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Supporting Information

Insights into the local structure of dopants, doping efficiency, and luminescence properties of lanthanide-doped $CsPbCl_3$ perovskite nanocrystals

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Experimental Section

Materials.

All chemicals, cesium carbonate (Cs_2CO_3, 99.99%, Aladdin), lead (II) chloride ($PbCl_2$, 99.999%, Alfa Aesar), ytterbium chloride ($YbCl_3$, 99.99%, Alfa Aesar), lanthanum chloride ($LaCl_3$, 99.99%, Alfa Aesar), lead(II) acetate trihydrate ($Pb(Ac)_2$•$3H_2O$, 99.999%, Acros), poly(methyl methacrylate) (PMMA, Average Mw ~350000 by GPC, Aldrich), 1-octadecene (ODE, 90%, Alfa Aesar), oleic acid (OA, 90%, Alfa Aesar), oleylamine (OAm, 80-90%, Acros), tri-n-octylphosphine (TOP, 90%, Alfa Aesar), benzoyl chloride (99%, Sigma-Aldrich), methyl acetate (MA, 99%, Alfa Aesar), n-hexane (Hex, ⩾98.0%(GC), Aladdin) and toluene (AR, QS), were used without purification unless otherwise noted.

Synthesis of La-doped $CsPbCl_3$ NCs: La-doped $CsPbCl_3$ NCs were synthesized by using the molar ratio of $LaCl_3$:$PbCl_2$ of 1:1. $PbCl_2$ (0.1521 g), $LaCl_3$ (0.1341 g), ODE (10 mL), OAm (1.6 mL), OA (1.6 mL), and TOP (2 mL) were added into a 50 mL three-neck round-bottomed flask, degassed at 120 ^oC for 1 h, and then heated at 120 ^oC under N_2. Then, 1.6 mL of dried OAm and 1.6 mL of dried OA were slowly injected into the solution. Ten minutes later, the temperature was raised to 225 ^oC. Then, 1.6 mL of dried OAm and 1.6 mL of dried OA were slowly injected into it again and kept at 225 ^oC for 5 min. Finally, the Cs-oleate (1.035 mL, 0.15 M in ODE) was quickly injected and 1 min later the reaction mixture was cooled down by ice-water bath. To purify the NCs, the crude solution was separated by centrifuging for 5 min at 12000 rpm. After centrifugation, the supernatant was discarded and this process was repeated two more times to remove residual reaction mixture. Then the precipitate was redispersed in 0.75 mL hexane and 0.75 mL MA and centrifuged again for 5 min at 12000 rpm, and the supernatant was discarded. Subsequently, the particles were redispersed in 1 mL hexane and centrifuged for 5 min at 12000 rpm, and the supernatant was reserved and denoted S-La-1. After repeating the previous step for two more times, different NC sets were collected, which are denoted S-La-2 and S-La-3, respectively.

Synthesis of Yb-doped $CsPb(Cl,Br)_3$ NCs: Yb-doped $CsPb(Cl,Br)_3$ NCs were synthesized by using the molar ratio of $YbCl_3$:$PbBr_2$ of 1:1. $YbCl_3$ (0.1328 g), $PbBr_2$ (0.1744 g), ODE (10 mL), OAm (1.6 mL), OA (1.6 mL), and TOP (2 mL) were added into a 50 mL three-neck round-bottomed flask, degassed at 120 ^oC for 1 h, and then heated at 120 ^oC under N_2. Then, 1.6 mL of dried OAm and 1.6 mL of dried OA were slowly injected into it. Ten minutes later, the temperature was raised to 215 ^oC. Then, 0.4 mL of dried OAm and 0.4 mL of dried OA were slowly injected into the reaction mixture and kept it at 215 ^oC for 5 min. Finally, the Cs-oleate (0.9 mL, 0.15 M in ODE) was quickly injected and 1 min later the reaction mixture was cooled down by ice-water bath. To purify the NCs, the crude solution was separated by centrifuging for 5 min at 12000 rpm. After centrifugation, the supernatant was discarded and this process was repeated two more times to remove residual reaction mixture. Then the precipitate was redispersed in 0.75 mL hexane and 0.75 mL MA and centrifuged again for 5 min at 12000 rpm, and the supernatant was discarded. Subsequently, the particles were redispersed in 1.5 mL hexane and centrifuged for 5 min at 12000 rpm, and the supernatant was reserved. After repeating the previous step for three more times, different NC sets were collected, which are denoted S(Cl/Br)-Yb-2, S(Cl/Br)-Yb-3, and S(Cl/Br)-Yb-4, respectively.

