Electronic Supplementary Information

Halide Exchange Mediated Cation Exchange Facilitates Room Temperature Co-doping of d-and f-Block Elements in Cesium Lead Halide Perovskite Nanoparticles

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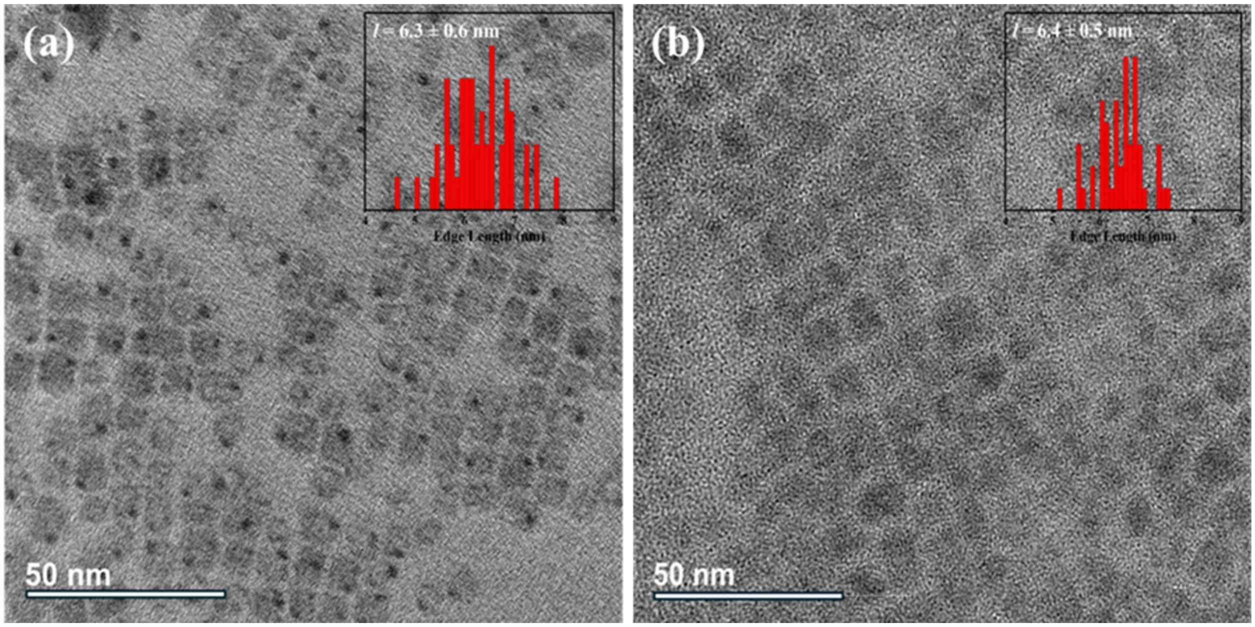


Figure S1. TEM images of (a) $CsPbBr_3$ NPs and (b) $CsPbBr_3/MnCl_2YbCl_3$ NPs are shown along with their size distributions (inset).

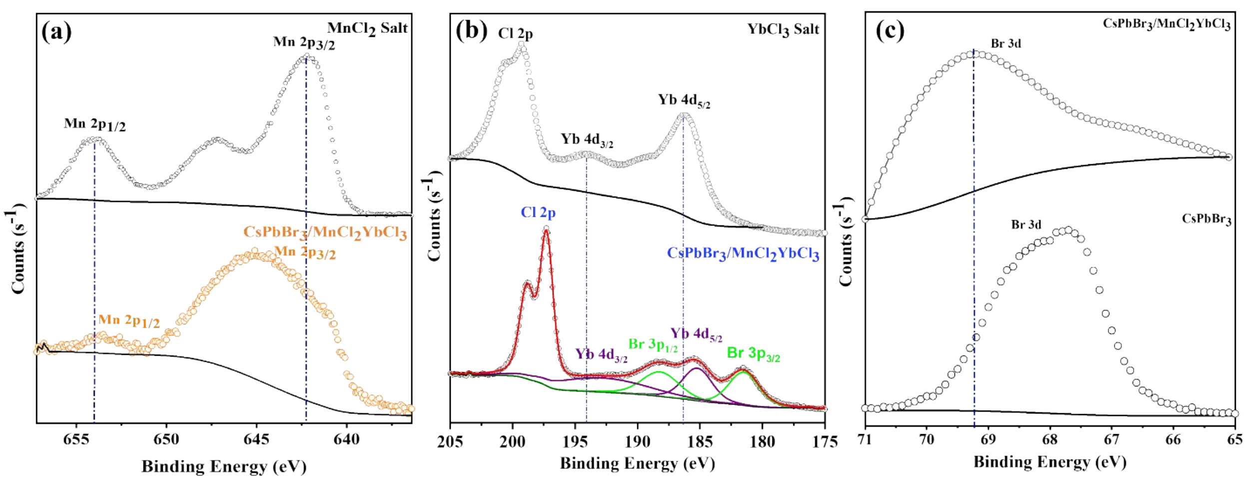
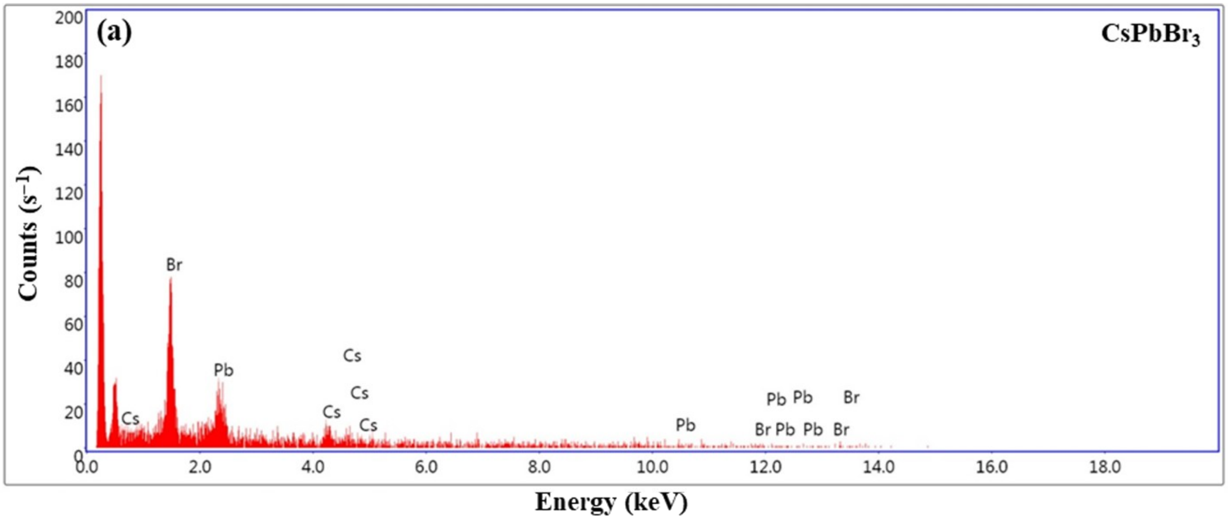


