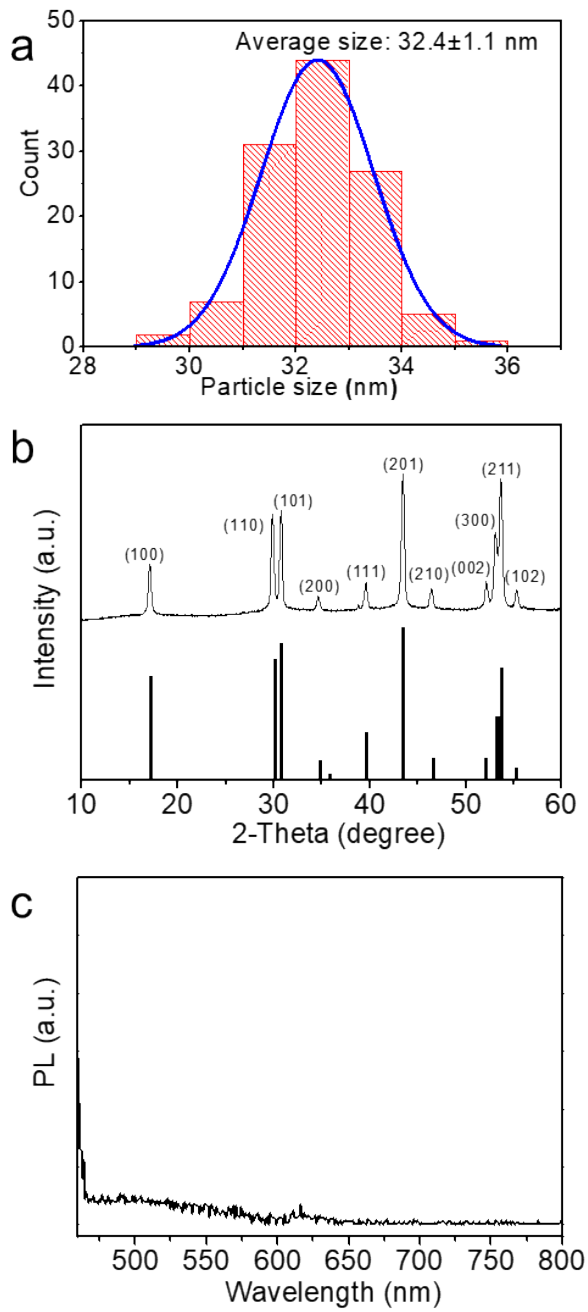

Figure S4. $NaYF_4$: Yb/Tm UCNP. (a) Statistical distribution histogram of $NaYF_4$: Yb/Tm nanocrystals (average size: 32.4±1.1 nm), (b) XRD pattern of $NaYF_4$: Yb/Tm nanocrystals and standard PXRD pattern of hexagonal $NaYF_4$:Yb/Tm nanocrystals (PDF NO. 16-0334), (c) Emission spectra of $NaYF_4$:Yb/Tm nanocrystals under excitation at 450 nm.

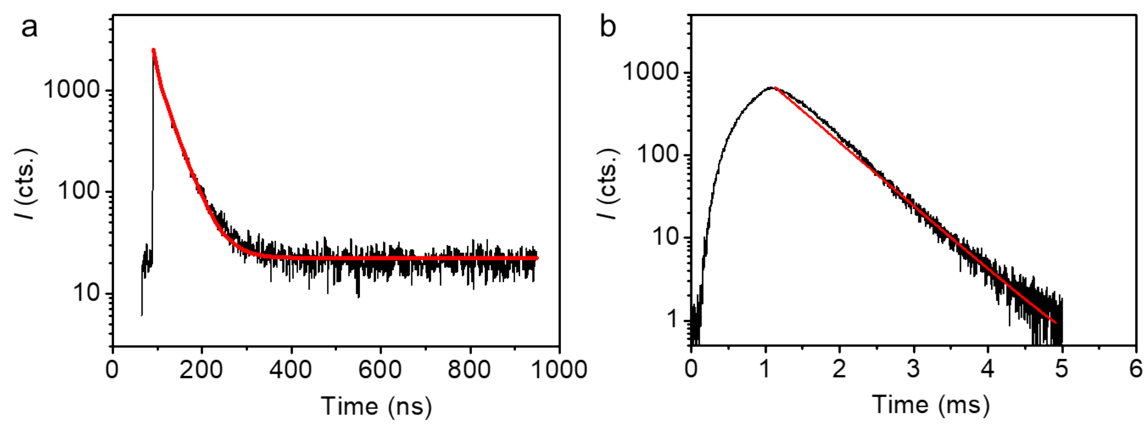

Figure S5. Fluorescence decay and fitting curves. (a) Time-resolved fluorescence decay and fitting curve of $CsPbBr_3$ nanocrystals (excitation at 365nm, emission at 513 nm), (b)Time-resolved fluorescence decay and fitting curve of $CsPbBr_3$/UCNP mixture ($CsPbBr_3$,14.1mmol/L; UCNP, 12.5 mmol/L) (excitation at 980nm, emission at 513 nm).

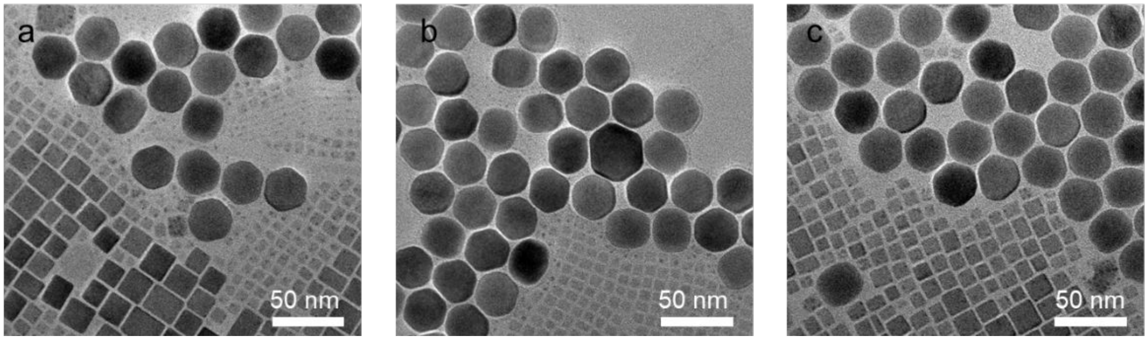

Figure S6. TEM image of $CsPbX_3$ nanocrystals with varying halide compositions mixed with $NaYF_4$: 30%Yb, 0.5%Tm nanocrystals. (a) Cl/Br = 2/1, (b) Cl or I/Br = 0/1, (c) I/Br = 2/1.

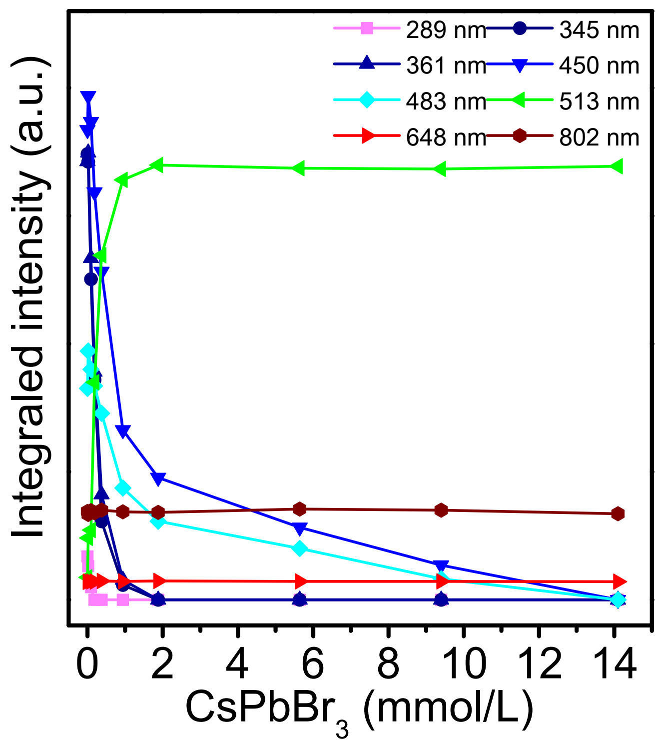

Figure S7. Integrated intensity of Tm^{3+} emissions at 289nm, 347nm, 362nm, 450nm, 483nm, 648nm, and 802 nm and $CsPbBr_3$ emission at 513 nm with different concentrations.

