

Supporting Information

Lanthanide-doping Enables Kinetic Control Growth of Deep-blue Two-monolayered CsPbBr₃ Perovskite Nanoplatelets

Qinxuan Cao,^{a‡} Asif Ilyas,^{a‡} Shuai Zhang,^b Zhijie Ju,^a Fangling Sun,^c Tianyu Liu,^c Yang(Michael) Yang,^c Yunhao Lu,^{*d} Xinfeng Liu,^{*b} and Renren Deng^{*a}

Supplementary Methods

Synthesis of undoped 2 ML CsPbBr₃ nanoplatelets (2- and 3-ML fragments): The synthetic method for the preparation of undoped 2- and 3-ML CsPbBr₃ fragments is identical to the method for the synthesis of 2 ML CsPbBr₃:Ln³⁺ nanoplatelets, except that the Ln precursor solution was replaced by a mixed ligand precursor (0.6 mL DMF, 0.1 mL OA, and 0.6 mL OAm) containing no Ln(NO₃)₃.

Synthesis of undoped 3 ML CsPbBr₃ nanoplatelets: In a typical experiment, 110 mg of PbBr₂ (0.3 mmol) was dissolved into DMF (1.50 mL). After complete dissolving of PbBr₂, OA (0.15 mL) and OAm (1.5 mL) were added. Subsequently, 0.40 mL of the CsBr stock solution was added to form admixed reaction precursor. Then, 0.70 mL of the reaction precursor was quickly added to 10 mL of toluene under continuous stirring at room temperature. After the reaction for 30 s, 10 mL of acetonitrile was added to terminate the reaction. The resulted nanocrystals were separated by centrifugation at 4000 rpm for 6 min and redispersed in 5 mL toluene for further experiments.

Synthesis of CsPb(Br_{0.25}Cl_{0.75})₃ mixed halide perovskite nanocrystals: CsPb(Br_{0.25}Cl_{0.75})₃ nanocrystals were synthesized by a hot injection method reported by Kovalenko *et al.*^[1] In a typical experiment, Cs₂CO₃ (0.41 g; 1.25 mmol) was first added into a 50 mL 3-neck flask containing ODE (20 mL) and OA (1.25 mL). The mixture was stirred at 120 °C under vacuum for 30 min to remove any residue water in the reactants, followed by heated at 150 °C under nitrogen atmosphere for another 30 min. The resulting Cs-oleate solution was used as the cesium precursor for the synthesis. For the preparation of CsPb(Br_{0.25}Cl_{0.75})₃, PbBr₂ (0.14 mmol) and PbCl₂ (0.42 mmol) were added into a 50 mL 3-neck flask containing a mixing solution of ODE (15 mL), OA (1.5 mL) and OAm (1.5 mL), followed by vacuum treatment at 120 °C for 1 h. Subsequently, the temperature was increased to 150 °C under N₂ flow and 1.20 mL of the as-prepared cesium precursor was quickly injected. After 5 s of the reaction, the mixture was

cooled in the ice-water bath. The as-obtained nanocrystals were precipitated by adding acetone (1:1, v./v.) and collected by centrifugation at 7000 rpm for 8 minutes. The nanocrystals were redispersed in 30 mL of toluene to result a clean transparent colloidal suspension.

Preparation of 2 ML CsPbBr₃:Lu³⁺ ink: To prepare stable nanoplatelet ink for encrypted information storage, the toluene suspension of the as-prepared 2 ML CsPbBr₃:Lu³⁺ nanoplatelets was mixed with a commercially available PMMA ethyl lactate solution (Microchem, 950K A4) with a volume ratio of 1:1. The admixed solution was used as perovskite ink for further experiments.

Calculations for reaction energy barriers: The theoretical model was built based on the assumption that the doping-coverage of Lu³⁺ kept the same for 2 ML, 3 ML and 2.5 ML CsPbBr₃ structures. The kinetic model well explains the dynamic stability as well as the preserved electronic properties with growth of the crystal in the Z-direction (001). For the execution of theoretical calculations, we constructed a large supercell of the cubic CsPbBr₃ with a size $5 \times 5 \times 1$, where one Pb site is substituted by an Lu atom in accordance with the experimentally measured doping concentration. The supercell of 2 ML and 3 ML consist of fifty and seventy-five octahedral respectively. We considered an intermediate state (2.5 ML) to find the energy-barrier which hinder the transformation of 2 ML into 3 ML. The 2.5 ML state is 2ML of CsPbBr₃ crystal with an extra [PbBr₆]⁴⁺ octahedron on its surface. We also considered the experimentally predicted in-plane lattice parameters for calculations regarding 2 ML and 3 ML perovskites. The first principles DFT calculations were carried out in the Vienna Ab initio Simulation Package (VASP), using the projector augmented wave method. The exchange-correlation function based on Perdew-Burke-Ernzerhof (PBE) was included regarding the on-site coulomb interaction for the localized f electrons of lanthanide metals. The Hubbard U value was considered to be 5 eV for the Lu atom. The cut-off energy for the basis function was set as 300 eV for dealing the valance electrons. A $3 \times 3 \times 1$ Monkhorst-Pack k-point mesh was used for the Brillouin zone sampling. A $5 \times 5 \times 1$ cells were relaxed until the total energy of the structures and the force on each atom converges to the 10^{-4} eV and 0.01 eV/Å, respectively.

