Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Surface Pre-optimization of Mixed Halide Perovskite Toward High Photoluminescence Quantum Yield in Whole Blue Spectrum Range

Chao Luo,[†] Wen Li,[†] Da Xiong,[†] Ji Fu,[‡] and Weiqing Yang[*, †]

[†] Key Laboratory of Advanced Technologies of Materials (Ministry of Education), School of Materials Science and Engineering, State Key Laboratory of Traction Power, Southwest Jiaotong University, Chengdu 610031, PR China
[‡] The Graduate School of Information, Production and Systems, Waseda University, 2-7 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135, Japan

Experiment section

Materials. Cesium carbonate (Cs_2CO_3, 99%), lead chloride ($PbBr_2$, 99%), lead bromide ($PbBr_2$, 99%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OAm, 80%-90%), trioctylphosphine (TOP, 95%) were purchased from Shanghai Aladdin Industrial Corporation Co., Ltd. Praseodymium chloride ($PrCl_3 \cdot 4H_2O$, 99%) were purchased from Xinzheng Rare Earth New Material Co., Ltd. The water crystallization of $PrCl_3 \cdot 4H_2O$ was evaporated by vacuum bake at 80 °C. All the materials were used directly without further purification.

Preparation of Cesium-Oleate Solution. Cs_2CO_3 (0.4 g), OA (2.5 mL), and ODE (20 mL) were loaded in a 100 ml three-neck flask and degassed for five minutes, and then heated to 120°C for 1 hour under Ar_2 atmosphere, followed by heating to 150°C until all Cs_2CO_3 reacted with OA. The Cs-oleate solution was stored at room temperature but must be preheated to more than 120°C before using.

Synthesis of $CsPbBr_3$ QDs. $PbBr_2$ (0.4 mmol, 0.1468 g), ODE (10 mL), dried OA (1.0 mL) and OAm (1.0 mL) were loaded into a 100 mL three-necked flask and heated to 120°C for 1 hour under Ar_2 atmosphere. Afterwards, the temperature was increased to 185°C, Cs-oleate (1.0 mL) swiftly injected, and 5 seconds later the reaction mixture was immediately cooled by cold-water bath.

Synthesis of $CsPbCl_3$ QDs. $PbCl_2$ (0.4 mmol, 0.11g) ODE (10 mL) were loaded into a 100 mL three-necked flask and heated to 120°C, and then dried OA (1.0 mL) and OAm (1.0 mL) were added into the flask. After 10 minutes, TOP (1 ml) was injected into the flask for 40 minutes under Ar_2 atmosphere. Afterwards, the temperature was increased to 200°C, Cs-oleate (1.0 mL) swiftly injected, and 2 minutes later the reaction mixture was immediately cooled by cold-water bath.

Synthesis of $PrCl_3$ doped $CsPbCl_3$ QDs. $PbCl_2$ (0.4 mmol, 0.11g) ODE (10 mL) were loaded into a 100 mL three-necked flask and heated to 120°C, and then dried OA (1.0 mL) and OAm (1.0 mL) were added into the flask. After 10 minutes, TOP (1 ml) was injected into the flask for 40 min under Ar_2 atmosphere. Meanwhile, different amounts of $PrCl_3$ (0.5, 0.8, 1.2, 1.5 mmol) were dissolved in ODE (10 mL) at 160°C for 1 hour under Ar_2 and then reduced the temperature to 130°C. After that, injected the $PrCl_3$ solution into the $PbCl_2$ solution with a syringe and stirred for 300 minutes at 120°C under Ar_2 atmosphere. Afterwards, heated the mixture solution to 200°C, Cs-oleate (1.0 mL) swiftly injected, and 2 minutes later the reaction mixture was immediately cooled by cold-water bath.

Purification. All the precipitates were collected from the crude solution by centrifuging at 8000 rpm for 10 minutes to discard the supernatant containing unreacted precursor and byproducts. After that, 10 mL of toluene was added into the precipitates to wash them by 10000 rpm for 10 minutes. And then the precipitates were re-dispersed in 10 ml toluene for washing once again at 10000 rpm for 10 minutes. At last, collected the supernatant.

Fabrication of ultraflexible planar photodetectors. After depositing Au directly on flexible adhesive tape-paper by magnetron sputtering, we cut out a gap (30 μm) between the two gold electrodes by cold laser marking machine. It is worth noting that the power of the laser must be accurately controlled so as not to destroy the substrate. And then, the pristine and optimized $CsPbCl_3$ solution was dripped into the gap by a miniature syringe. At last, the devices were dried under vacuum at 80 °C for 10 minutes.