Figure S2. A comparison of the (a) Mn 2p XPS signatures between $MnCl_2$ salt (black circles) and $CsPbBr_3/MnCl_2YbCl_3$ NPs (orange circles), (b) Yb 4d XPS signatures between $YbCl_3$ salt (black circles) and $CsPbBr_3/MnCl_2YbCl_3$ NPs (fitted with purple solid line) and Br 3d XPS between $CsPbBr_3$ NPs and $CsPbBr_3/MnCl_2YbCl_3$ NPs are shown. The dotted lines in panels a-c indicate the shift in the binding energies between the different systems. The black solid lines denote the baseline. In panel b, the spectrum is shown in black circles and the envelope of the fit is shown in red solid line.



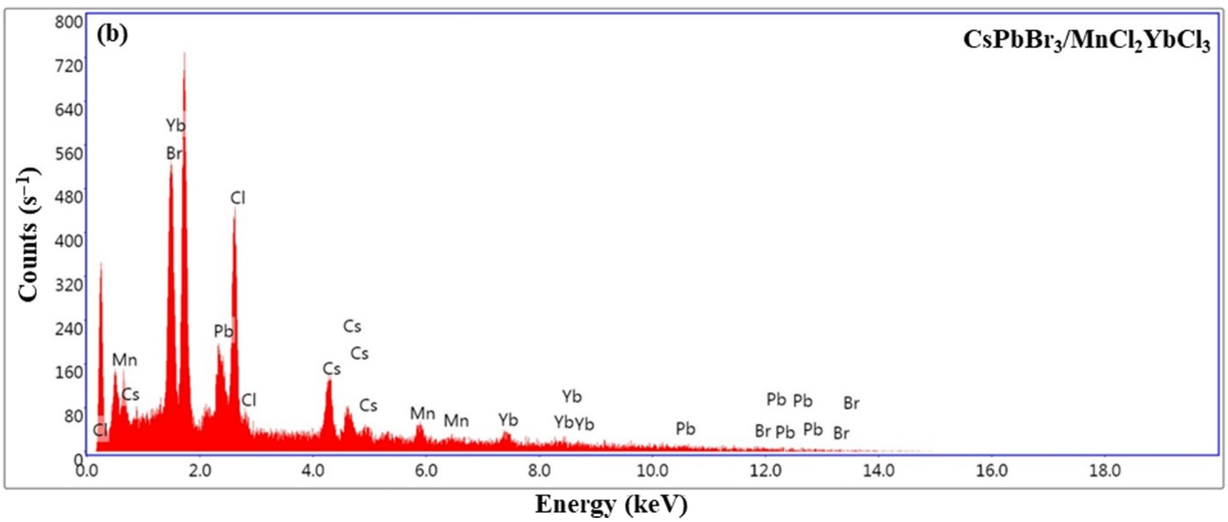


Figure S3. EDS signatures of (a) $CsPbBr_3$ NPs and (b) $CsPbBr_3/MnCl_2YbCl_3$ NPs are shown.

Table S1. Atomic percentages of the different elements are shown.

System	Cs	Pb	Br	Cl	Mn	Yb
$CsPbBr_3$	17.7	18.9	63.4	--	--	--
$CsPbBr_3/MnCl_2YbCl_3$	16.7	5.5	5.7	53.3	9.3	9.5
$CsPbCl_3$	18.1	16.3	--	65.6		
$CsPbCl_3/MnCl_2YbCl_3$	13.2	11.3		67.4	4.7	3.4
	Cs	**Pb**	**Br**	**Cl**	**Eu**	**Tb**
$CsPbCl_3/EuCl_3TbCl_3$	15.2	6.3	--	65.7	6.3	6.5

An error of ~10% is encountered while calculating the atomic percentage.