We calculated the ground state (GS) state energy of the 2 ML, 3 ML CsPbBr₃ with and without doping as mentioned in Figure 3a in the main text. The results depict that both 2 ML and 3 ML with Lu doping are more stable than their counterpart in pure form. However, the doping sedates the transformation of 2 ML into 3 ML. To investigate the reason that why 2 ML becomes stable

with doping, we calculate the GS energy of 2.5 ML states both for doped and un-doped cases. Interestingly, we found that the energy barrier gets higher with introducing the dopant atom as shown in the Figure 3a. As a result, 2 ML becomes kinetically more stable with doping since the higher barrier slows down the transformation process.

Density of states (DOS) calculation: We compared the electronic properties of the 2 ML CsPbBr₃ nanocrystal before and after doping with Lu³⁺ by the PBE+U method. Although, the PBE+U method is not suitable to compute the actual bandgap, it can be meaningful for comparison of the electronic properties of the few-monolayer CsPbBr₃ with its thickness. For this purpose, we calculate the density of states (DOS) as shown in the Figure 4b. The DFT results demonstrate that the doping does not influence the band gaps significantly. It is due to the fact that the Lu atom creates its states in the conduction band as shown with the red lines in Figure 4b. On the basis of our DFT results, it can be concluded that the low doping of rare earth metals not only stabilizes 2 ML CsPbBr₃ nanocrystal but also preserve its electronic properties. These results are well consistent with our experimental observations.

Kinetic modelling of the formation reaction of CsPbBr₃ nanoplatelets: We developed a kinetic model to describe the formation reaction process of nanoplatelets with various thickness. We assumed that only nanoplatelets thicker than 2 ML can be stable under the given reaction conditions. $[N_m]$ ($m = 0, 2, 2.5, 3$) was defined to represent the concentration of monomers ($m=0$) and nanoplatelets with m ML thickness. Note that $[N_{2.5}]$ refers to the concentration of a 2, 3-ML hybrid intermediate state (2.5 ML) during the transformation from 2 ML to 3 ML structures. Considering a layer-by-layer growing process of the reaction, the evolution of different $[N_m]$ should satisfy following equations,

$$\frac{d[N_0]}{dt} = k_2'[N_2] + k_{2.5}'[N_{2.5}] + k_3'[N_3] - k_2[N_0] - k_{2.5}[N_0][N_2] - k_3[N_0][N_{2.5}] \quad (S1)$$

$$\frac{d[N_2]}{dt} = k_2[N_0] + k_{2.5}'[N_{2.5}] - k'[N_2] - k_{2.5}[N_0][N_2] \quad (S2)$$

$$\frac{d[N_{2.5}]}{dt} = k_{2.5}[N_0][N_2] + k_3'[N_3] - k_{2.5}'[N_{2.5}] - k_3[N_0][N_{2.5}] \quad (S3)$$

$$\frac{d[N_3]}{dt} = k_3[N_0][N_{2.5}] - k_3'[N_3] \quad (S4)$$

where k_m and k'_m are the rate constants for attachment and detachment, respectively. The k_m can be described according to the Arrhenius equation,

$$k_m = c_0 e^{\left(-\frac{\Delta E_m^{barrier}}{RT}\right)} \quad (S5)$$

in which c_0 is a constant depending on the features of the reactions, $\Delta E_m^{barrier}$ is the energy barrier between the reaction states, R is the molar gas constant of 8.314 (J·mole⁻¹·K⁻¹), and T is the temperature (K).