Synthesis of Yb-doped $CsPbCl_3$ NCs under Cl-poor conditions: For this purpose, we used one modified hot-injection method to readily control Cl- amount in the reaction. The key is to use $Pb(Ac)_2\cdot 3H_2O$ instead of $PbCl_2$ as a precursor to create Cl-poor condition in the synthesis. Briefly, $Pb(Ac)_2\cdot 3H_2O$ (0.2074 g), $YbCl_3$ (0.1527 g), ODE (10 mL), OAm (1.6 mL), OA (1.6 mL), TOP (2 mL) were added into a 50 mL three-neck round-bottomed flask and dried under vacuum for 1 h at 120 ^{o}C, while keeping all the other parameters consistent with the "Synthesis of Yb-doped $CsPbCl_3$ NCs" as described above. The collected NCs were denoted S-Cl-poor-*x*, where *x* represent the CNT of NCs dispersed in 1.5 mL hexane. The samples synthesized under Cl-poor condition, S-Cl-poor-2 was used for the detailed characterizations. We note that the sizes of S-Cl-poor-2 and S-Yb-4 are similar, suggesting comparable growth rates of these NCs.

Synthesis of $CsPbCl_3$ NCs: $PbCl_2$ (0.1521 g), ODE (10 mL), OAm (1.6 mL), OA (1.6 mL), and TOP (2 mL) were added into a 50 mL 3-neck round-bottomed flask, degassed at 120 ^{o}C for 1 h, and then heated at 120 ^{o}C under N_2. Then, 1.6 mL of dried OAm and 1.6 mL of dried OA were slowly injected into it. After 10 min, the temperature was raised to 215 ^{o}C and kept at 240 ^{o}C for 5 min. Finally, the Cs-oleate (1.035 mL, 0.15 M in ODE) was quickly injected and 1 min later the reaction mixture was cooled down by ice-water bath. To purify the NCs, the crude solution was separated by centrifuging for 5 min at 12000 rpm. After centrifugation, the supernatant was discarded and this process was repeated two more times to remove residual reaction mixture. Then the precipitate was redispersed in 0.75 mL hexane and 0.75 mL MA and centrifuged again for 5 min at 12000 rpm, and the supernatant was discarded. Subsequently, the particles were redispersed in 1.5 mL hexane and centrifuged for 5 min at 12000 rpm, and the supernatant was reserved. After repeating the previous step for three more times, different NC sets were collected. The collected NCs were denoted S-*x*, where *x* represents the CNT of NCs dispersed in 1.5 mL hexane. We stress that the concentrations of the precursors and the reaction temperature in this synthesis are slightly higher than those commonly used, which is critical to obtain NC sets with different average sizes and narrow size distribution.

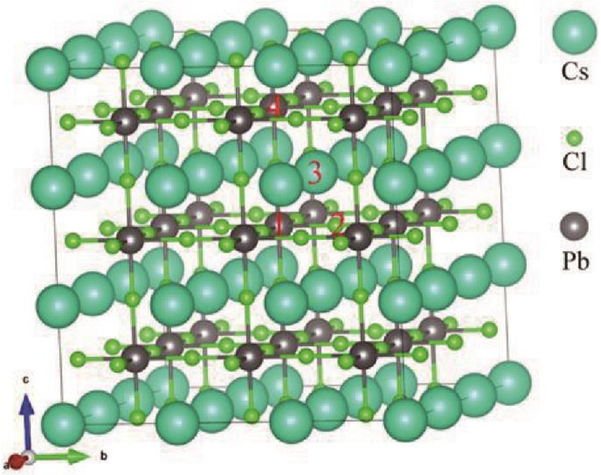

Figure S1. The 3x3x3 $CsPbCl_3$ supercell. Numbers 1, 2, 3 and 4 represent the positions of Yb dopant, Cl vacancy, Cs vacancy and Pb vacancy used in our calculations, respectively.

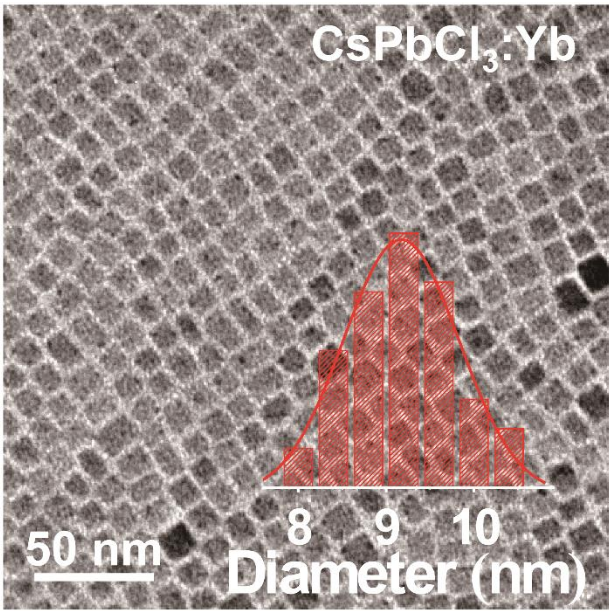

Figure S2. TEM images of $CsPbCl_3$:Yb samples, the average size and standard deviation is 9.17±0.03 nm. Note that the average size is obtained by Gaussian fitting.