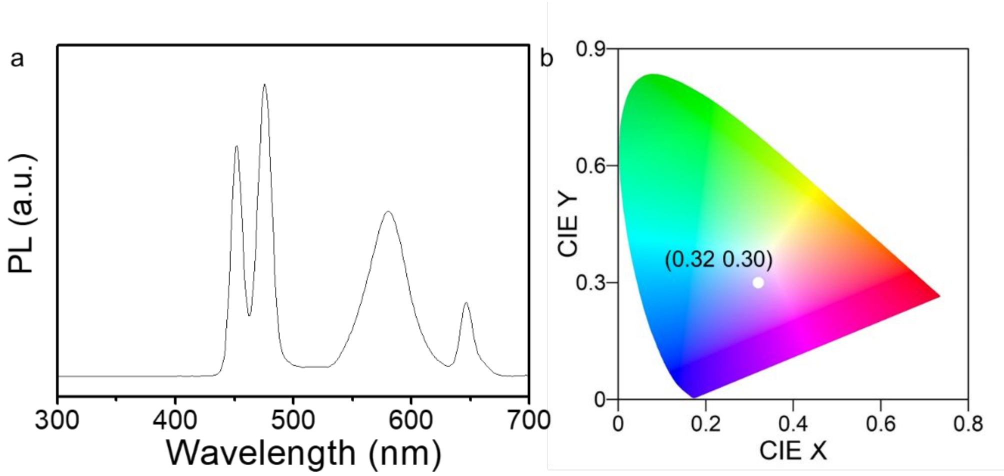

Figure S8. Fluorescence emission of mixed UCNP and PQD. (a) Emission spectra of $CsPbBr_{1.5}I_{1.5}$ nanocrystals mixed with $NaYF_4$: Yb,Tm nanocrystals ($CsPbBr_{1.5}I_{1.5}$, 5.64 mmol/L; UCNP, 12.5 mmol/L) under 980 nm excitation, (b) Corresponding color gamut of the emission colors from the samples in (a).

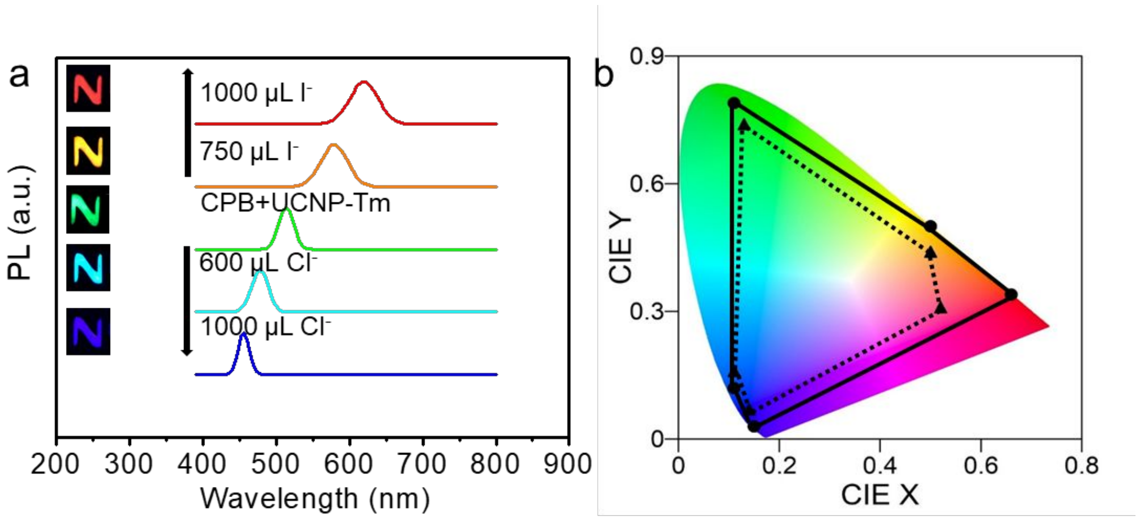

Figure S9. Tunable emissions of PQD. (a) Fluorescence emission spectra of $CsPbBr_3$ (14.1 mmol/L) mixed with $NaYF_4$:Yb,Tm UCNPs (12.5 mmol/L) by adding different amount of halide ions under 365 nm excitation. the panel shows the pattern of letter N in A (N, $CsPbBr_3$+$NaYF_4$:Yb/Tm), (b) Corresponding color gamut of the emission colors from the samples in 2d (circle) and S9 a (triangle).

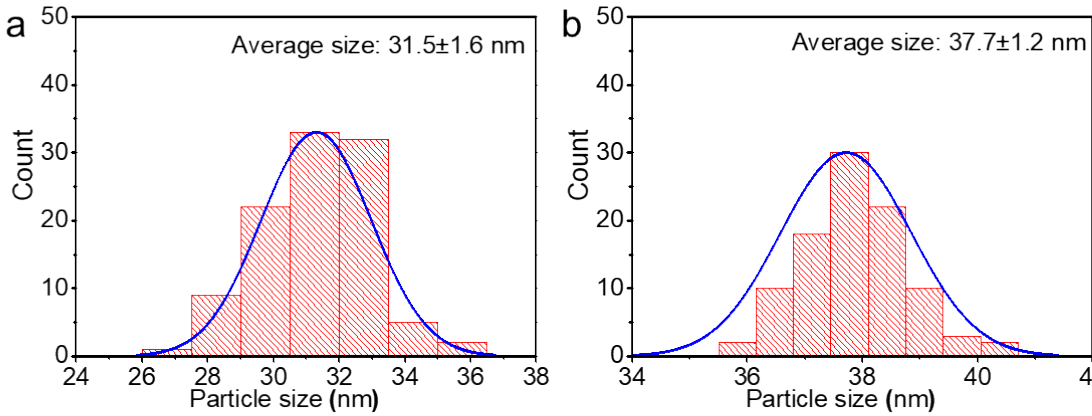

Figure S10. Statistical distribution histograms. (a) heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm nanocrystals, (b) heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm nanocrystals.

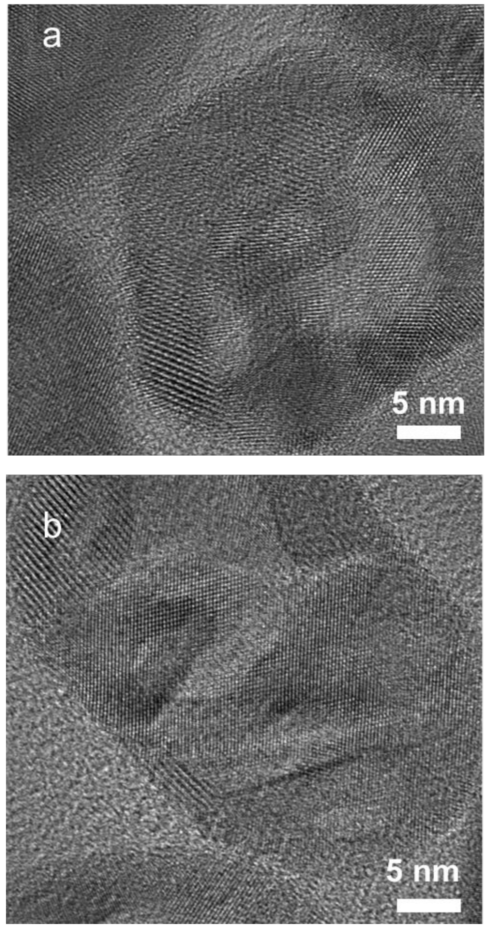

Figure S11. HRTEM images. (a) heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm nanocrystals, (b) heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm nanocrystals.