For simplicity, we assumed that c_0 is the same for reactions with and without dopants. As the lanthanide dopants increase the energy barrier $\Delta E_{2.5}^{barrier}$ from 0.03 to 0.17 eV during the formation of 2.5 ML intermediates from 2 ML nanoplatelets. It is possible to validate the change of reaction rates in forming the 2.5 ML intermediates by

$$\frac{k_{2.5,undoped}}{k_{2.5,doped}} = e^{\left(-\frac{\Delta E_{2.5,undoped}^{barrier} + \Delta E_{2.5,doped}^{barrier}}{RT}\right)} \quad (S6)$$

The temporal dependence of the population densities indicating the kinetic evolution of $[N_m]$ can be calculated using MATLAB.

Excited state decay time analysis

The transient absorption decay time are fitted by using Gaussian response function convoluted with a triple exponential decay function of

$$y = y_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}} \quad (S7)$$

The average lifetime (the finite portion) is defined as:

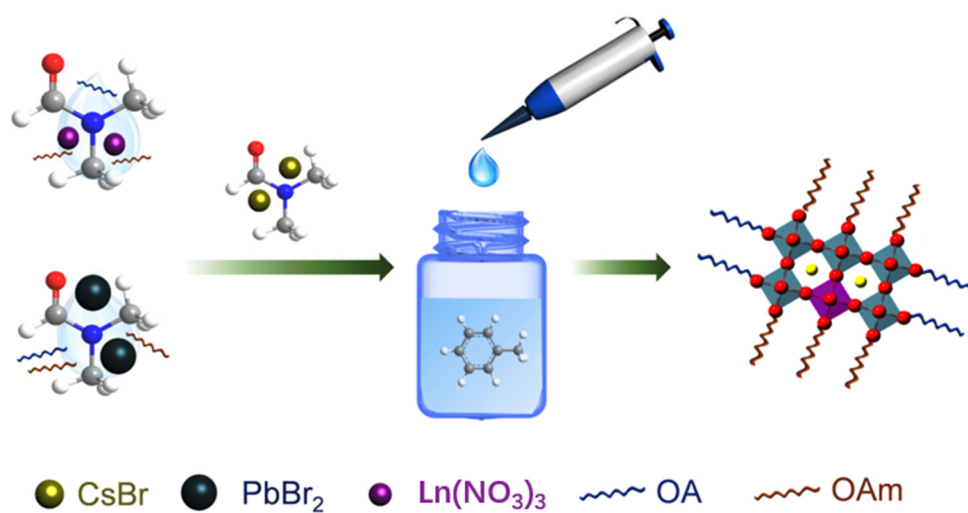
$$\tau_A = \frac{A_1 * \tau_1^2 + A_2 * \tau_2^2 + A_3 * \tau_3^2}{A_1 * \tau_1 + A_2 * \tau_2 + A_3 * \tau_3} \quad (S8)$$

The weighting parameters of $A_{1/2/3}\%$ are calculated as:

$$A_{1/2/3} \% = \frac{A_{1/2/3}}{A_1 + A_2 + A_3} * 100 \% \quad (S9)$$

The PL decay time are fitted with a double exponential decay function of

$$y = y_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} \quad (S10)$$



Scheme S1. Schematic illustration for synthesis of CsPbBr₃:Ln³⁺ (Ln = Lu, Gd, Nd) nanoplatelets.