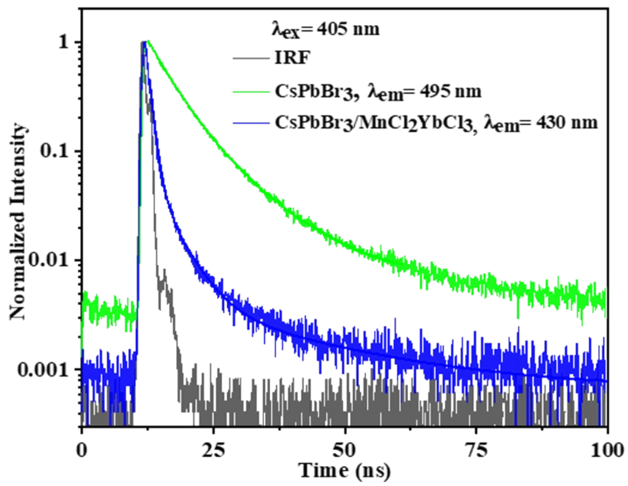


Figure S4. Emission decay profiles of $CsPbBr_3$ NPs (green) and $CsPbBr_3/MnCl_2YbCl_3$ NPs (blue) are shown. The NPs were dispersed in toluene for acquiring the spectra.

Table S2. Lifetime parameters of the different NPs.[1]

System	a_1	τ_1(ns)	a_2	τ_2(ns)	a_3	τ_3(ns)	$<\tau>$(ns)
$CsPbBr_3$ λ_{em} = 495 nm	0.65 ± 0.07	0.44 ± 0.03	0.32 ± 0.02	5.10 ± 0.43	0.03 ± 0.002	17.36 ±1.50	2.44 ± 0.22
$CsPbBr_3/MnCl_2YbCl_3$ λ_{em} = 430 nm	0.93 ± 0.08	0.72 ± 0.12	0.06 ± 0.01	2.80 ± 0.10	0.01 ± 0.001	15.20 ± 2.20	0.98 ± 0.20
$CsPbCl_3$ λ_{em} = 430 nm	0.95 ± 0.01	0.94 ± 0.04	0.04 ± 0.007	5.10 ± 0.42	0.01 ± 0.002	24.0 ± 4.4	1.33 ± 0.14
$CsPbCl_3/MnCl_2YbCl_3$ λ_{em} = 430 nm	0.93 ± 0.01	0.96 ± 0.04	0.06 ± 0.005	5.10 ± 0.60	0.01 ± 0.001	30.36 ± 0.40	1.50 ± 0.16

[1]The decays are fitted to a multiexponential model using the equation $I(t) = \Sigma a_i \exp(-t/\tau)$, where $\Sigma a_i = 1$ and $<\tau> = a_1\tau_1 + a_2\tau_2 + a_3\tau_3$ with τ_1, τ_2, and τ_3 being the three lifetime components having relative amplitudes a_1, a_2, and a_3 respectively. $\chi^2 \leq 1.2$

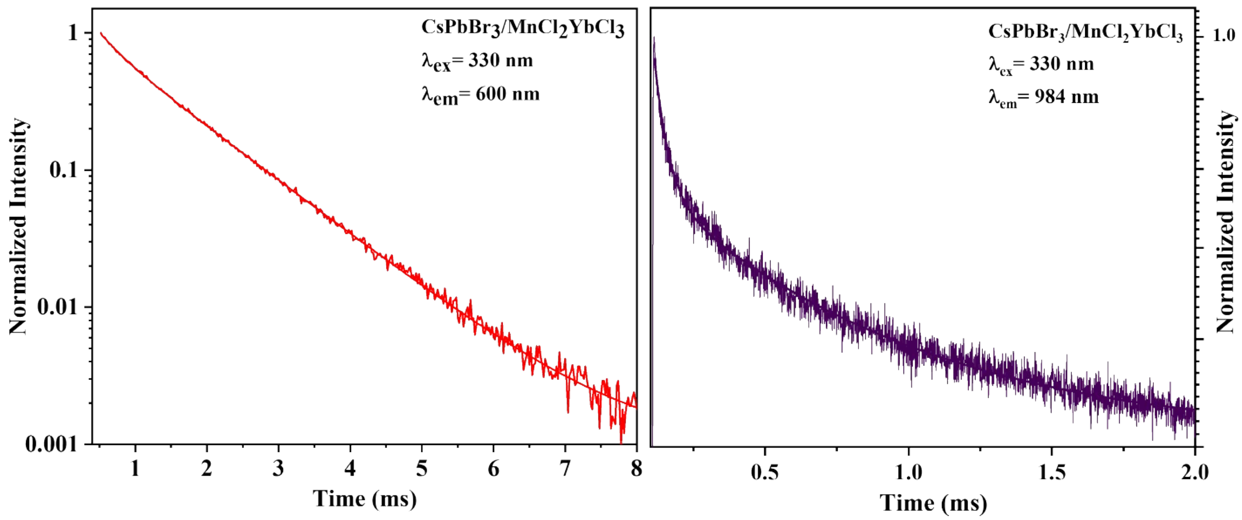


Figure S5. Mn^{2+} (left) and Yb^{3+} (right) emission decay profiles in $CsPbBr_3/MnCl_2YbCl_3$ NPs are shown. The NPs were dispersed in toluene for acquiring the spectrum.