Characterization. The crystal structure and phase composition were determined by the XPert Pro (Holland) X-ray diffract meter with Cu Ka1 radiation (λ=0.154 nm). The crystal structure and grain size were determined by TEM (FEI Tecnai G2 F20) with acceleration voltage of 200KV. The element compositions of the products were examined by ICP-OES (Agilent 720). The UV absorption spectrum were obtained by UV-2500 (shimadzu corporation). The photoluminescence and photoluminescence excitation were investigated at room temperature using FLS980 (Edinburgh Instruments) spectrometer with a 450 W Xenon lamp. Decay times were obtained with a Xenon flash lamp as a light source at room temperature (FLS 980). The absolute PLQYs of the QDs colloids were measured on Edinburgh-FLS 980 spectrometer by a integrating sphere (The standard solvent is toluene).

Detailed calculation of the average lifetime, radiative and nonradiative decay rates.

The radiative and nonradiative decay rate were calculated by PLQYs and the $\boldsymbol{\tau}_{\mathbf{ave}}$. As we know, PLQY is defined as the number of photons emitted compared to the number of photons absorbed. Both the radiative recombination and the nonradiative recombination will depopulate the excited state. Therefore, the PLQY can also be defined as the ratio of the radiation recombination to the total recombination, which could be expressed as follows: [1]

$$PLQY = \frac{\Gamma_{rad}}{\Gamma_{rad} + \Gamma_{non-rad}}$$

(1)

in which Γ_{rad} and $\Gamma_{non-rad}$ are the radiative recombination rate and the nonradiative recombination rate, respectively.

The lifetime of the excited state is the average time that the photon spends in the excited state before returning to the ground state. The average lifetime is the inverse of the total recombination rate, given by:

$$\tau_{ave} = \frac{1}{\Gamma_{rad} + \Gamma_{non-rad}} \tag{2}$$

Where τ_{ave} could be calculated by the time-resolved PL decay information fitting. Therefore, we can calculate radiative and nonradiative recombination rates by the following equation:

$$\Gamma_{rad} = \frac{PLQY}{\tau_{ave}} \tag{3}$$

$$\Gamma_{non-rad} = \frac{1}{\tau_{ave}} - \Gamma_{rad} = \frac{1 - PLQY}{\tau_{ave}} \tag{4}$$

Urbach energies (E_U) calculation.

The E_U was calculated by plotting the absorption coefficient as a function of photon energy, which can be extracted by fitting the exponential part of the Urbach tail and be derived from the following equation:[2]

$$\alpha(E) = \alpha_0 exp[\sigma(T)\frac{E - E_0}{K_BT}] \tag{5}$$

where K_B is the Boltzmann constant, T is the absolute temperature and E_U is defined as：

$$E_U = \frac{K_B T}{\sigma(T)} \tag{6}$$

Table S1. ICP-OES element proportion analysis.

Sample	**$PrCl_3$:$PbCl_2$**	**Molar ratio (Pr:Pb)**
Pr-7%	1.25:1	0.07:1
Pr-16%	2:1	0.16:1
Pr-20%	3:1	0.20:1
Pr-23%	3.75:1	0.23:1

Table S2. The emission peak and PLQY of $CsPbBr_xCl_{3-x}$ in previous reports.

Composition	**Emission peak (nm)**	**QY (%)**	**Ref.**
$CsPbBrCl_2$	435	22	[3]
$CsPbBrCl_2$	430	65	[4]
$CsPbBrCl_2$	430	37	[5]
$CsPbBrCl_2$	444	36	[6]
$CsPbBr_{1.5}Cl_{1.5}$	455	37	[7]
$CsPbBr_{1.5}Cl_{1.5}$	464	61	[6]
$CsPbBr_{1.5}Cl_{1.5}$	457	15	[5]
$CsPbBr_{1.5}Cl_{1.5}$	460	60	[4]
$CsPbBr_2Cl$	481	61	[6]
$CsPbBr_2Cl$	480	40	[4]

$CsPb_2Cl_xBr_{5-x}$	450	49	[8]
$CsPbBr_{2.52}Cl_{0.48}$	485	30	[7]
$CsPbBr_{2.34}Cl_{0.66}$	500	9	[7]

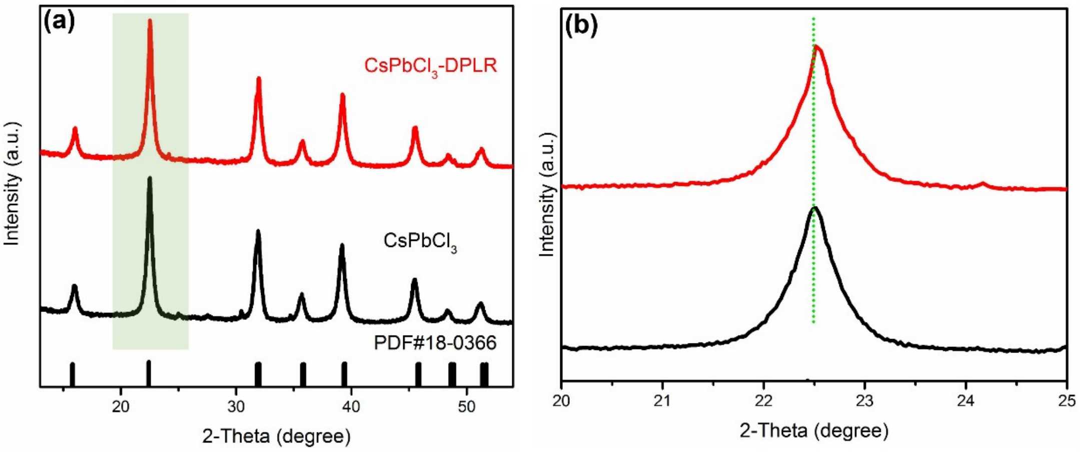

Fig. S1 XRD patterns of pristine and DPLR optimized $CsPbCl_3$.