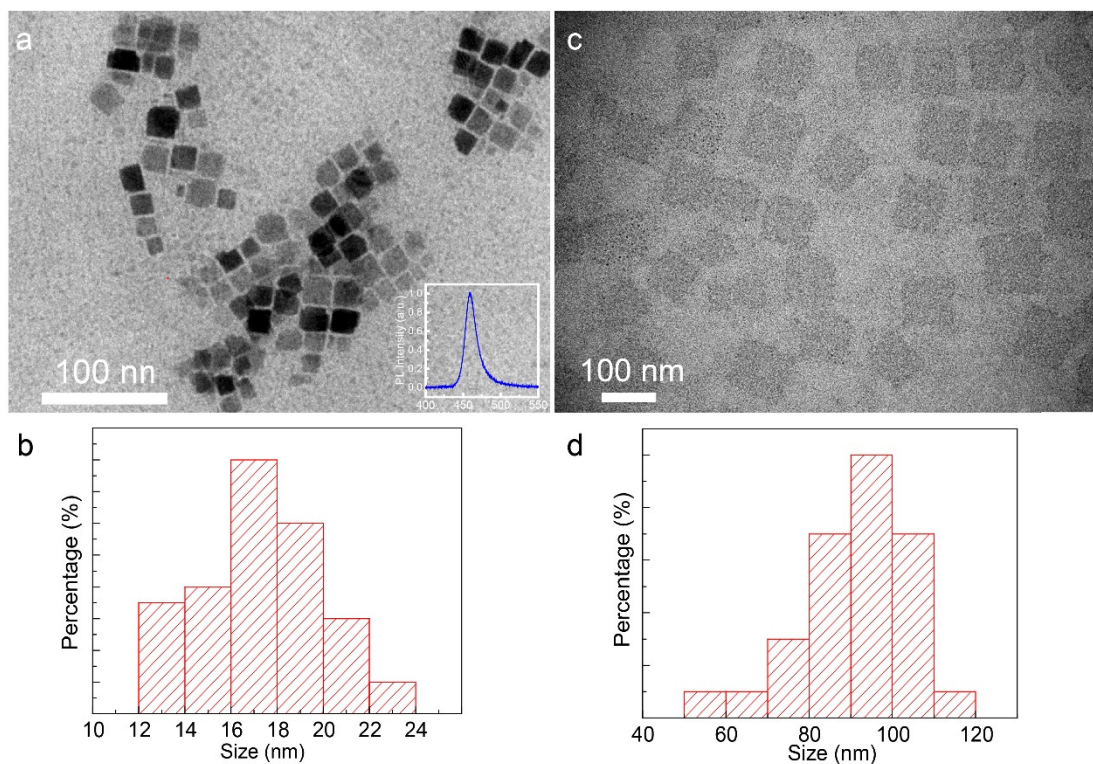


Figure S1. (a) TEM image and the PL spectrum (inserted) of 3 ML CsPbBr₃ nanoplatelets. (b) Corresponding size distribution of 3 ML CsPbBr₃ nanoplatelets shown in TEM image in a. The average size of the nanoplatelets is determined to be 17 ± 3 nm. (c) TEM image of representative 2 ML CsPbBr₃:Lu³⁺ (11.7 mol%) nanoplatelets (d) Corresponding size distribution of the 2 ML CsPbBr₃: Lu³⁺ shown in c. The average size of the nanoplatelets is determined to be 92 ± 13 nm.

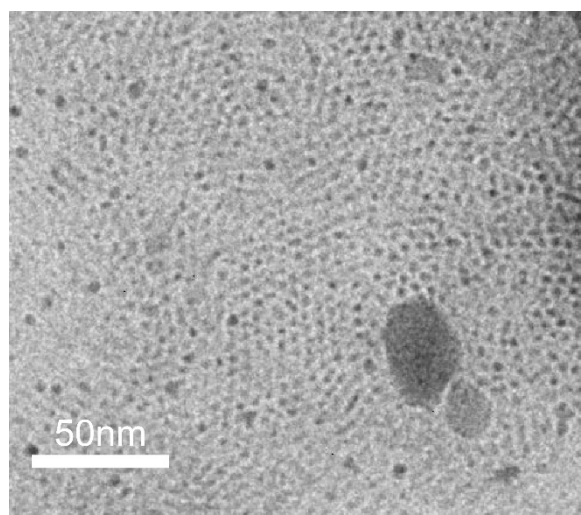


Figure S2. TEM image of 2- and 3-ML CsPbBr₃ fragments synthesized in the absence of Lu³⁺ dopants.

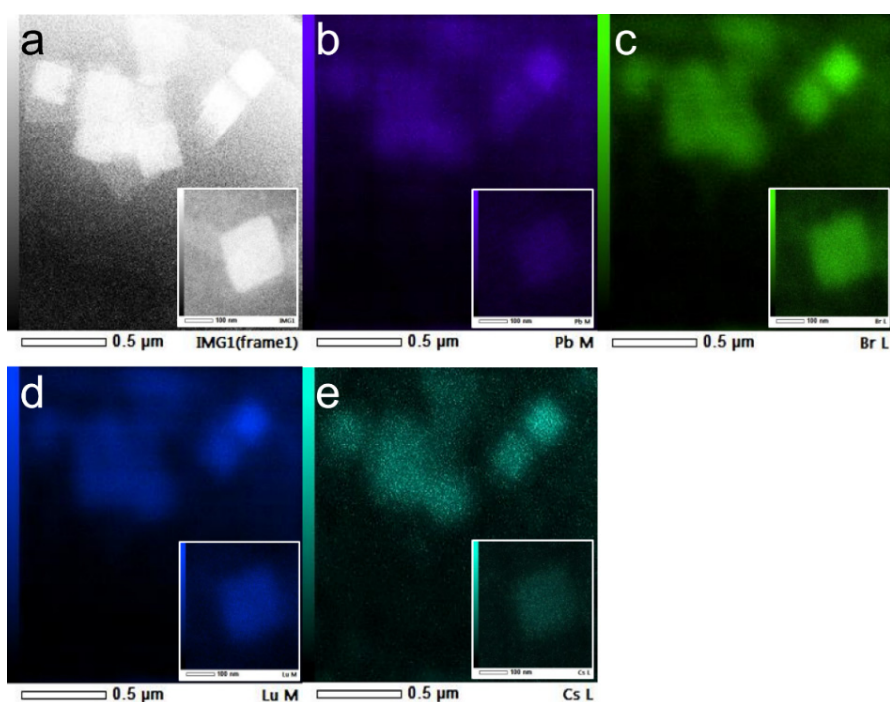


Figure S3. (a) STEM image and (b-e) corresponding EDS elemental mapping of the as-synthesized 2 ML CsPbBr₃:Lu³⁺ (11.7 mol%) nanoplalelets.