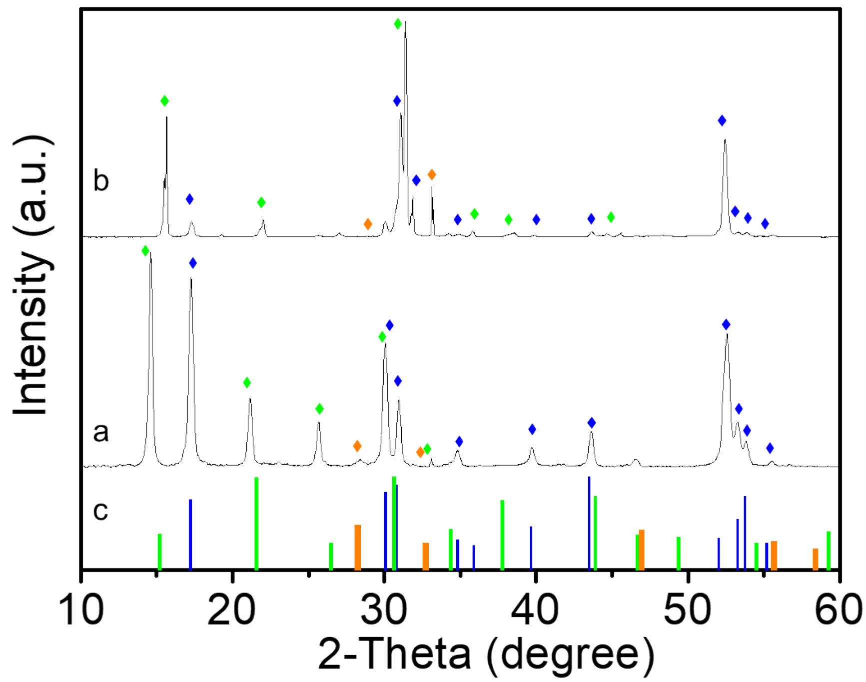

Figure S12. X-ray diffraction (XRD) patterns. (a) heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm nanocrystals , (b) heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm nanocrystals , (c) hexagonal phase $NaYF_4$, blue color (JCPDF NO. 16-0334)； cubic phase $NaYF_4$, orange color (JCPDF NO. 77-2042)； cubic phase $CsPbBr_3$, green color (JCPDF NO. 54-0752).

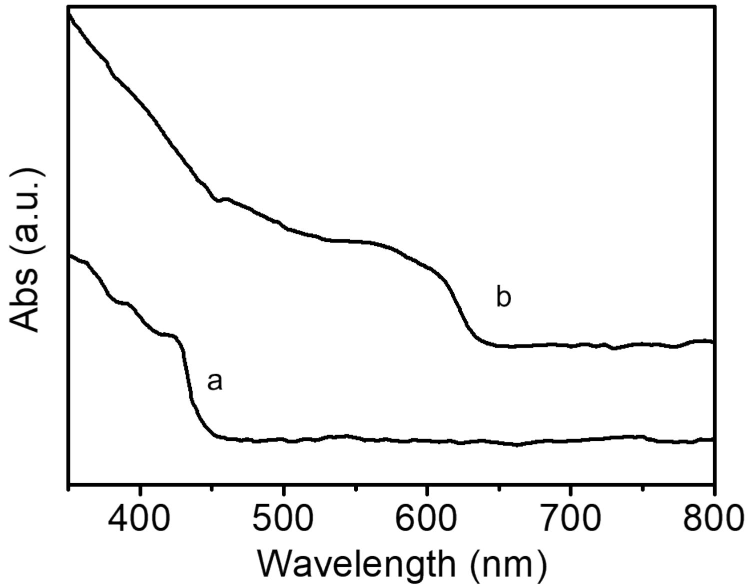

Figure S13. UV-Vis absorption spectra. (a) heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm nanocrystals , (b) heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm nanocrystals

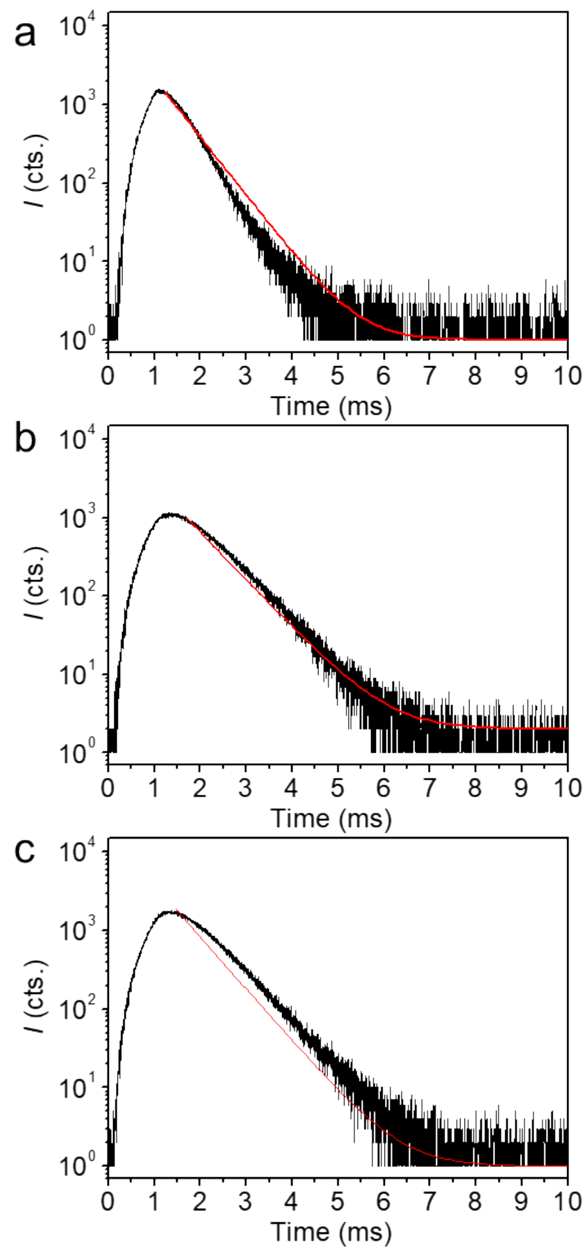

Figure S14. Time-resolved fluorescence decay and fitting curves. (a) $CsPbBr_1Cl_2$/ $NaYF_4$: 30%Yb,0.5%Tm mixture, (b) $NaYF_4$:30%Yb,0.5%Tm nanoparticles, and (c) $CsPbBr_1I_2$/ $NaYF_4$: 30%Yb,0.5%Tm mixture under 980 nm excitation (monitored at the emission of 478 nm).

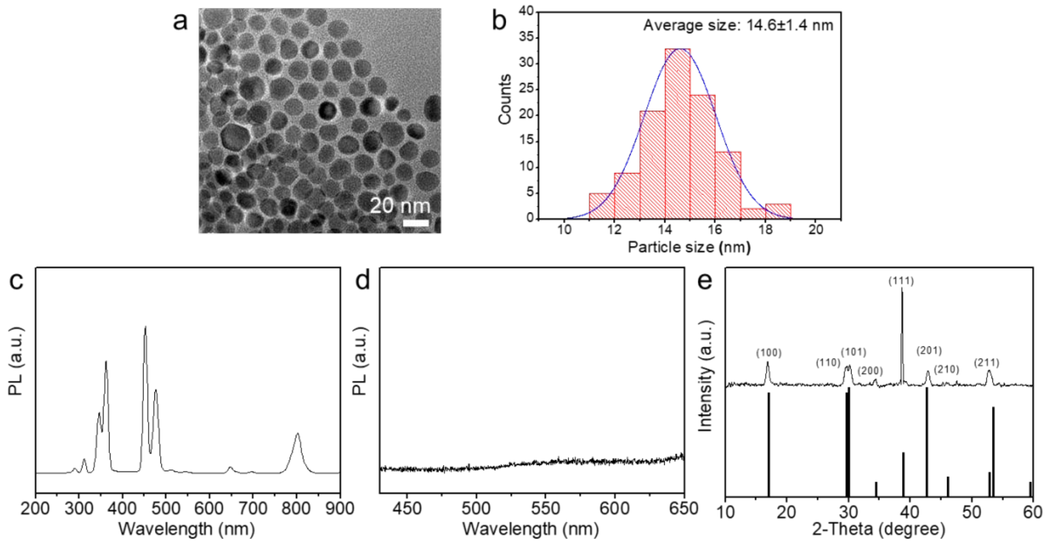

Figure S15. (a) TEM image of $NaGdF_4$:30%Yb,0.5%Tm nanocrystals at 300 ℃ for 60 min; (b) Histograms representing statistical distribution of the nanocrystals in a; (c) and (d) Fluorescence emission spectra of $NaGdF_4$:30%Yb,5%Tm nanocrystals at 300 ℃ for 60 min under 980 nm and 365 nm excitations respectively, (the illustration in C shows $NaGdF_4$:30%Yb,5%Tm nanocrystals dispersed in cyclohexane under 980 nm excitation at room temperature); (e) XRD pattern of $NaGdF_4$:30%Yb,0.5%Tm nanocrystals at 300 ℃ for 60 min and standard PXRD pattern of Hexagonal phase $NaGdF_4$ (JCPDF NO. 27-0699).