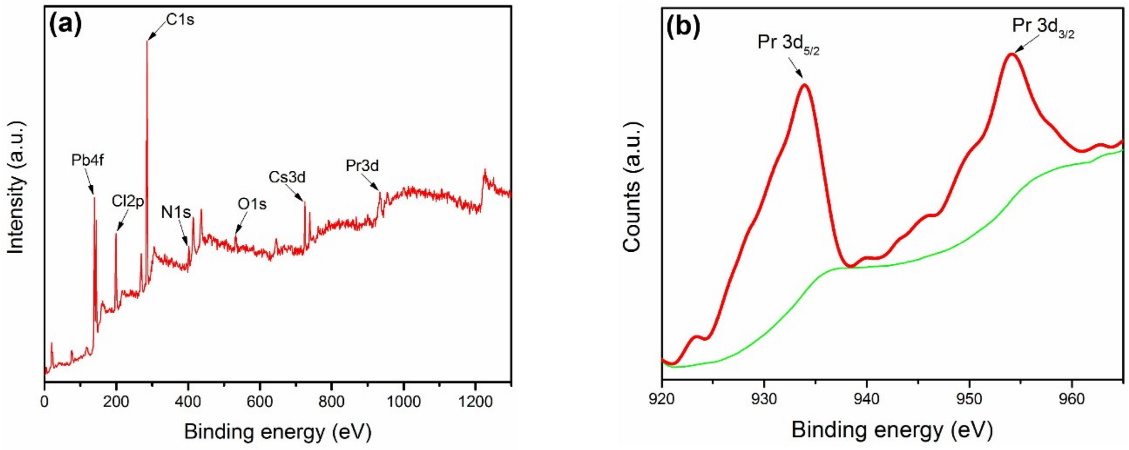

Fig. S2 XPS survey images of DPLR optimized $CsPbCl_3$. (a) Full spectrum. (b) Spectrum of Pr $3d_{5/2}$ and Pr $3d_{3/2}$.

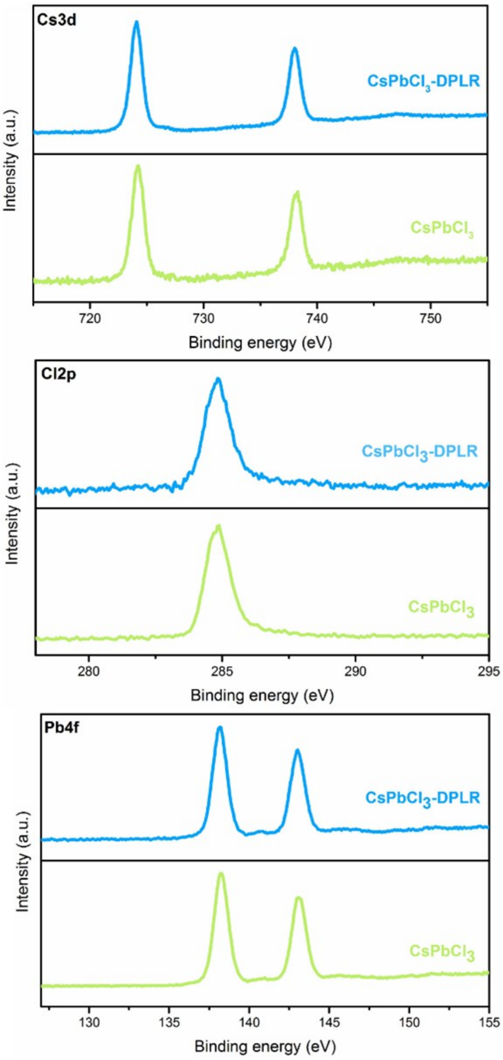

Fig. S3 The XPS results of Cs3d, Cl2p and Pb4f before and after DPLR optimization.