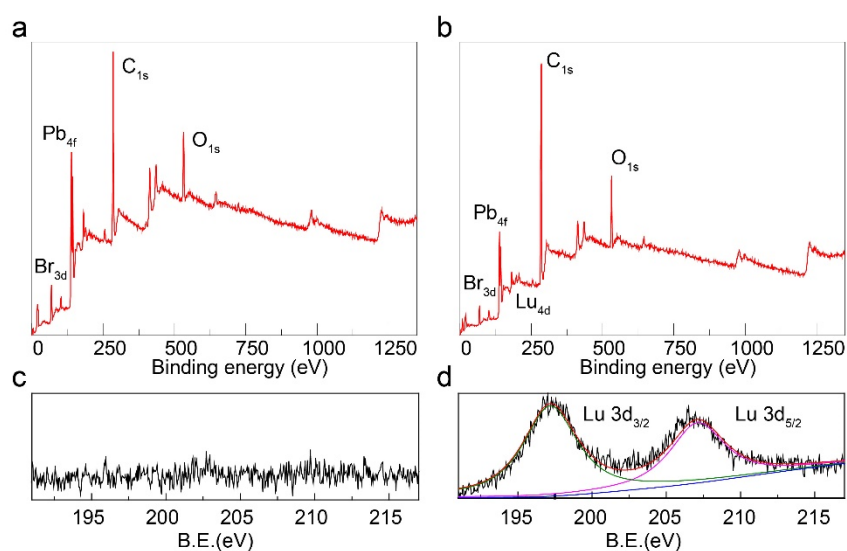


Figure S4. XPS spectra of (a) undoped CsPbBr₃ nanoplalelets and (b) CsPbBr₃:Lu³⁺ (11 mol%) nanoplalelets. High-resolution Lu_{3d} XPS spectra of (c) undoped CsPbBr₃ nanoplalelets and (d) CsPbBr₃:Lu³⁺ (11 mol%) nanoplalelets.