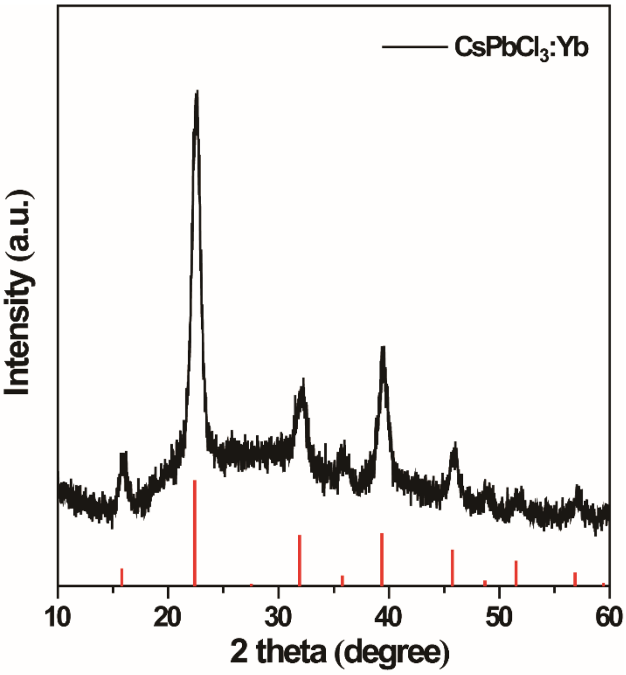

Figure S3. XRD pattern of the CsPbCl$_3$:Yb NCs. The red vertical line at the bottom is the XRD pattern of CsPbCl$_3$ corresponding to ICSD: 201251 (Cubic, Pm-3m).

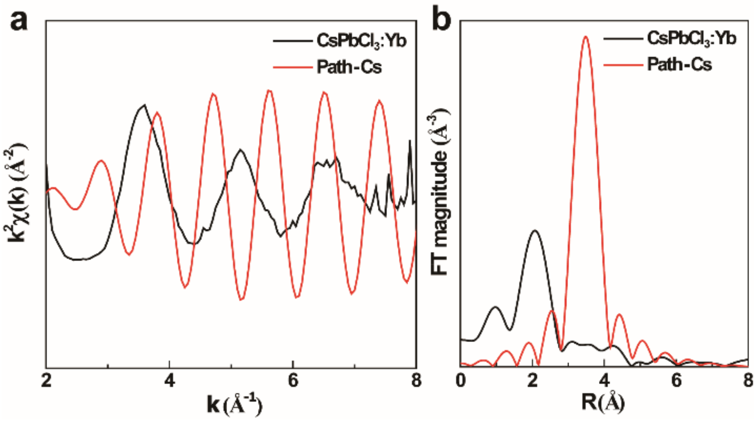

Figure S4. a. k^2-weighted Yb L_{III}-edge EXAFS. **b.** corresponding FTs of CsPbCl$_3$:Yb. The red line is the path corresponding to the model where Yb replaces Cs.

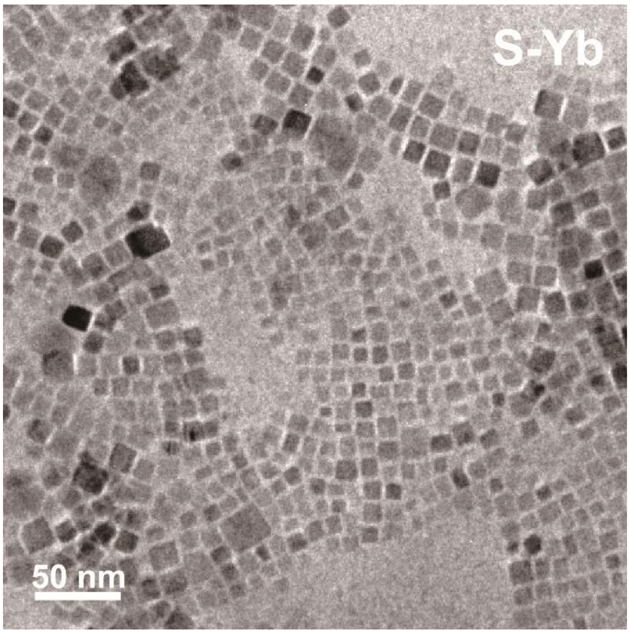

Figure S5. TEM images of the Yb-doped NCs with a wide size distribution. The sample for the TEM measurement was prepared by dispersing the precipitate obtained from centrifuging the NC solution with 0.75 mL hexane and 0.75 mL MA. That is, these NCs correspond to the precipitate before the attainment of S-Yb-*x*.