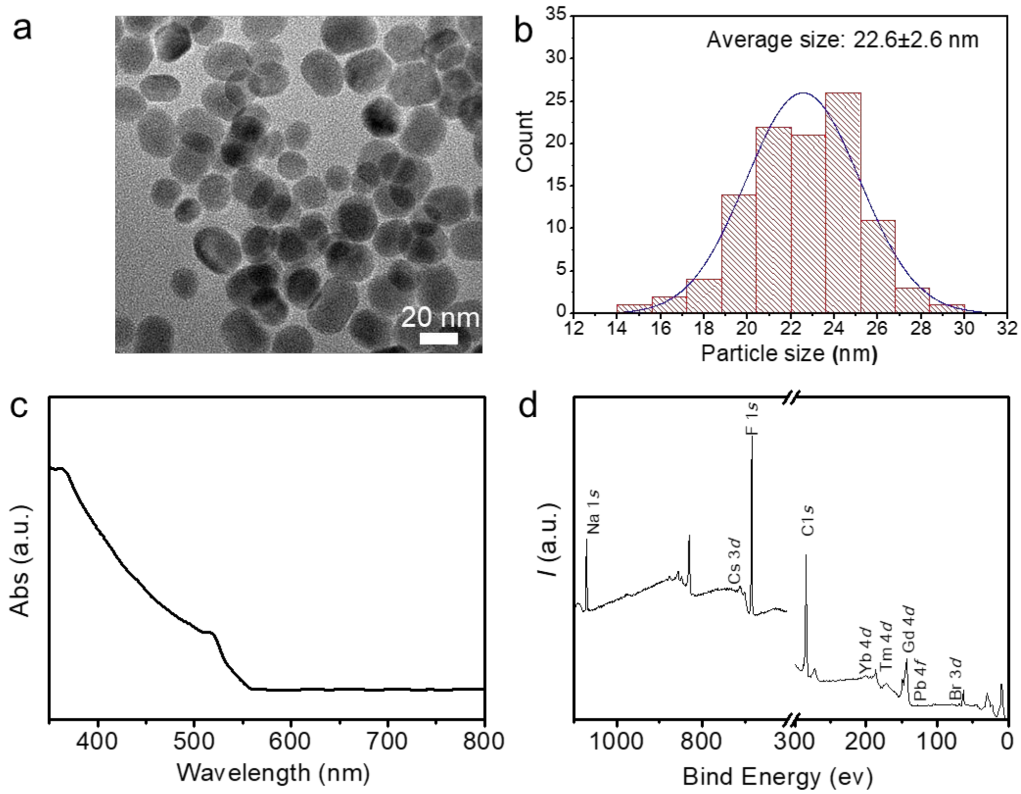

Figure S16. (a) TEM image of heterostructured $CsPbBr_3$-$NaGdF_4$: Yb,Tm nanocrystals; (b) Histograms representing statistical distribution of the nanocrystals in a; (c) UV-Vis absorption spectra of heterostructured $CsPbBr_3$-$NaGdF_4$: Yb,Tm nanocrystals. (d) X-ray photoelectron spectroscopy (XPS) spectra of heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm hybrid nanocrystals. The presence of Cs, Pb Br, F, Na, Gd, Tm and Yb in the nanocrystals is confirmed.

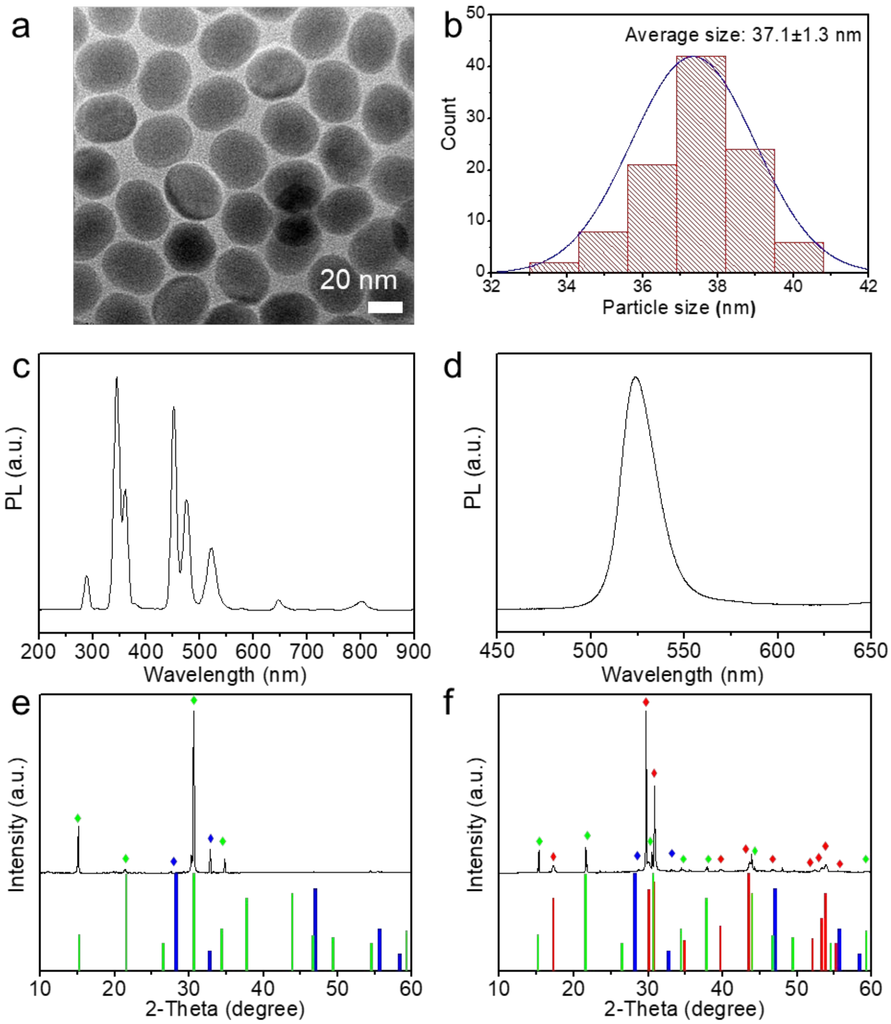

Figure S17. (a) TEM image of heterostructured $CsPbBr_3$-$NaYF_4$: Yb,Tm nanocrystals; (b) Histograms representing statistical distribution of the nanocrystals in a; (c) and (d) Fluorescence emission spectra of heterostructured $CsPbBr_3$-$NaYF_4$: Yb,Tm nanocrystals under 980 nm and 365 nm excitations, respectively; (e) and (f) X-ray diffraction (XRD) patterns of heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals at 250 ℃, and 300 ℃ for 60 min, respectively; Hexagonal $NaYF_4$, red color (JCPDF NO. 16-0334), cubic $NaYF_4$, blue color (JCPDF NO. 77-2042), cubic $CsPbBr_3$, green color (JCPDF NO. 54-0752).