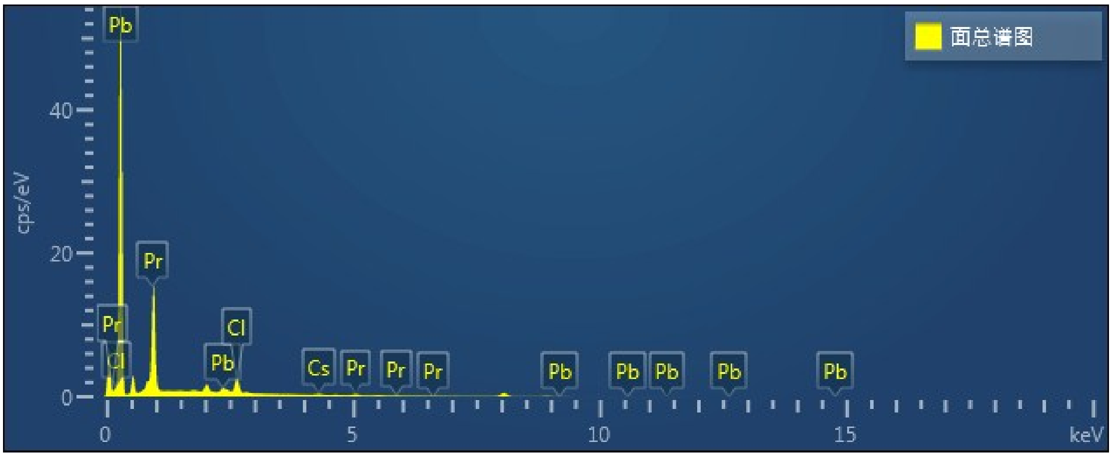

Fig. S4 EDS mapping full spectrum of DPLR optimized $CsPbCl_3$.

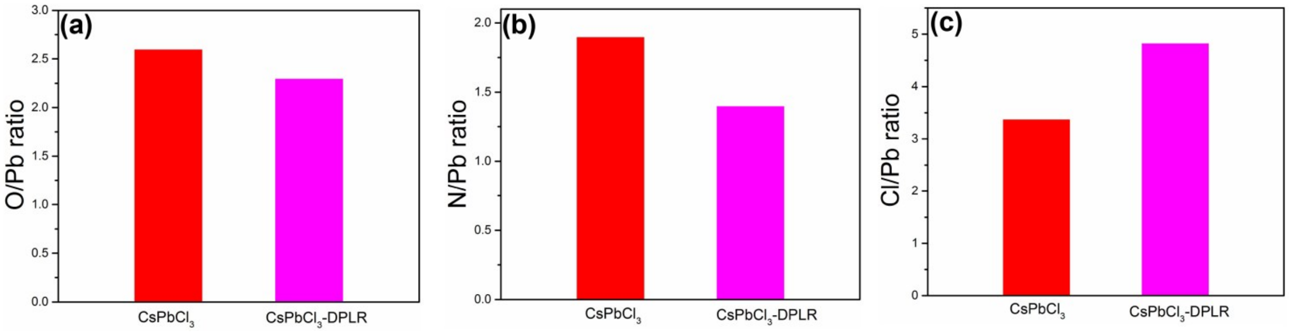

Fig. S5 The XPS quantitative analysis of DPLR optimized CsPbCl3, elements ratio of (a) O to Pb. (b) N to Pb. (c) Cl to Pb.

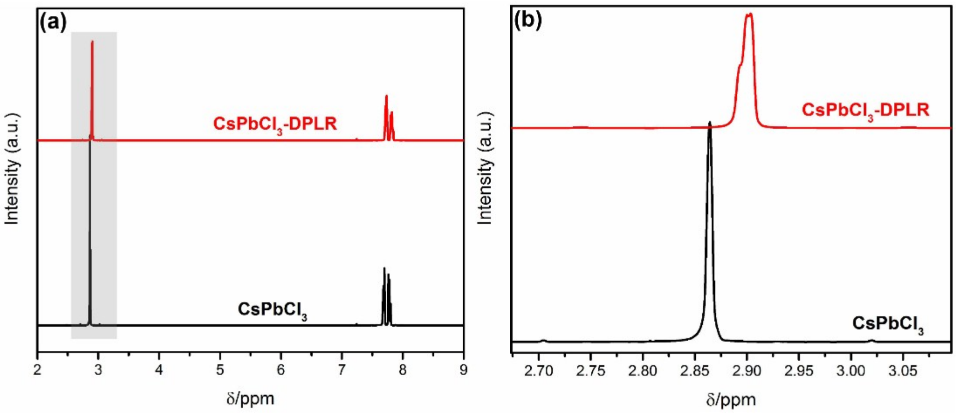

Fig. S6 The ^1H NMR spectrum of $CsPbCl_3$ QDs before and after DPLR optimization.