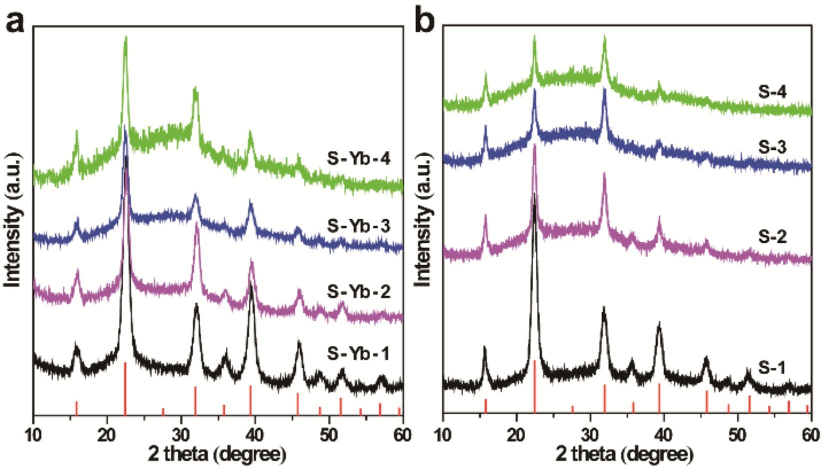

Figure S6. XRD patterns of the S-Yb-*x* (a) and S-*x* samples (b). The red vertical line at the bottom is the XRD pattern of $CsPbCl_3$ corresponding to ICSD: 201251 (Cubic, Pm-3m).

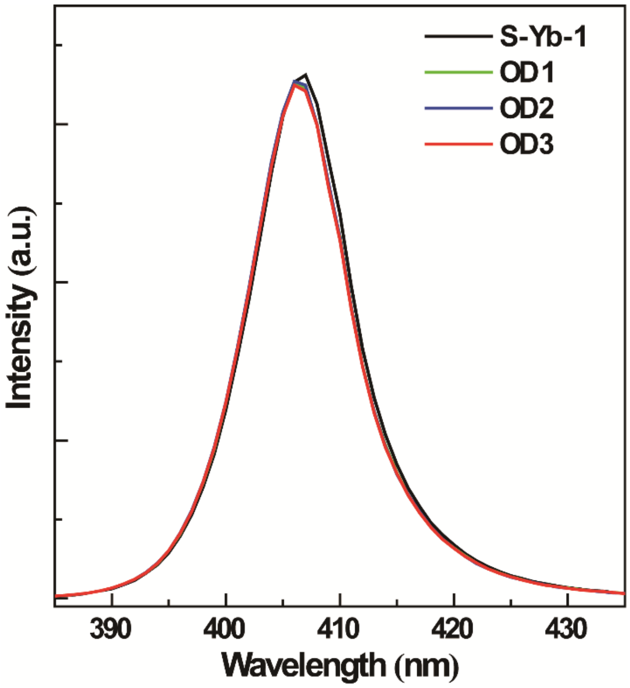

Figure S7. PL spectra of S-Yb-1, OD1, OD2, and OD3. All PL spectra were measured under the same optical density of NC solutions.

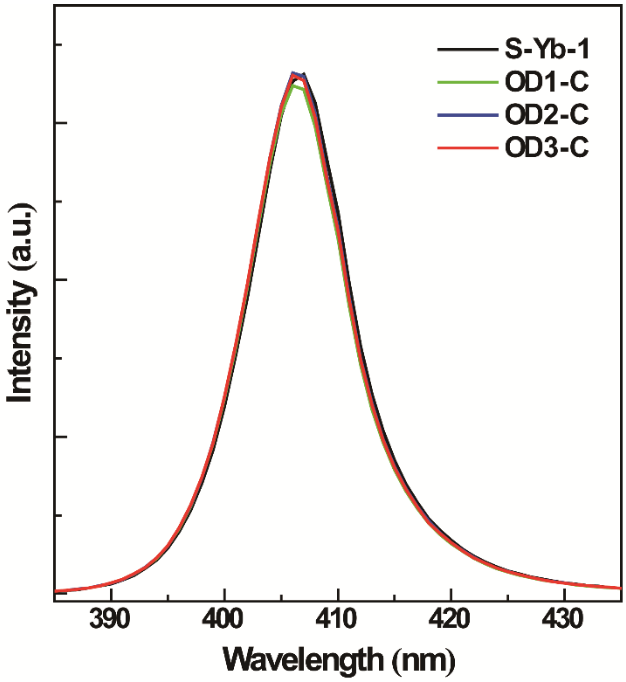

Figure S8. PL spectra of S-Yb-1, OD1-C, OD2-C, and OD3-C. All PL spectra were measured under the same optical density of NC solutions.