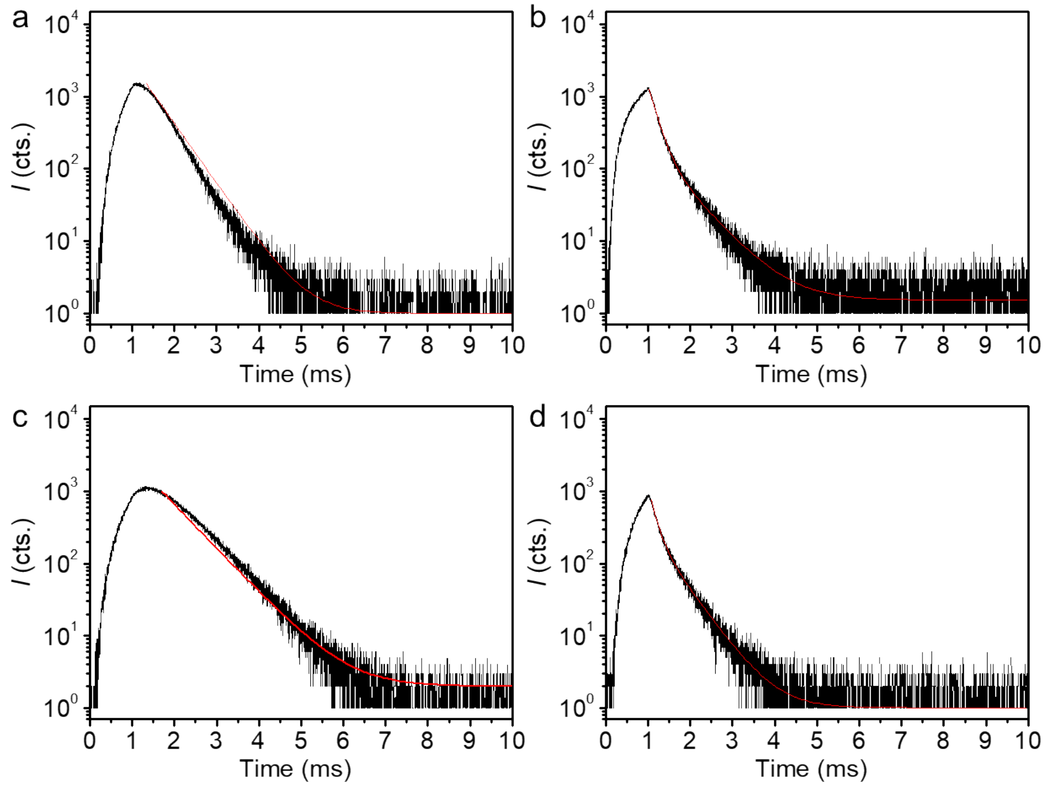

Figure S18. Time-resolved fluorescence decay and fitting curve of $NaGdF_4$:30%Yb,0.5%Tm nanoparticles (a), the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals (b), $NaYF_4$:30%Yb,0.5%Tm nanoparticles (c), and the heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals (d) under 980 nm excitation (monitored at the emission of 478 nm).

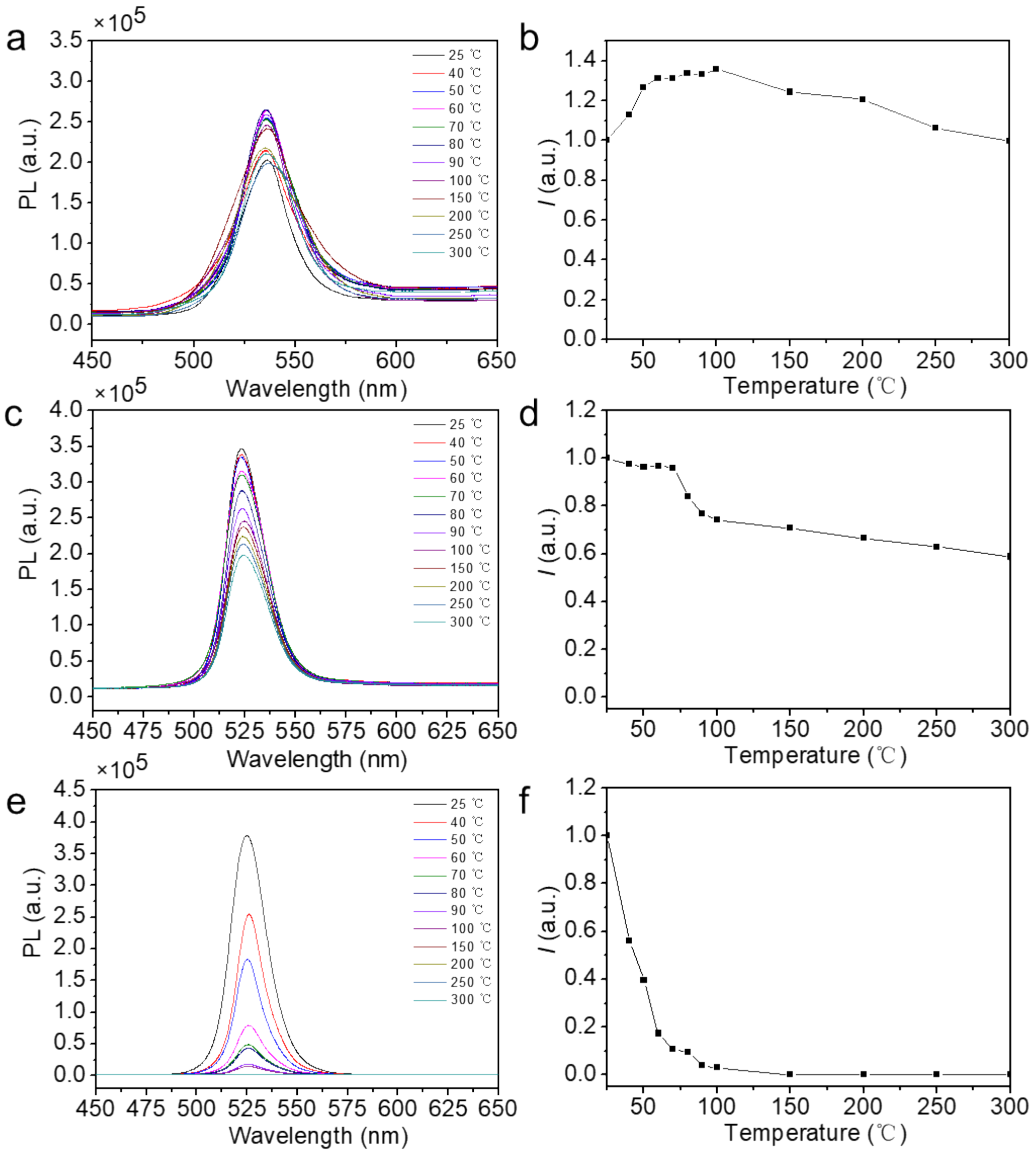

Figure S19. PL intensity monitoring the stabilities of the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals (a and b), the heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals (c and d), and the $CsPbBr_3$ nanocrystals (e and f) collected at different temperatures under 365 nm excitation.