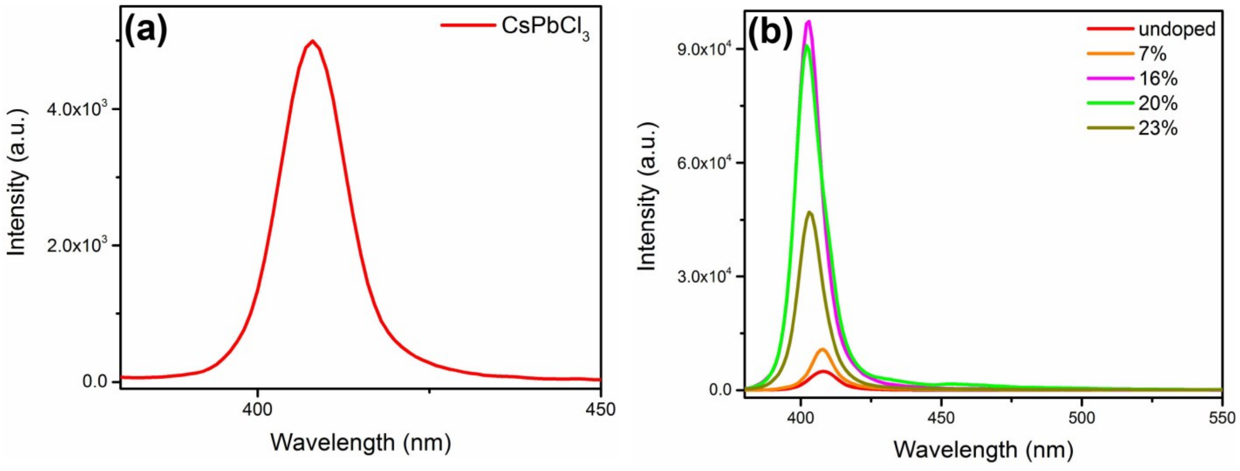

Fig. S7 The PL spectra of (a) pristine $CsPbCl_3$, (b) the DPLR optimized $CsPbCl_3$ with different $PrCl_3$ doping content, which reflects different degrees of DPLR optimization.

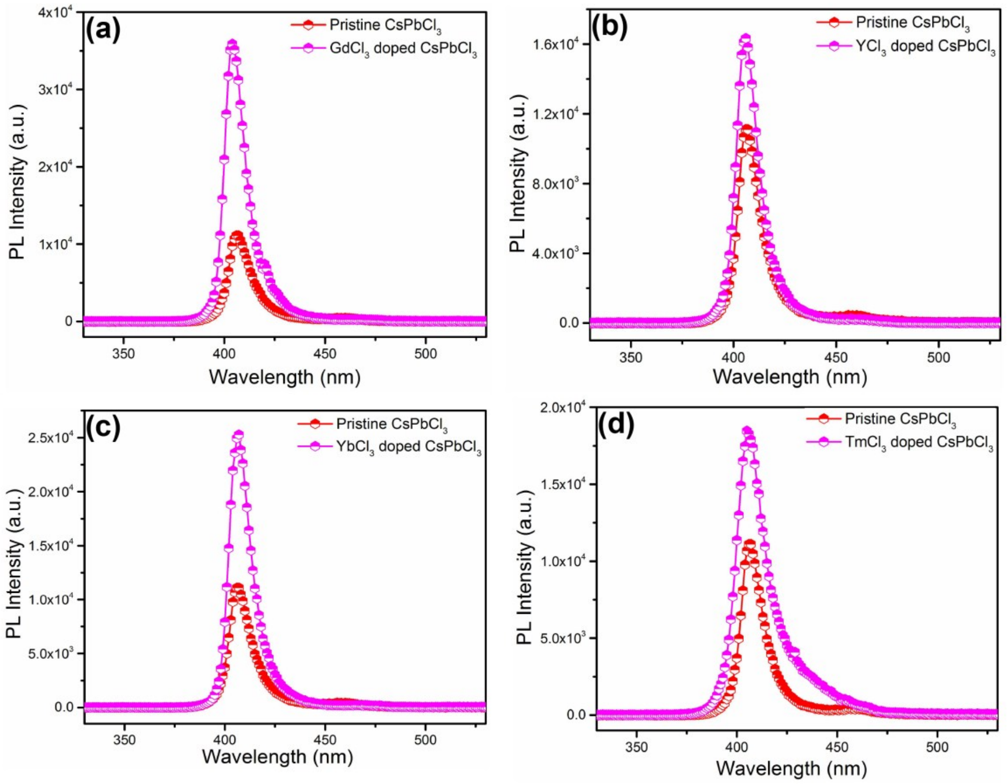

Fig. S8 The PL spectrum of pristine and different trivalent metal optimized $CsPbCl_3$. (a) $GdCl_3$. (b) YCl_3 (c) $YbCl_3$ (d) $TmCl_3$.