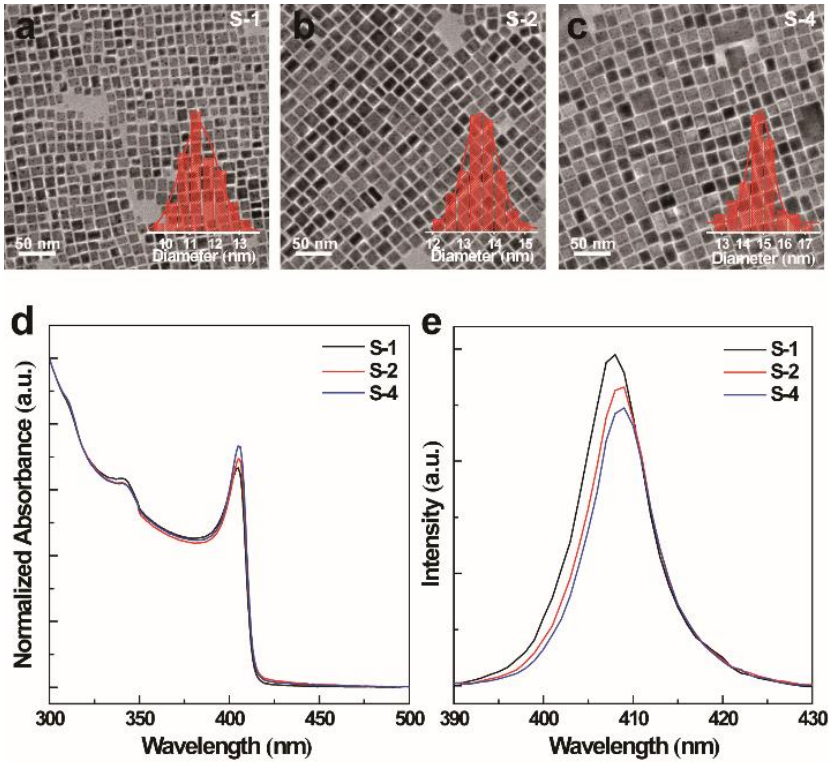

Figure S9. a-c. TEM images of S-1 (**a**), S-2 (**b**), and S-4 (**c**). Insets show the histograms of edge lengths of NCs. The average sizes and standard deviations for S-1, S-2, and S-4 are 11.37±0.07 nm, 13.57±0.03 nm, 14.84±0.06 nm, respectively. Note that the average sizes are obtained by Gaussian fitting. **d, e.** Absorption (**d**), visible PL spectra (**e**) of S-1, S-2, and S-4. The excitation wavelength for PL is 375 nm. The FWHMs of PL for S-1, S-2, and S-4 are 9.8 nm, 9.5 nm, 9.4 nm, respectively. All PL spectra were measured under the same optical density of NC solutions. We note that with the increase of CNT, the size of undoped $CsPbCl_3$ NCs increases, accompanying the weakened PL emission. Since all NCs are from the same synthesis batch, we thus conclude that a fast growth rate of NCs can introduce more structural defects. That is, larger NCs have more defects.

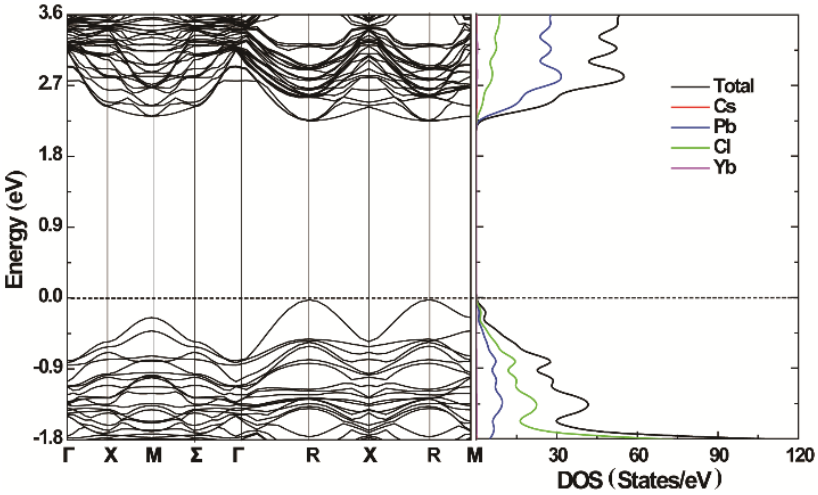

Figure S10. Band structure and DOS of Yb-doped $CsPbCl_3$ with a Pb vacancy. It is obvious that the Pb vacancy does not introduce any in-gap state. The dotted line represents the Fermi level.