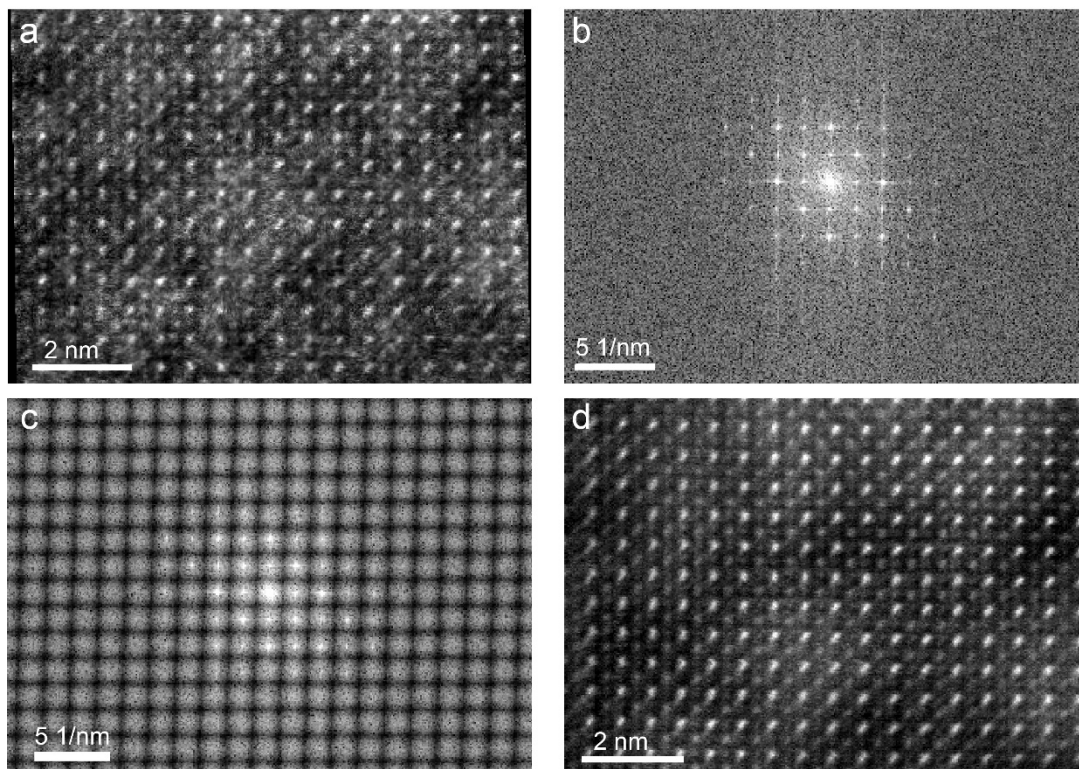


Figure S5. HAADF-STEM image processing of 2 ML CsPbBr₃:Lu³⁺ (11 mol%) nanoplatelets. (a) The original high-resolution HAADF-STEM image. (b) Fast Fourier transform diffractogram of **a**. (c) A mask array was applied on image in **b** to remove the background noises. (d) Inversed fast Fourier transform image of **c**.

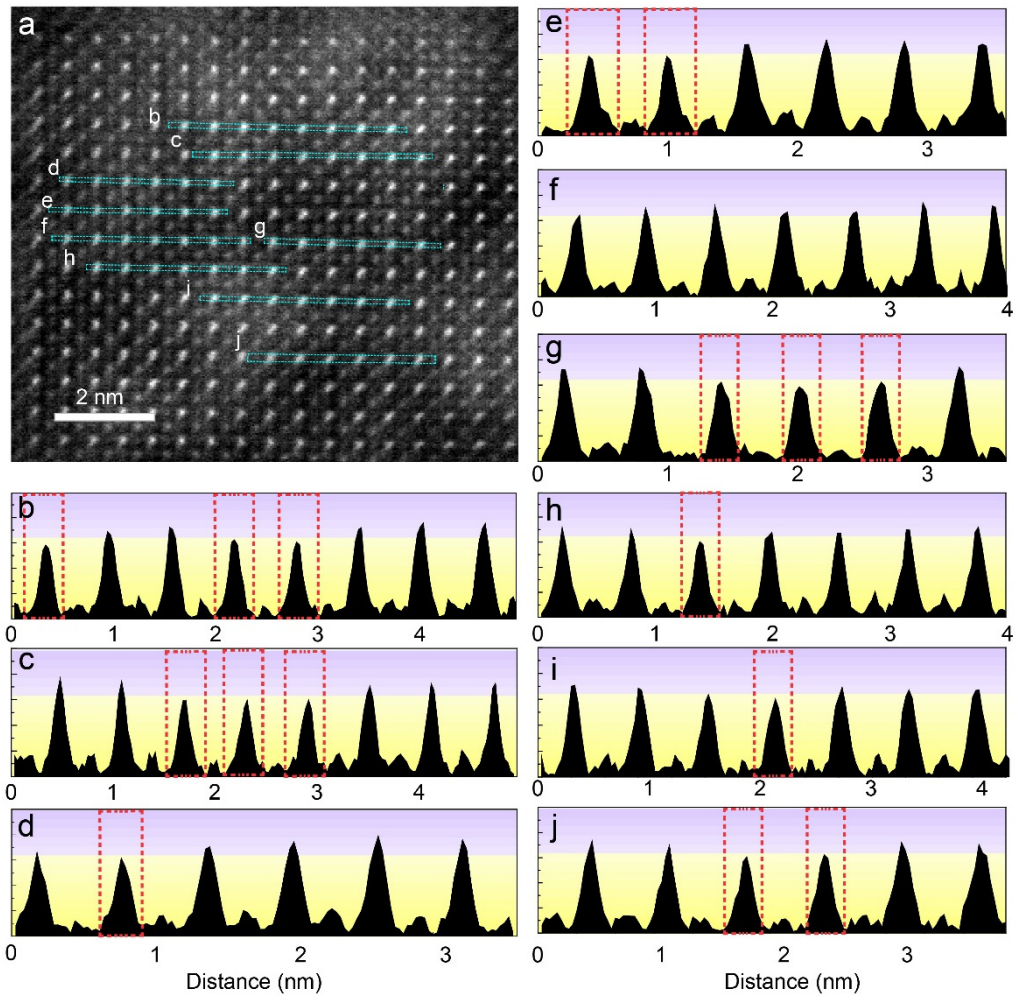


Figure S6. (a) Processed HAADF-STEM image taken in (001) incidence showing the projected atomic arrangement of the as-prepared 2 ML CsPbBr₃:Lu³⁺ nanoplatelets. (b-j) Corresponding intensity profiles of selected-area indicated in a. The intensity profiles indicate the signal intensity variation of atoms across the selected area. The possible sites for Lu³⁺ substitutions are circled by red dash lines.