Table S3. Mn^{2+} and Yb^{3+} lifetime parameters of the different NPs.[1]

System	a_1	τ_1(ms)	a_2	τ_2(ms)	<τ>(ms)
$CsPbBr_3/MnCl_2YbCl_3$ λ_{em} = 600 nm	0.20 ± 0.01	0.30 ± 0.01	0.80 ± 0.01	1.10 ± 0.10	0.94 ± 0.08
$CsPbBr_3/MnCl_2YbCl_3$ λ_{em} = 984 nm	0.43 ± 0.04	0.047 ± 0.005	0.57 ± 0.06	0.82 ± 0.07	0.49 ± 0.05
$CsPbCl_3/MnCl_2YbCl_3$ λ_{em} = 600 nm	0.28 ± 0.02	0.21 ± 0.01	0.72 ± 0.06	1.2 ± 0.10	0.92 ± 0.09
$CsPbCl_3/MnCl_2YbCl_3$ λ_{em} = 984 nm	0.30 ± 0.02	0.07 ± 0.006	0.70 ± 0.05	0.94 ± 0.80	0.68 ± 0.06

[1]The decays are fitted to a multiexponential model using the equation $I(t) = \Sigma a_i \exp(-t/\tau)$, where $\Sigma a_i = 1$ and $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2$ with τ_1 and τ_2 being the two lifetime components having relative amplitudes a_1 and a_2 respectively. $\chi^2 \leq 1.3$

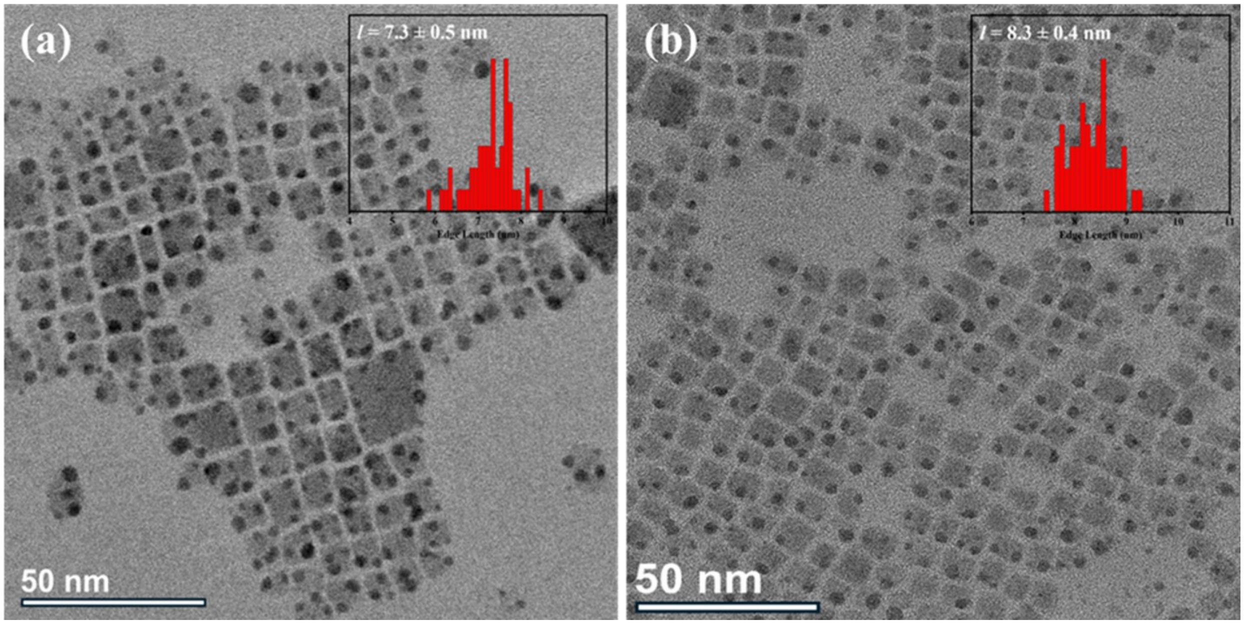


Figure S6. TEM images of (a) $CsPbCl_3$ NPs and (b) $CsPbCl_3/MnCl_2YbCl_3$ NPs are shown along with their size distributions (inset).