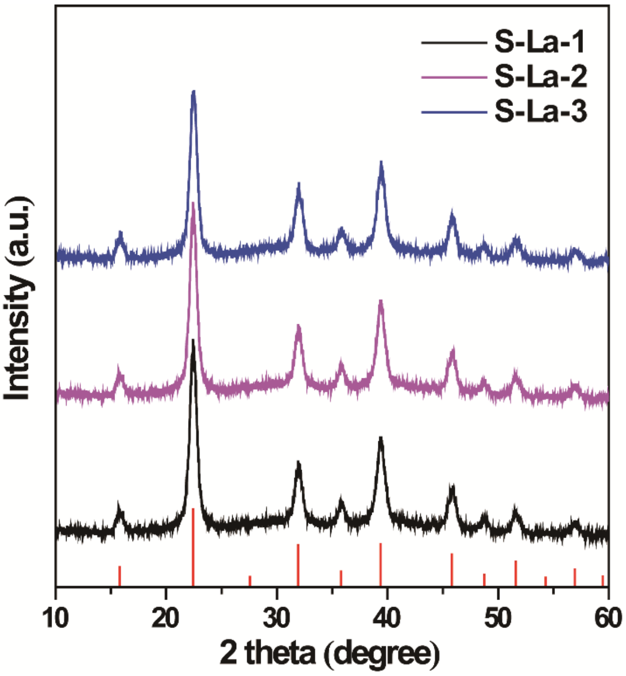

Figure S11. XRD patterns of S-La-*x*. The red vertical line at the bottom is the XRD pattern of $CsPbCl_3$ corresponding to ICSD: 201251 (Cubic, Pm-3m).

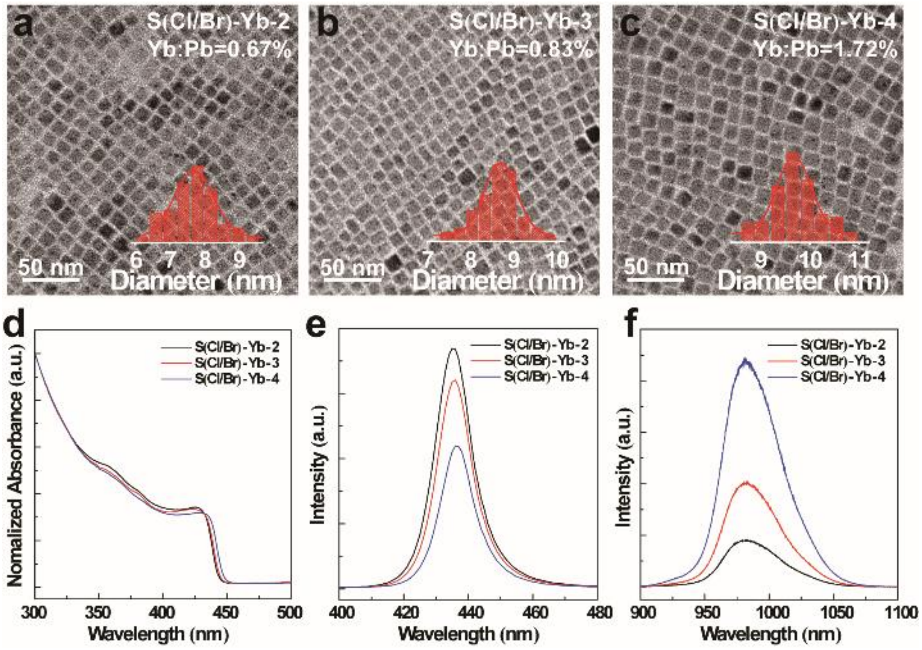

Figure S12. a-c. TEM images of S(Cl/Br)-Yb-2 (**a**), S(Cl/Br)-Yb-3 (**b**), and S(Cl/Br)-Yb-4 (**c**). The Yb concentrations are indicated in the TEM images. Insets show the histograms of edge lengths of NCs. The average sizes and standard deviations for S(Cl/Br)-Yb-2, S(Cl/Br)-Yb-3, and S(Cl/Br)-Yb-4 are 7.70±0.06 nm, 8.70±0.03 nm, 9.68±0.04 nm, respectively. Note that the average sizes are obtained by Gaussian fitting. **d-f**. Absorption (**d**), visible (**e**) and near-infrared (**f**) PL spectra of S(Cl/Br)-Yb-2, S(Cl/Br)-Yb-3, and S(Cl/Br)-Yb-4. The excitation wavelength for PL is 375 nm. The FWHMs of PL for S(Cl/Br)-Yb-2, S(Cl/Br)-Yb-3, and S(Cl/Br)-Yb-4 are 14.6 nm, 14.0 nm, 13.7 nm, respectively. The visible PLQYs for S(Cl/Br)-Yb-2, S(Cl/Br)-Yb-3, and S(Cl/Br)-Yb-4 are 78.0%, 59.3%, and 45.9%, respectively. All PL spectra were measured under the same optical density of NC solutions.