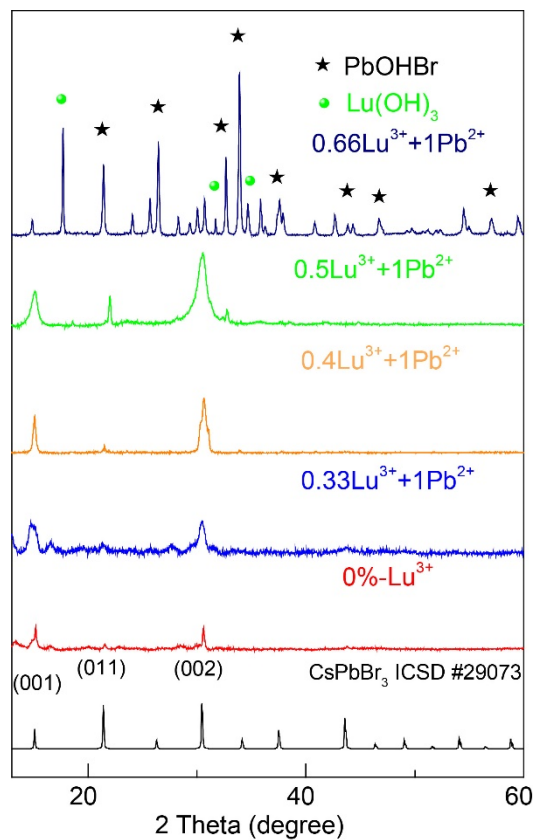


Figure S7. XRD patterns of the CsPbBr₃ nanocrystals obtained from reactions containing various Lu³⁺ and Pb²⁺ molar ratios.

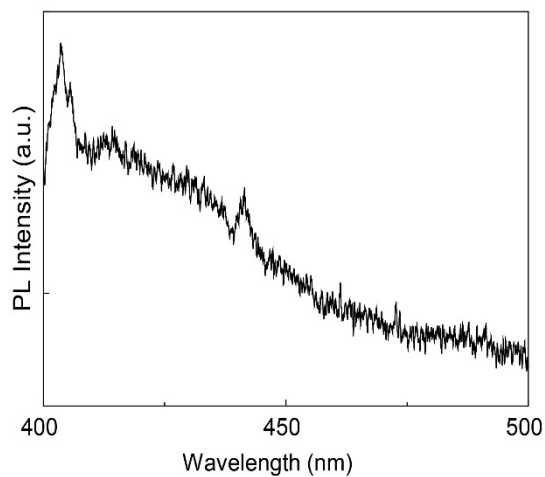


Figure S8. PL spectrum of the CsPbBr₃ product obtained under a Lu³⁺: Pb²⁺ molar ratio of 0.66: 1. It is clear that high content of Lu³⁺ hampers the formation of CsPbBr₃ nanocrystals resulting in a featureless emission. The PL spectrum was recorded under a laser excitation at 360 nm.