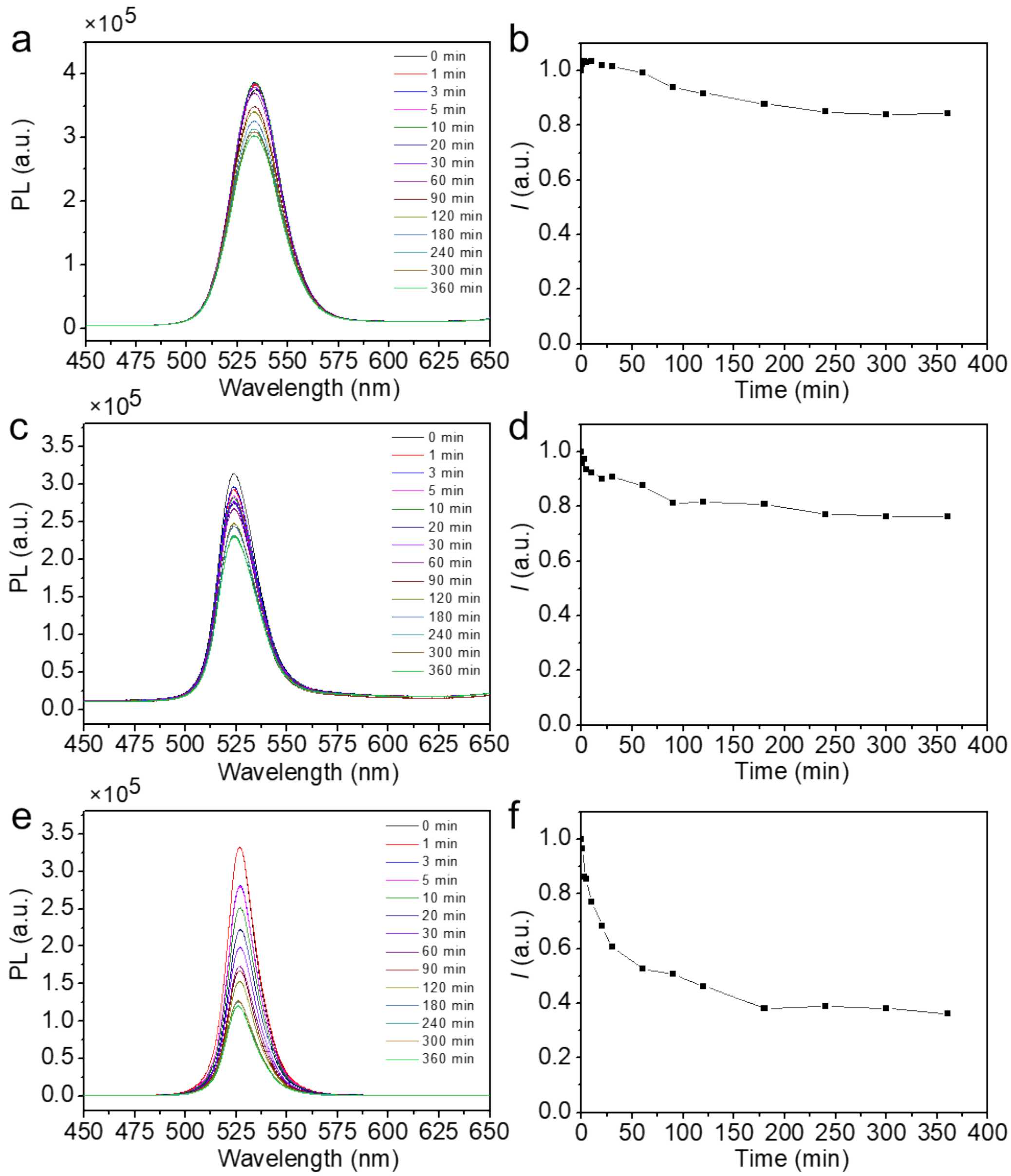

Figure S20. PL intensity monitoring the stabilities of the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals (a and b), the heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals (c and d), and the $CsPbBr_3$ nanocrystals (e and f) under ultraviolet light continuous irradiation.

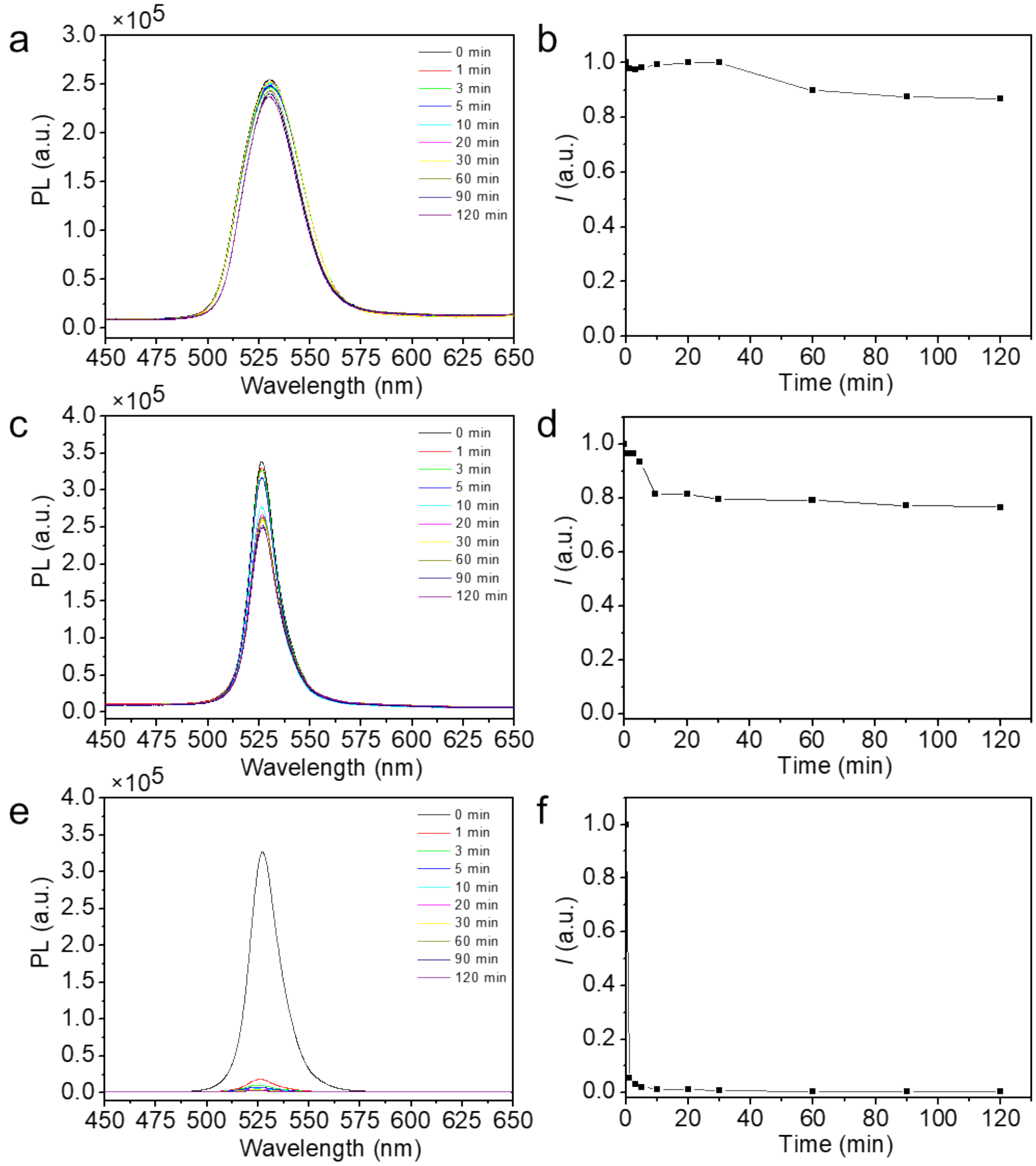

Figure S21. PL intensity monitoring the stabilities of the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals (a and b), the heterostructure composite of $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals (c and d), and the $CsPbBr_3$ nanocrystals (e and f)) in cyclohexane and ethanol (v/v = 1 : 1) mixed solvent under 365 nm excitation.