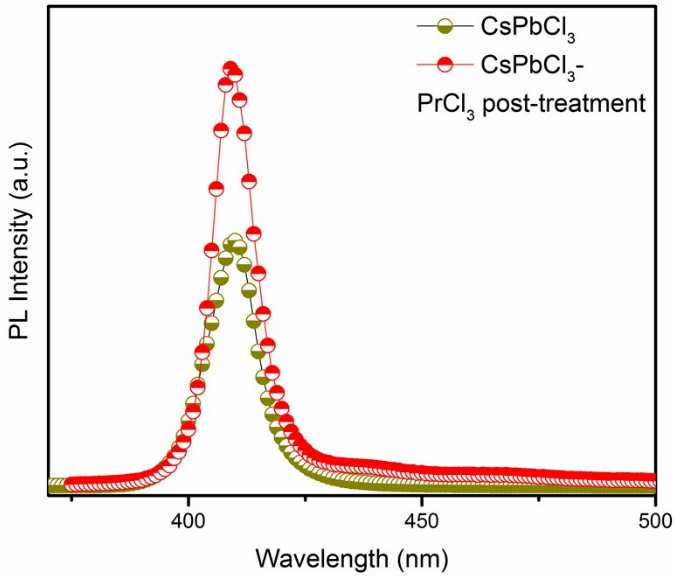

Fig. S9 The PL spectrum of pristine and PrCl3 post-treatment $CsPbCl_3$.

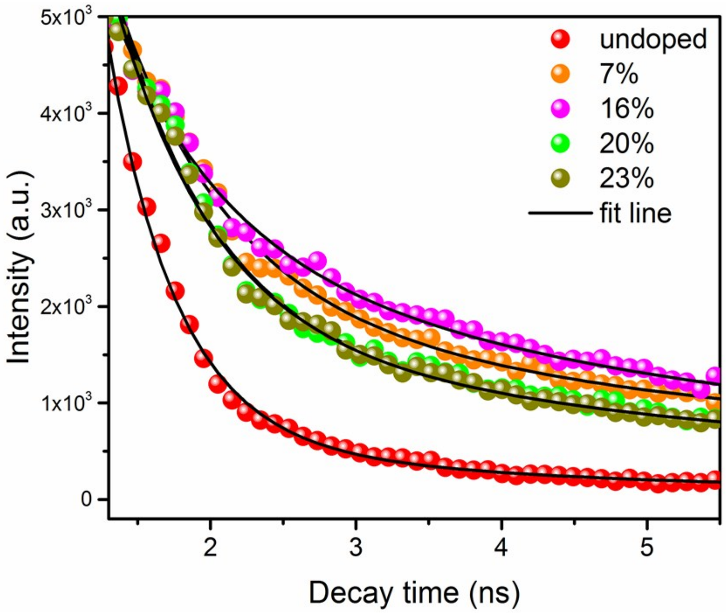

Fig. S10 The PL decay of DPLR optimized $CsPbCl_3$ with different $PrCl_3$ doping content, which reflects different degrees of DPLR optimization.

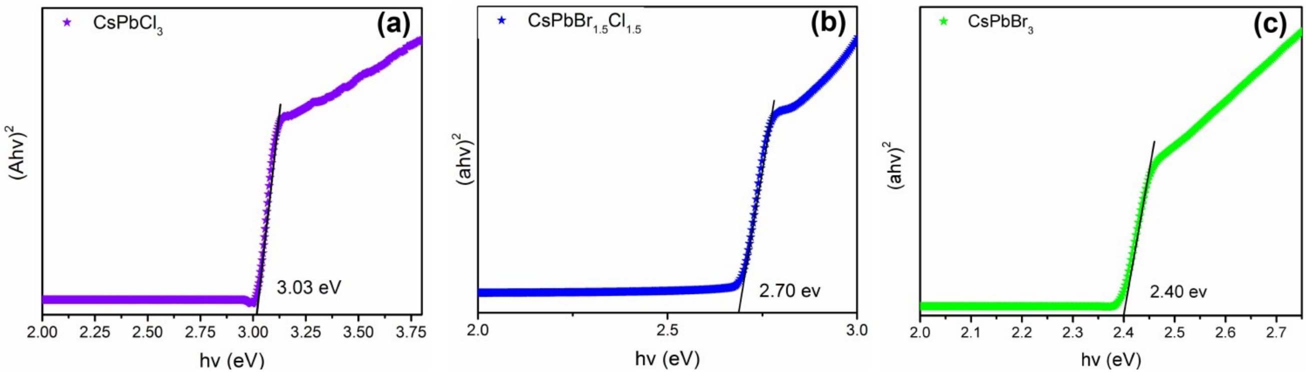

Fig. S11 The Tauc Plot of (a) $CsPbCl_3$. (b) $CsPbBr_{1.5}Cl_{1.5}$. (c) $CsPbBr_3$.