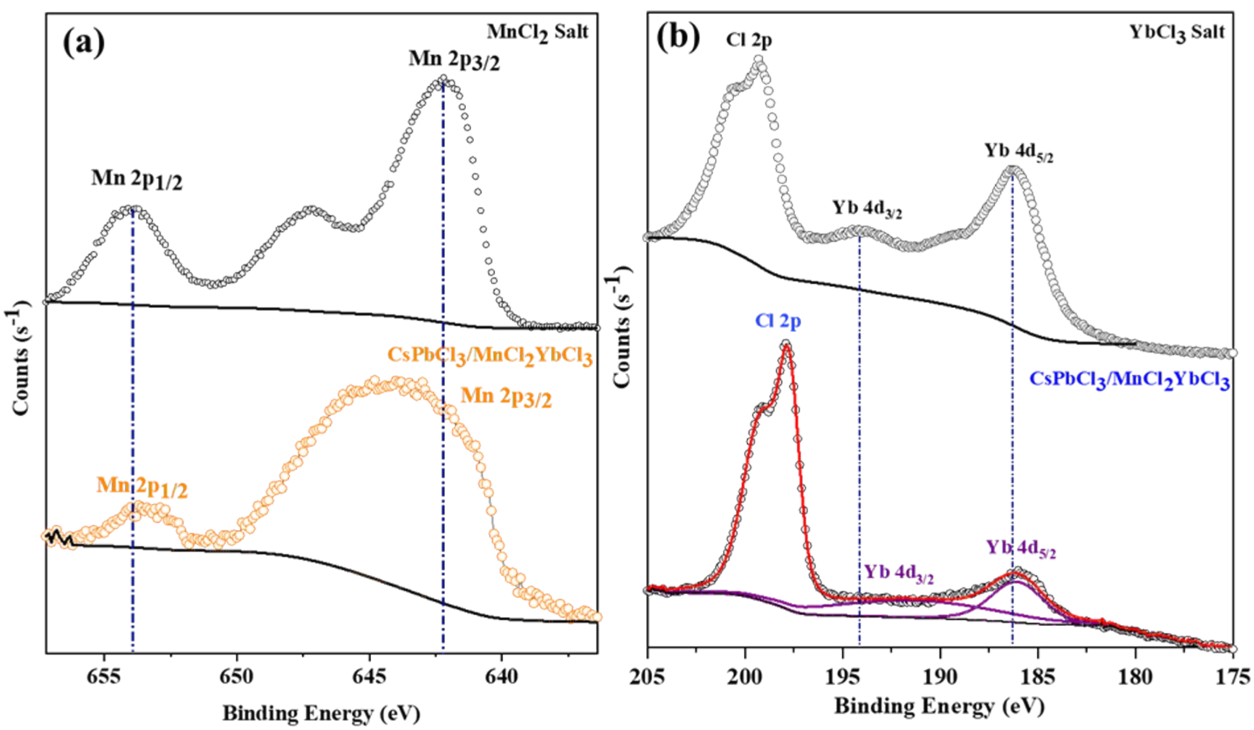


Figure S7. A comparison of the (a) Mn 2p XPS signatures between $MnCl_2$ salt (black circles) and $CsPbCl_3/MnCl_2YbCl_3$ NPs (orange circles) and (b) Yb 4d XPS signatures between $YbCl_3$ salt (black circles) and $CsPbCl_3/MnCl_2YbCl_3$ NPs (fitted with purple solid line) are shown. The dotted lines in panels a-b indicate the shift in the binding energies between the precursors and the NPs. The black solid lines denote the baseline. In panel b, the spectrum is shown in black circles and the envelope of the fit is shown in red solid line.

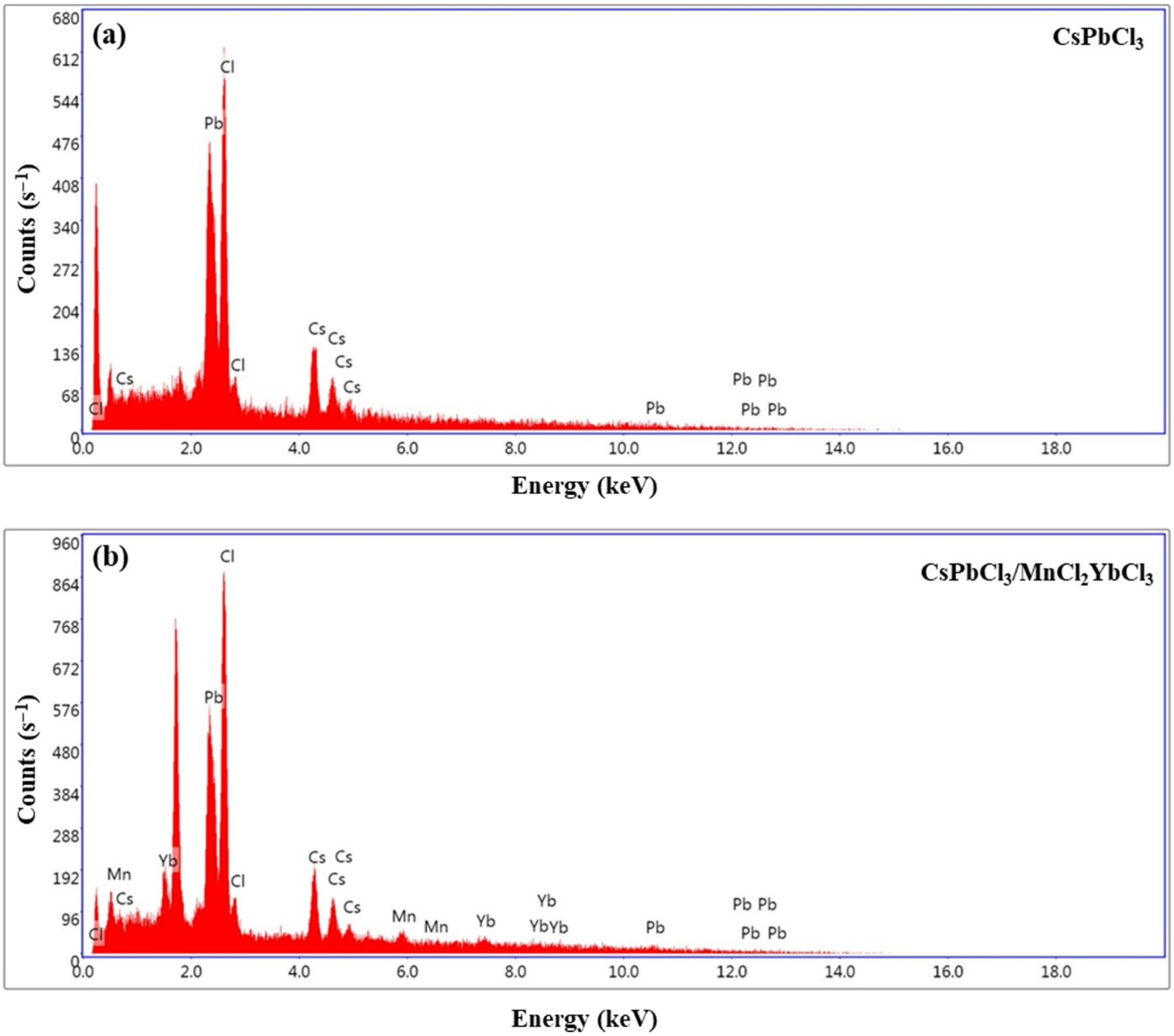


Figure S8. EDS signatures of (a) $CsPbCl_3$ NPs and (b) $CsPbCl_3/MnCl_2YbCl_3$ NPs are shown.