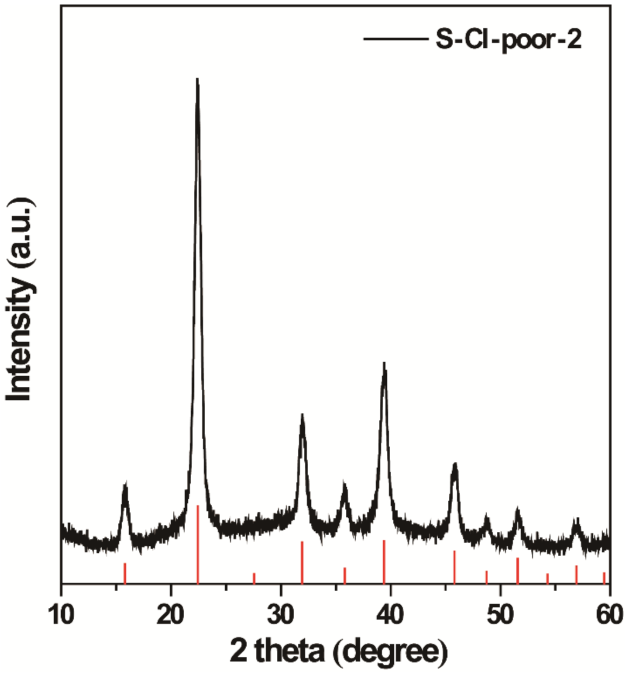

Figure S13. XRD pattern of S-Cl-poor-2. The red vertical line at the bottom is the XRD pattern of $CsPbCl_3$ corresponding to ICSD: 201251 (Cubic, Pm-3m).

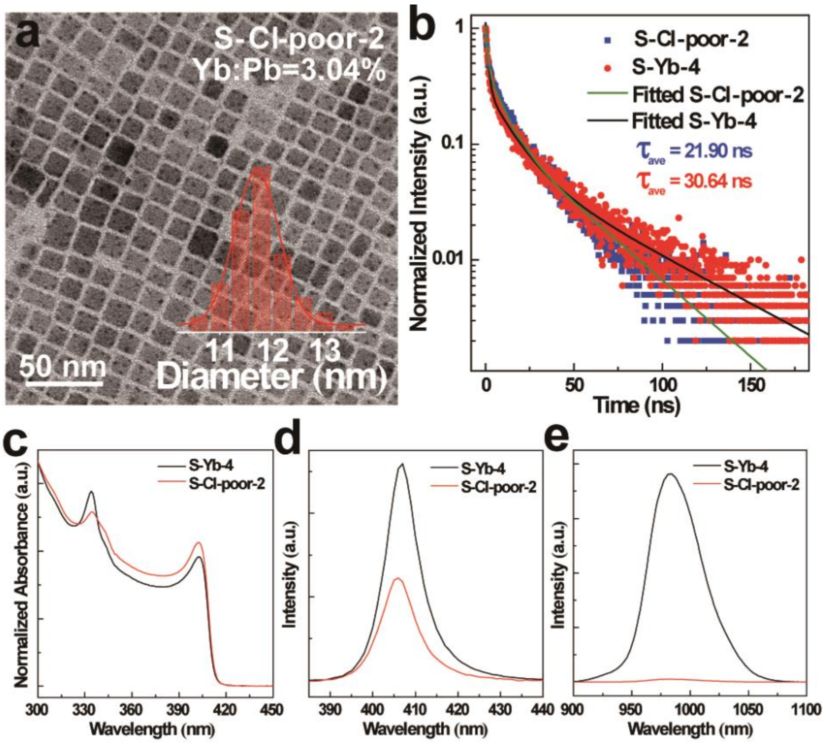

Figure S14. a. TEM image of S-Cl-poor-2. The Yb concentration is indicated in the TEM image. Inset shows the histogram of edge length of NCs. The average size and standard deviation is 11.71±0.03 nm. **b.** Time-resolved PL of S-Cl-poor-2; the monitored wavelength is 407 nm. **c-e** Absorption (**c**), visible (**d**) and near-infrared (**e**) PL spectra of S-Cl-poor-2. We note that the sizes of S-Yb-4 and S-Cl-poor-2 are similar; the TEM image of S-Yb-4 is shown in Figure 1e. However, the Yb concentration in S-Cl-poor-2 synthesized under Cl-poor conditions is much higher than that of S-Yb-4 synthesized under Cl-rich conditions. All PL spectra were measured under the same optical density of NC solutions. The visible PLQY of S-Cl-poor-2 is 23.8%. It is obvious that the PL intensity of S-Cl-poor-2 is much weaker than that of S-Yb-4 in the visible and NIR, which can be attributed to the increase of the concentration of deep defect states in S-Cl-poor-2 owing to Cl-poor growth conditions. This result further corroborates that a higher-concentration defects favor a higher doping efficiency.