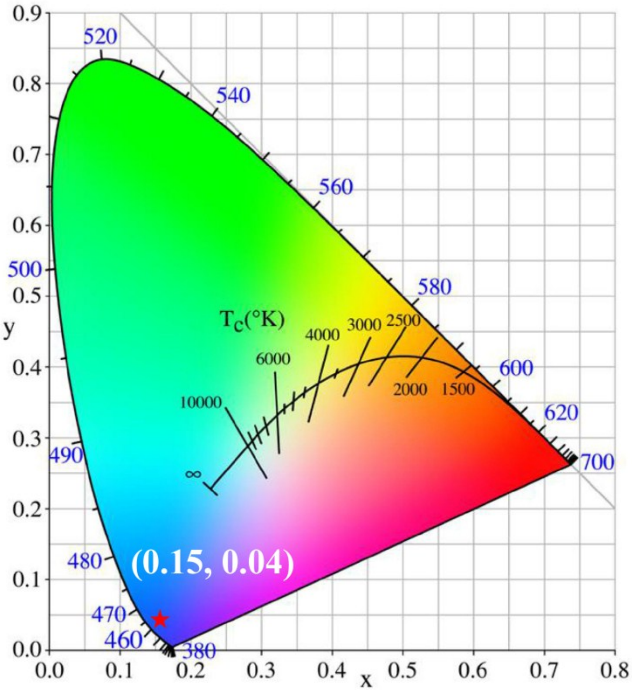

Fig. S12 The Commission Internationale de l’ Eclairage (CIE) color coordinate of as-synthesized $CsPbBr_{1.5}Cl_{1.5}$.

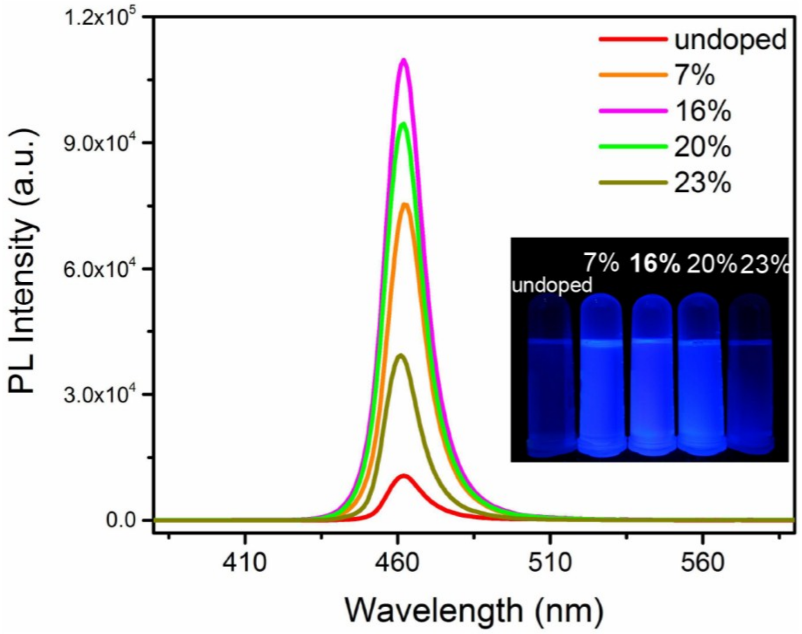

Fig. S13 The PL spectra of DPLR optimized $CsPbBr_{1.5}Cl_{1.5}$ with different $PrCl_3$ doping content, which reflects different degrees of DPLR optimization.

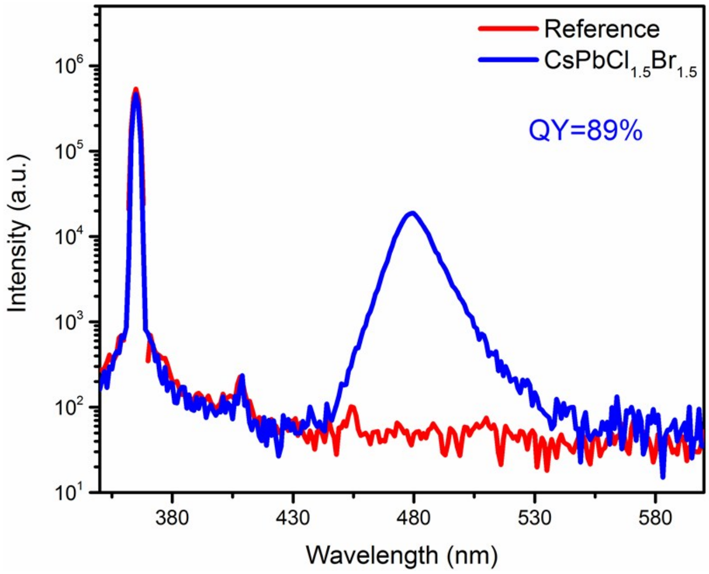

Fig. S14 The absolute PLQY measurements of $CsPbBr_{1.5}Cl_{1.5}$ QDs.