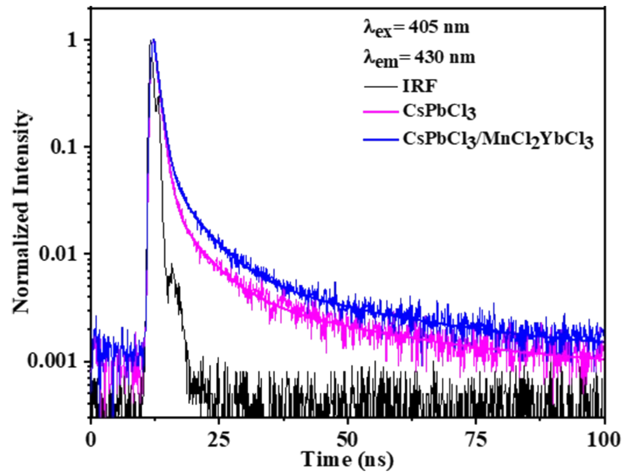


Figure S9. Emission decay profiles of $CsPbCl_3$ NPs (magenta) and $CsPbCl_3/MnCl_2YbCl_3$ NPs (blue) are shown. The NPs were dispersed in toluene for acquiring the spectra.

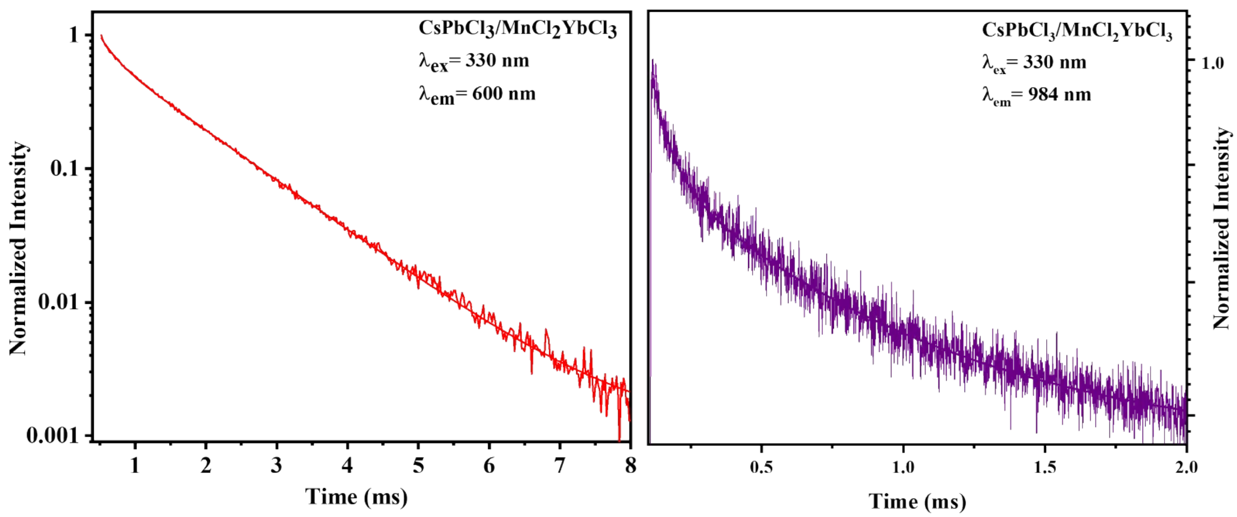


Figure S10. Mn^{2+} (left) and Yb^{3+} (right) emission decay profile in $CsPbCl_3/MnCl_2YbCl_3$ NPs are shown. The NPs were dispersed in toluene for acquiring the spectrum.