Table S1. The number of atoms, lattice parameters (a = b = c, and volume V) and Bader charge in the 3x3x3 supercell before and after introducing the vacancy/dopant. V_{Cl}, V_{Cs}, and V_{Pb} represent the models of $CsPbCl_3$ supercells with Cl, Cs, and Pb vacancies, respectively. The terms of “Supercell” and “Yb-doped” represent the models without any defect and with Yb dopant, respectively. Yb-V_{Cl}, Yb-V_{Cs}, and Yb-V_{Pb} represent the models of Yb-doped $CsPbCl_3$ supercells with Cl, Cs, and Pb vacancies, respectively.

		Supercell	V_{Cl}	V_{Cs}	V_{Pb}	Yb-doped	Yb-V_{Cl}	Yb-V_{Cs}	Yb-V_{Pb}
Number of atoms	Cl	81	80	81	81	81	80	81	81
	Cs	27	27	26	27	27	27	26	27
	Pb	27	27	27	26	26	26	26	25
	Yb	0	0	0	0	1	1	1	1
a=b=c (Å)		17.164	17.074	17.055	17.020	17.065	17.064	17.039	17.028
V (Å^3)		5056.648	4978.312	4978.312	4930.434	4969.613	4929.952	4947.228	4931.493
Bader charge (*e*)	Cl	7.628	7.696	7.647	7.649	7.759	7.7587	7.729	7.649
	Cs	8.117	8.120	8.098	8.104	8.111	8.121	8.101	8.108
	Pb	2.999	3.105	2.783	2.757	2.900	2.823	2.778	2.716
	Yb	-	-	-	-	6.629	6.588	6.627	6.630
Valence states	Cl	-0.628	-0.696	-0.647	-0.649	-0.759	-0.7587	-0.729	-0.649
	Cs	+0.883	+0.880	+0.902	+0.896	+0.889	+0.879	+0.899	+0.892
	Pb	+1.001	+0.895	+1.217	+1.243	+1.100	+1.177	+1.222	+1.284
	Yb	-	-	-	-	+1.371	+1.412	+1.373	+1.370

Table S2. Sizes, product yields, and Yb/Pb ratios of Yb-doped $CsPbCl_3$ NCs.

Sample	Average size (nm)	Amount/synthesis (g)	Product yield (%)[a]	Molar ratio (Yb:Pb)
S-Yb-1	8.35	0.0244	10.52	0.62%
S-Yb-2	9.33	0.0084	3.64	0.94%
S-Yb-3	11.07	0.0056	2.42	1.04%
S-Yb-4	11.35	0.0047	2.03	1.21%

[a] The product yield was calculated by dividing the obtained powder by the total amount of Cs, Pb and Cl in the reaction system.

Table S3. Fitted lifetimes and calculated average lifetimes (τ_{ave}) at 407 nm for Yb-doped $CsPbCl_3$ NCs.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{ave} (ns)
S-Yb-1	0.06	43.62	0.26	12.18	0.79	1.33	22.55
S-Yb-2	0.11	37.68	0.24	9.30	0.69	0.88	25.41
S-Yb-3	0.06	54.10	0.23	14.82	0.81	1.40	29.24
S-Yb-4	0.07	53.10	0.23	13.22	0.80	1.30	30.64

Table S4. Fitted lifetimes and calculated average lifetimes (τ_{ave}) at 980 nm for Yb-doped $CsPbCl_3$ NCs.

Sample	A_1	τ_1 (ms)	A_2	τ_2 (ms)	A_3	τ_3 (ms)	τ_{ave} (ms)
S-Yb-1	0.24	0.66	0.71	2.10	0.0240	6.05	2.30
S-Yb-2	0.24	0.73	0.73	2.28	0.0081	11.66	2.59
S-Yb-3	0.22	0.65	0.73	2.31	0.0110	19.16	3.99
S-Yb-4	0.17	0.51	0.77	2.19	0.0220	14.64	4.06

Table S5. Fitted lifetimes and calculated average lifetimes (τ_{ave}) at 407 nm for La-doped $CsPbCl_3$ NCs.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{ave} (ns)
S-La-1	0.30	7.12	0.66	0.95	0.07	29.04	15.60
S-La-2	0.31	8.59	0.69	1.39	0.07	33.40	17.16
S-La-3	0.36	7.08	0.54	1.06	0.10	35.48	21.67