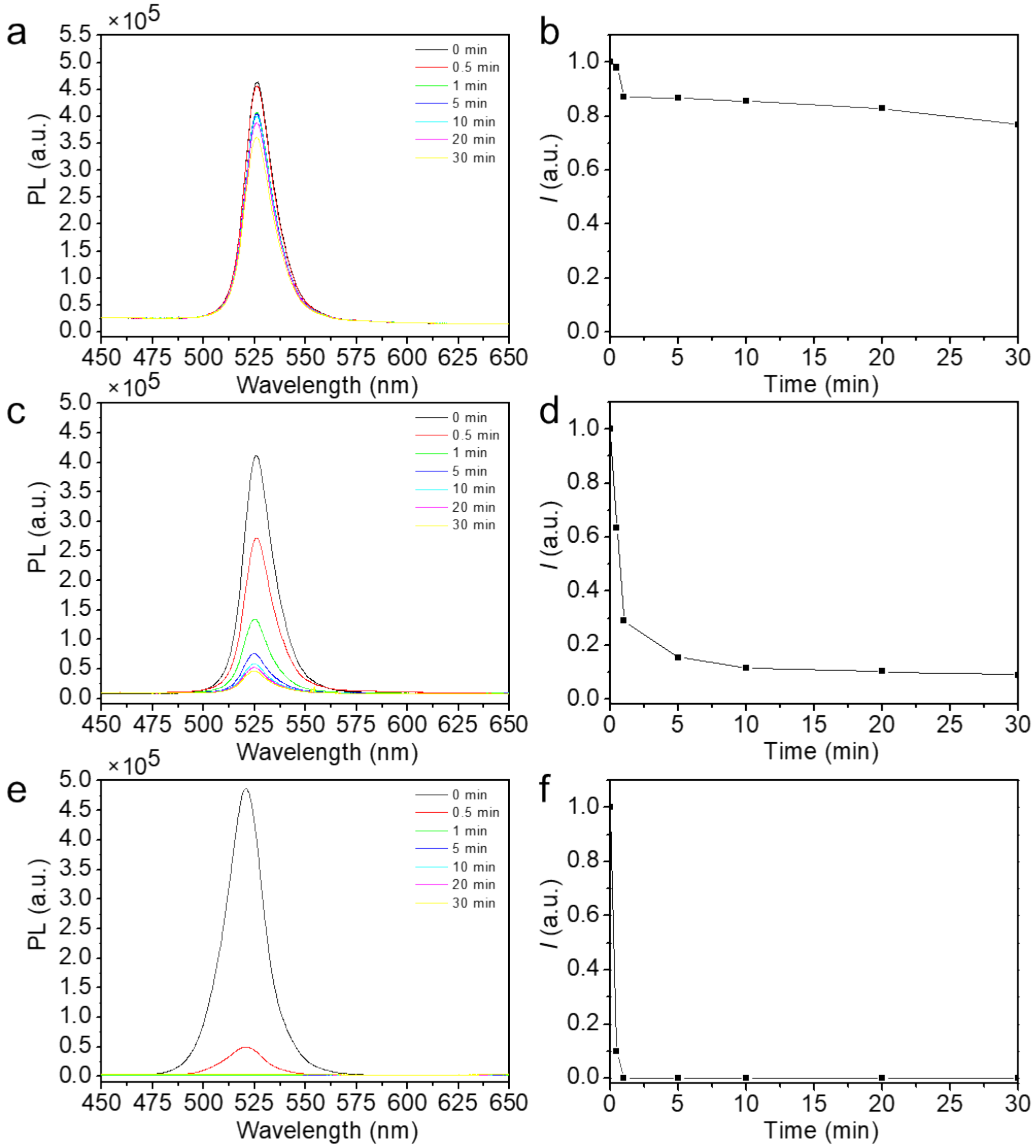

Figure S22. PL intensity monitoring the stabilities of the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals (a and b), the heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals (c and d), and the $CsPbBr_3$ nanocrystals (e and f) in cyclohexane and ethanol (v/v = 1 : 9) mixed solvent under 365 nm excitation.

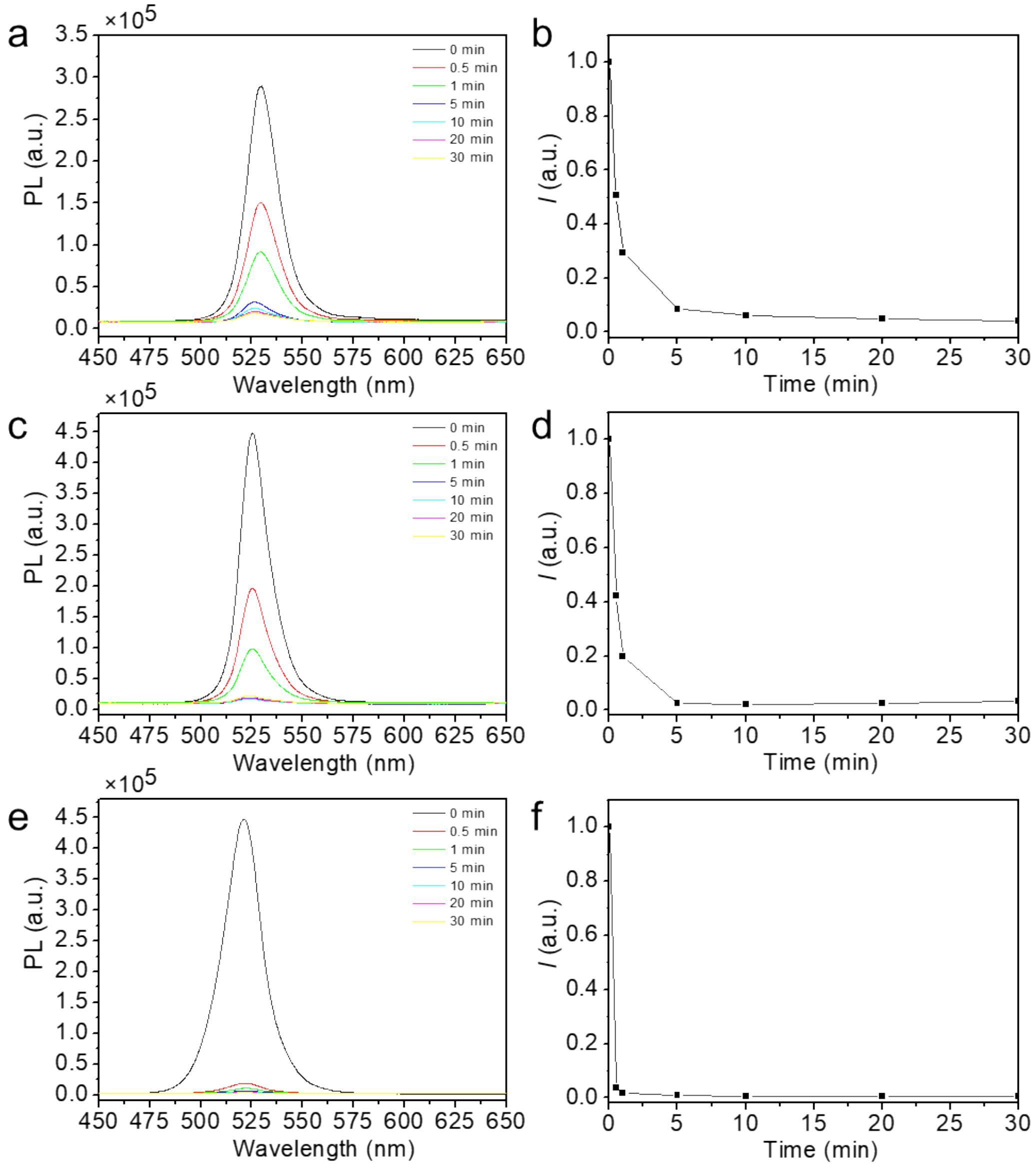

Figure S23. PL intensity monitoring the stabilities of the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals (a and b), the heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals (c and d), and the $CsPbBr_3$ nanocrystals (e and f) in water solvents under 365 nm excitation.

Table S1. Exponential fitting results of $CsPbBr_3$ and $CsPbBr_3$/UCNPs mixture.

Sample	**$CsPbBr_3$**	**$CsPbBr_3$/UCNPs mixture**
A_1	1702.8	675.9
τ_1 (ns)	34.1 (89%)	0.56×106 (100%)
A_2	959.0	⁄
τ_2 (ns)	7.6 (11%)	⁄
Average(ns)	31.1	0.56×10^6

*Time-resolved fluorescence decay curve of $CsPbBr_3$ was fitted by a double exponential (see eqs 1 and 2) function: $A(t) = A_0 + A_1 \exp-(t-t_0)/\tau_1 + A_2 \exp-(t-t_0)/\tau_2$ (eqs 1);

The average lifetime was calculated based on $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ (eqs 2).

Time-resolved fluorescence decay curve of $CsPbBr_3$/UCNPs mixture was fitted by a single exponential (see eqs 1 and 2) function: $A(t) = A_0 + A_1 \exp-(t-t_0)/\tau_1$ (eqs 1);

The average lifetime was calculated based on $\tau_{avg} = \tau_1$ (eqs 2);

Table S2. Chromaticity coordinates (CIE, 1931) of $CsPbBr_3$ nanocrystals of different concentrations mixed with $NaYF_4$:Yb,Tm UCNPs (12.5 mmol/L) under 980 nm excitation.