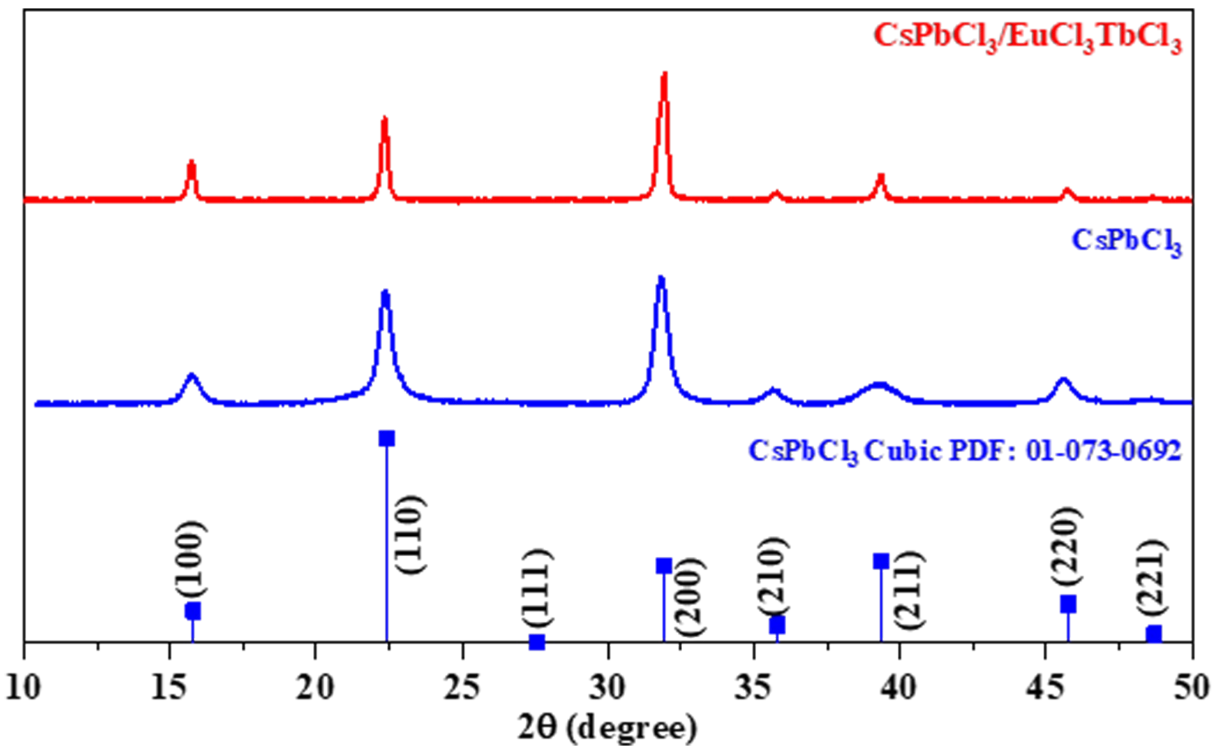


Figure S11. XRD patterns of the $CsPbCl_3$ and the $CsPbCl_3/EuCl_3TbCl_3$ NPs are shown.

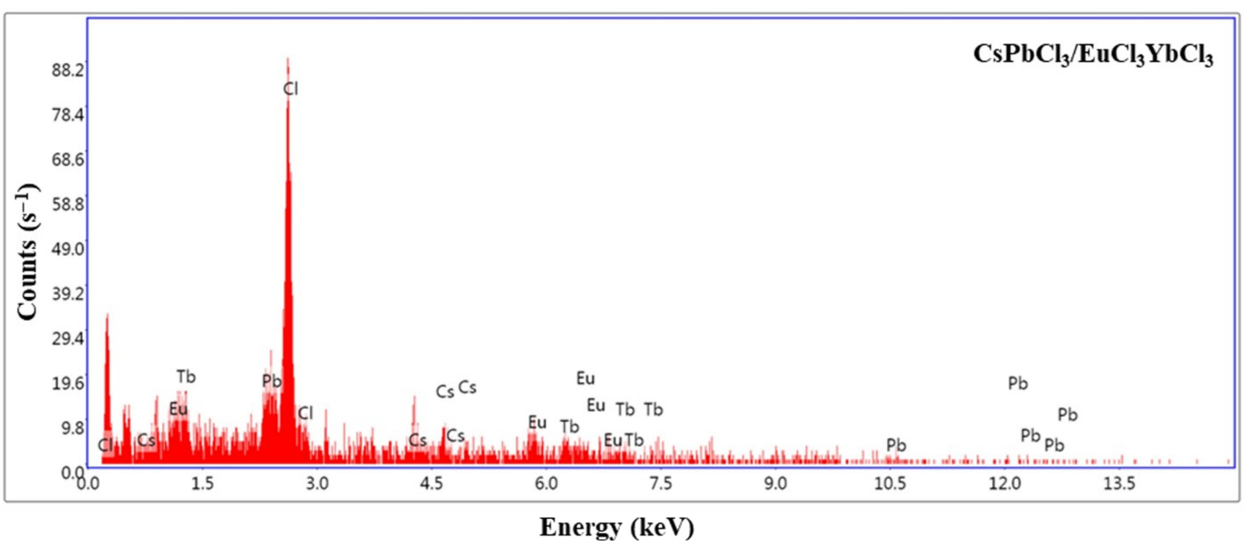


Figure S12. EDS signature of $CsPbCl_3/EuCl_3TbCl_3$ NPs is shown.

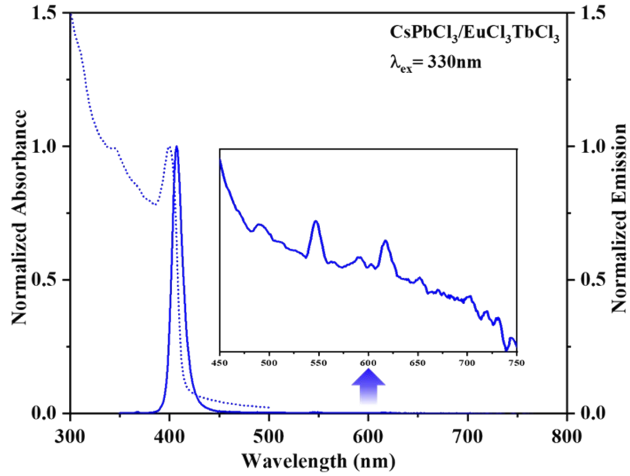


Figure S13. UV-vis absorption and steady-state emission spectra of $CsPbCl_3/EuCl_3TbCl_3$ NPs are shown.