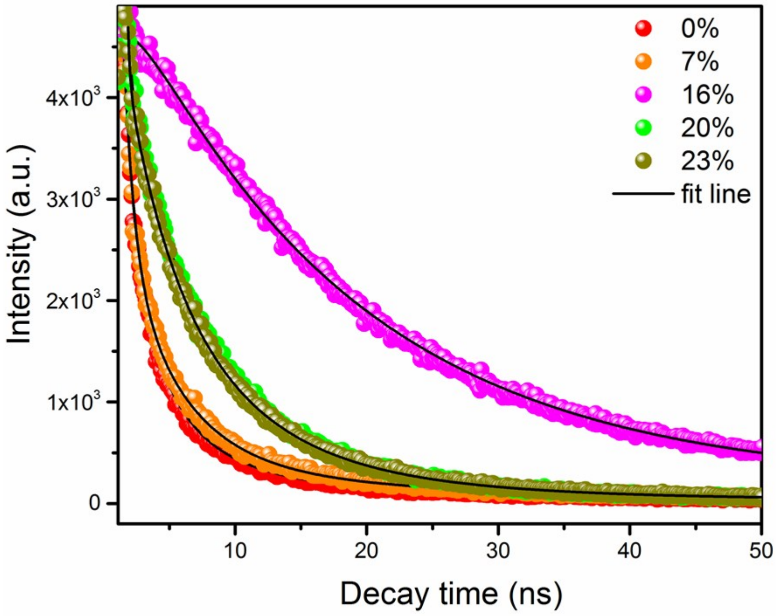

Fig. S15 The PL decay of DPLR optimized $CsPbBr_xCl_{3-x}$ with different $PrCl_3$ doping content, which reflects different degrees of DPLR optimization.

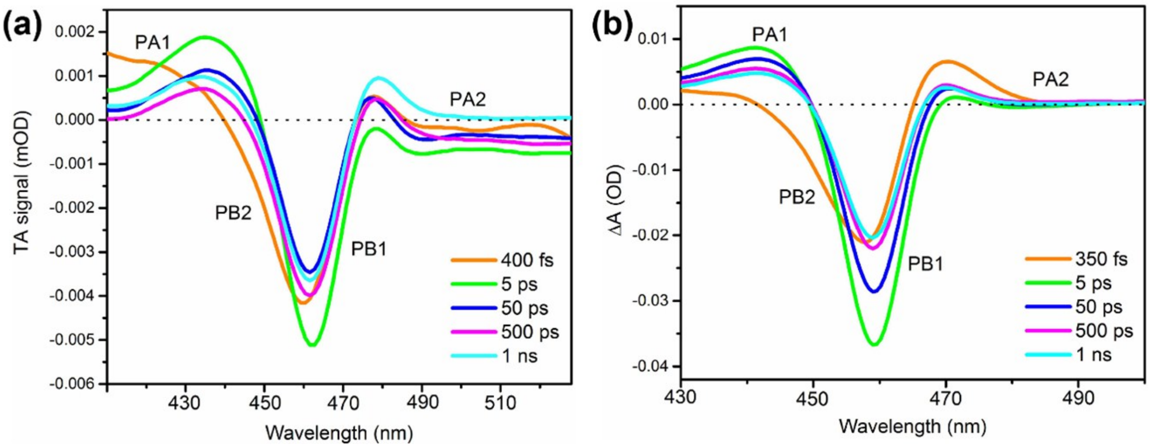

Fig. S16 The TA spectra of (a) pristine and (b) DPLR optimized $CsPbBr_{1.5}Cl_{1.5}$ with different probe delay times.

REFERENCES:

1. Z. J. Yong, S. Q. Guo, J. P. Ma, J. Y. Zhang, Z. Y. Li, Y. M. Chen, B. B. Zhang, Y. Zhou, J. Shu, J. L. Gu, L. R. Zheng, O. M. Bakr and H. T. Sun, *J. Am. Chem. Soc.*, 2018, **140**, 9942-9951.
2. Y. Wu, C. Wei, X. Li, Y. Li, S. Qiu, W. Shen, B. Cai, Z. Sun, D. Yang, Z. Deng and H. Zeng, *Acs Energy Lett.*, 2018, **3**, 2030-2037.
3. Y. S. Park, S. J.Guo, N. S. Makarov, V. I. Klimov, *ACS Nano,* 2015**,** ***9***, 10386-10393.
4. Y. Su, X. J. Chen, W. Y. Ji, Q. H. Zeng, Z. Y. Ren, Z. S. Su, L. Liu, *ACS Appl. Mater. Interfaces,* 2017, ***9***, 33020-33028.
5. P. C.Wang, B. H. Dong, Z. J. Cui, R. J. Gao, G. Su, W. Wang, L. X. Cao, *Rsc Adv.,* 2018, ***8***, 1940-1947.
6. W. Zheng, P. Huang, Z. Gong, D. Tu, J. Xu, Q. Zou, R. Li, W. You, J. G. Bunzli, X. Chen, *Nat. Commun.,* 2018, ***9***, 3462.
7. N. Soetan, A. Puretzky, K. Reid, A. Boulesbaa, H. F. Zarick, A. Hunt, O. Rose, S. Rosenthal, D. B. Geohegan, R. Bardhan, *ACS Photonics,* 2018, ***5***, 3575-3583.
8. H. Wu, S. H. Xu, H. B. Shao, L. Li, Y. P. Cui, C. L. Wang, *Nanoscale,* 2017, ***9***, 16858-16863.