CPB (mmol/L)	**CIE-X**	**CIE-Y**
0	0.15	0.05
0.019	0.15	0.05
0.094	0.14	0.09
0.188	0.14	0.12
0.376	0.13	0.18
0.94	0.12	0.3
1.88	0.12	0.38
5.64	0.11	0.47
9.4	0.11	0.61
14.1	0.13	0.74

Table S3. Chromaticity coordinates (CIE, 1931) of $CsPbBr_3$ nanocrystals (CPB) mixed with $NaYF_4$: Yb/Tm nanocrystals (UCNP-Tm, 14.1 mmol/L) by adding different amount of halide ions under 980 and 365 nm excitation.

Sample	**Ex: 980 nm**		**Ex: 365 nm**	
	CIE-X	**CIE-Y**	**CIE-X**	**CIE-Y**
Add 1000 μL Cl^-	0.14	0.07	0.15	0.03
Add 600 μL Cl^-	0.11	0.16	0.11	0.12
CPB+ UCNP-Tm	0.13	0.74	0.11	0.79
Add 750 μL I^-	0.5	0.44	0.5	0.5
Add 1000 μL I^-	0.52	0.31	0.66	0.34

Table S4. Exponential fitting results of the heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm nanocrystals and the heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm nanocrystals under 980 nm excitation (monitored at the emission of 478 nm).

Sample	**heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm**	**heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm**
A_1	15613	12308
τ_1 (ns)	0.42×10^6 (100%)	0.47×10^6 (100%)
Average(ns)	0.42×10^6	0.47×10^6

*Time-resolved PL decay curves of the heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm nanocrystals, and the heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm nanocrystals were fitted by a single exponential (see eqs 1 and 2) function: $A(t) = A_0 + A1\exp\text{-}(t\text{-}t_0)$ (eqs 1)

The average lifetimes were calculated using $t_{avg} = t_1$ (eqs 2);

Table S5. Exponential fitting results of $CsPbBr_1Cl_2/NaYF_4$: 30%Yb,0.5%Tm mixture, $NaYF_4$:30%Yb,0.5%Tm nanoparticles, and $CsPbBr_1I_2/NaYF_4$: 30%Yb,0.5%Tm mixture under 980 nm excitation (monitored at the emission of 478 nm).

Sample	**$CsPbBr_1Cl_2/NaYF_4$: 30%Yb,0.5%Tm mixture**	**$NaYF_4$:30%Yb,0.5%Tm**	**$CsPbBr_1I_2/NaYF_4$: 30%Yb,0.5%Tm mixture**
A_1	3934	10882.6	20258
τ_1 (ns)	0.42×10^6 (100%)	0.71×10^6 (100%)	0.64×10^6 (100%)
Average(ns)	0.61×10^6	0.71×10^6	0.64×10^6

*Time-resolved PL decay curves of $CsPbBr_1Cl_2$/ $NaYF_4$: 30%Yb,0.5%Tm mixture, $NaYF_4$:30%Yb,0.5%Tm nanoparticles, and $CsPbBr_1I_2$/ $NaYF_4$: 30%Yb,0.5%Tm mixture were fitted by a single exponential (see eqs 1 and 2) function: $A(t) = A_0 + A_1 \exp-(t-t_0)$ (eqs 1)

The average lifetimes were calculated using $t_{avg}= t_1$ (eqs 2);

Table S6. The FRET efficiency of $CsPbBr_1Cl_2$/ $NaYF_4$: 30%Yb,0.5%Tm mixture, $NaYF_4$:30%Yb,0.5%Tm nanocrystals, $CsPbBr_1I_2$/ $NaYF_4$: 30%Yb,0.5%Tm mixture, the heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm nanocrystals, and the heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm nanocrystals under 980 nm excitation.

τ and Eff	**$CsPbBr_1Cl_2$/ $NaYF_4$: 30%Yb,0.5% Tm mixture**	**$NaYF_4$:30%Yb ,0.5%Tm**	**$CsPbBr_1I_2$/ $NaYF_4$: 30%Yb,0.5%T m mixture**	**heterostructured $CsPbBr_1/Cl_2$-$NaYF_4$:Yb,Tm**	**heterostructured $CsPbBr_1/I_2$-$NaYF_4$:Yb,Tm**
τ_D (ns)	0.71×10^6	0.71×10^6	0.71×10^6	0.71×10^6	0.71×10^6
$\tau_{D\text{-}A}$ (ns)	0.61×10^6	/	0.64×10^6	0.42×10^6	0.47×10^6
$Eff = 1 - \tau_{D-A}/\tau_D$	14%	/	9.8%	41%	32%

Table S7 Atomic ratios in the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals determined based on XPS measurement.

Element	Atomic%
Cs 3*d*	0.27
Pb 4*f*	0.24
Br 3*d*	0.81
F 1s	61.86
Gd 4*d*	15.68
Na 1*s*	14.32
Yb 4*d*	5.18
Tm 4*d*	1.61

Table S8. PLQY of heterostructured nanocrystals before and after phase transition.

Before and after the phase transition	**Samples**	**Ex 365 nm-PLQY**	**Ex 980 nm-PLQY**
Before the phase transition	heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm-250 ℃	10%	/
	heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm-250 ℃	20%	/
heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm-300 ℃-60 min	heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm-300 ℃-60 min	19%	0.25%
	heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm-300 ℃-60 min	33%	0.13%

Table S9. Exponential fitting results of $NaGdF_4$:30%Yb,0.5%Tm nanoparticles, the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanoparticles, $NaYF_4$:30%Yb,0.5%Tm nanoparticles, and the heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanoparticles under 980 nm excitation (monitored at the emission of 478 nm).

Sample	**$NaGdF_4$:30%Yb,0.5%Tm**	**heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm**	**$NaYF_4$:30%Yb, 0.5%Tm**	**heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm**
A1	9580.8	269278.4	10882.6	807.5
τ1 (ns)	0.53×10^6 (100%)	0.18×10^6 (98%)	0.71×10^6 (100%)	0.15×10^6 (44%)
A2		882.5		274.6
τ2 (ns)		0.68×10^6 (2%)		0.53×10^6 (56%)
Average(ns)	0.53×10^6	0.19×10^6	0.71×10^6	0.36×10^6

*Time-resolved fluorescence decay curves of $NaGdF_4$:30%Yb,0.5%Tm nanocrystals and $NaYF_4$:30%Yb,0.5%Tm nanocrystals were fitted by a single exponential (see eqs 1 and 2) function: $A(t)=A_0+A_1\exp-(t-t_0)/\tau_1$ (eqs 1). The average lifetime was calculated using $\tau_{avg}=\tau_1$ (eqs 2).

*Time-resolved fluorescence decay curve of heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals, and heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals were fitted by a double exponential (see eqs 1 and 2) function: $A(t)=A_0+A_1\exp-(t-t_0)/\tau_1+A_2\exp-(t-t_0)/\tau_2$ (eqs 1). The average lifetime was calculated using $\tau_{avg}=(A_1\tau_1^2+A_2\tau_2^2)/(A_1\tau_1+A_2\tau_2)$ (eqs 2).

Table S10. The FRET efficiency of the heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm nanocrystals, and the heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm nanocrystals under 980 nm excitation.

τ and Eff	**$NaYF_4$:30%Yb,0.5%Tm**	**heterostructured $CsPbBr_3$-$NaGdF_4$:Yb,Tm**	**$NaYF_4$:30%Yb, 0.5%Tm**	**heterostructured $CsPbBr_3$-$NaYF_4$:Yb,Tm**
τ_D (ns)	0.53×10^6	0.53×10^6	0.71×10^6	0.71×10^6
$\tau_{D\text{-}A}$ (ns)	/	0.19×10^6	/	0.36×10^6
$Eff = 1 - \tau_{D\text{–}A}/\tau_D$	/	64.2%	/	49.3%