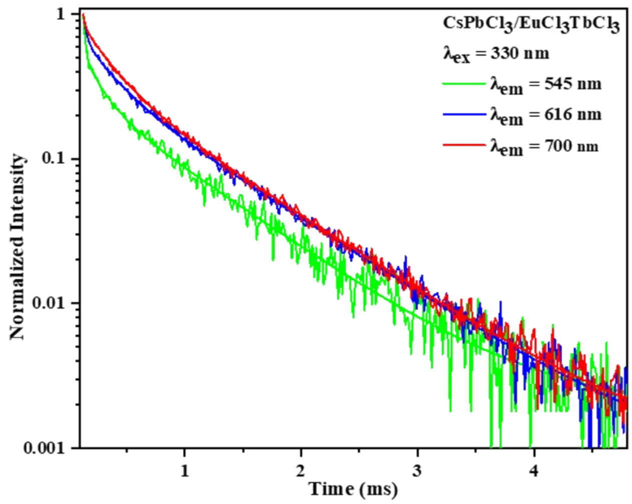


Figure S14. Eu^{3+} and Tb^{3+} decay profiles in $EuCl_3TbCl_3$ NPs are shown.

Table S4. Ln^{3+} (Ln = Eu, Tb) lifetime parameters of the different NPs.[1]

System	a_1	τ_1(ms)	a_2	τ_2(ms)	a_3	τ_3(ms)	<τ>(ms)
$CsPbCl_3/EuCl_3TbCl_3$ λ_{em} = 545 nm	0.68 ± 0.04	0.03 ± 0.007	0.17 ± 0.01	0.19 ± 0.04	0.15 ± 0.02	0.83 ± 0.08	0.18 ± 0.04
$CsPbCl_3/EuCl_3TbCl_3$ λ_{em} = 616 nm	0.49 ± 0.04	0.03 ± 0.004	0.25 ± 0.03	0.20 ± 0.03	0.26 ± 0.03	0.80 ± 0.09	0.26 ± 0.05
$CsPbCl_3/EuCl_3TbCl_3$ λ_{em} = 700 nm	0.44 ± 0.05	0.02 ± 0.003	0.33 ± 0.03	0.23 ± 0.02	0.23 ± 0.02	0.80 ± 0.07	0.27 ± 0.04

[1]The decays are fitted to a multiexponential model using the equation $I(t) = \Sigma a_i \exp(-t/\tau)$, where $\Sigma a_i = 1$ and $\langle\tau\rangle = a_1\tau_1 + a_2\tau_2 + a_3\tau_3$ with τ_1, τ_2, and τ_3 being the three lifetime components having relative amplitudes a_1, a_2, and a_3 respectively. $\chi^2 \leq 1.3$

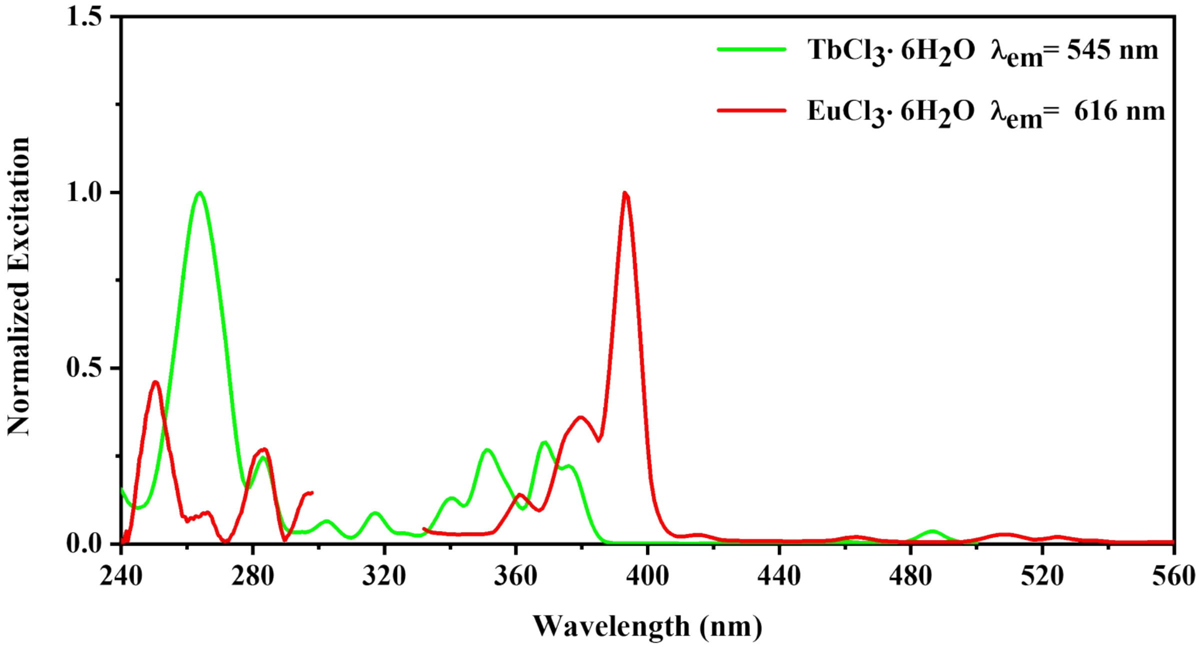


Figure S15. Excitation spectra of the $LnCl_3.6H_2O$ [Ln = Eu, Tb] in water is shown. For $EuCl_3.6H_2O$, the spectrum from 300-330 nm is broken to remove the contribution of the harmonic from the excitation source.