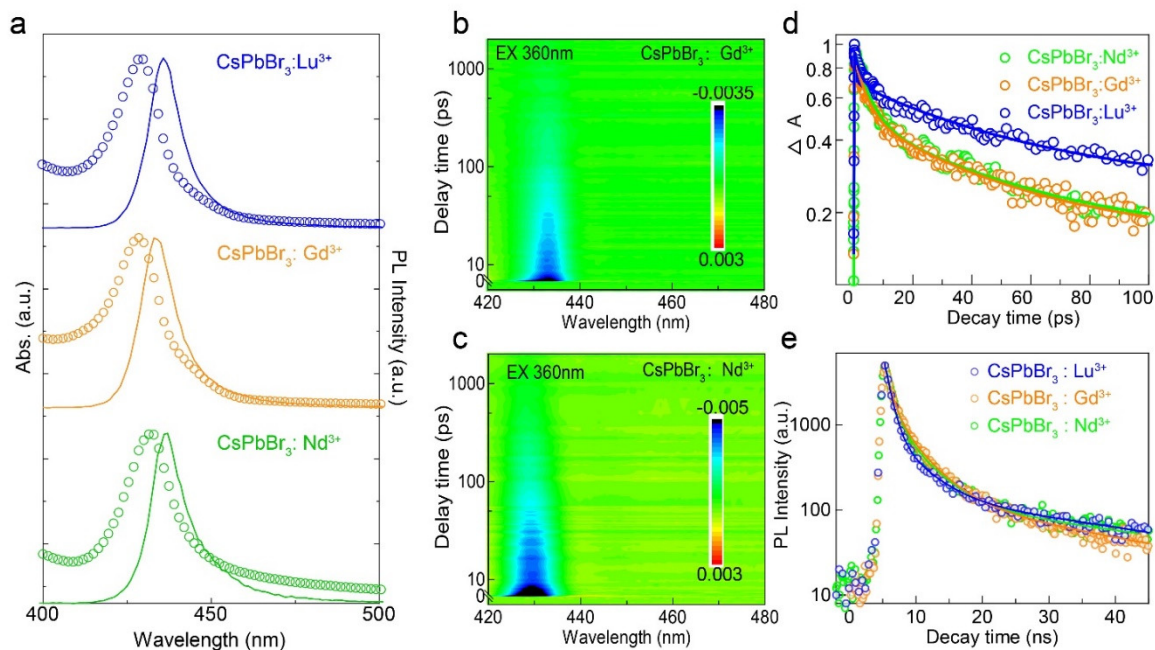


Figure S9. (a) Absorption and PL spectra of 2 ML CsPbBr₃:Ln³⁺ (Ln = Nd, Gd, Lu) nanoplatelets. (b) Transient absorption images of colloidal suspensions of 2 ML CsPbBr₃:Gd³⁺ and (c) 2 ML CsPbBr₃:Nd³⁺ nanoplatelets. (d) Transient absorption decay dynamics of 2 ML CsPbBr₃:Ln³⁺ (Ln = Nd, Gd, Lu) nanoplatelets at 431nm. (e) Photoluminescence decay curves of 2 ML CsPbBr₃:Ln³⁺ (Ln = Nd, Gd, Lu) nanoplatelets at 431nm. A 360-nm pump laser was used for the measurements.

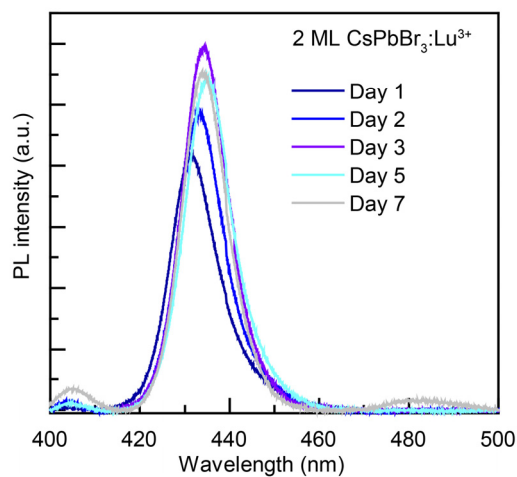


Figure S10 PL spectra evolution of colloidal suspension of 2 ML CsPbBr₃:Lu³⁺ nanoplatelets in pure toluene stored at ambient condition.

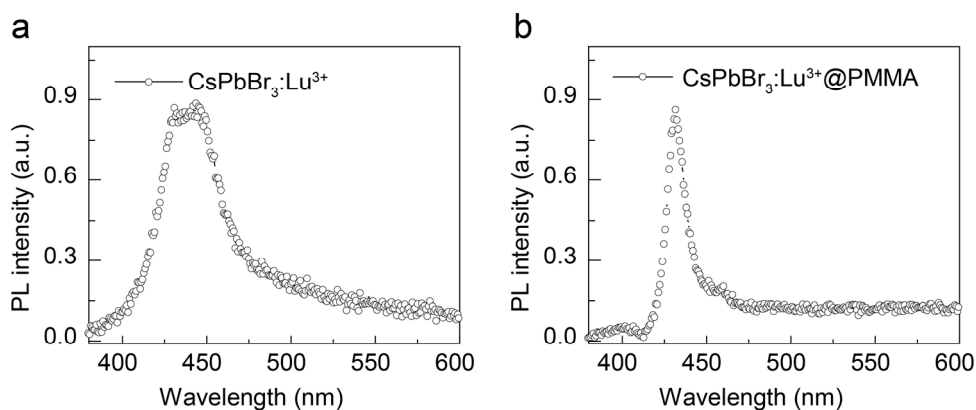


Figure S11. PL spectra of 2 ML CsPbBr₃:Lu³⁺ (11.7 mol%) nanoplalelets film made from (a) 2 ML CsPbBr₃:Lu³⁺ colloids without PMMA and (b) 2 ML CsPbBr₃:Lu³⁺ colloids with PMMA under excitation at 360 nm.

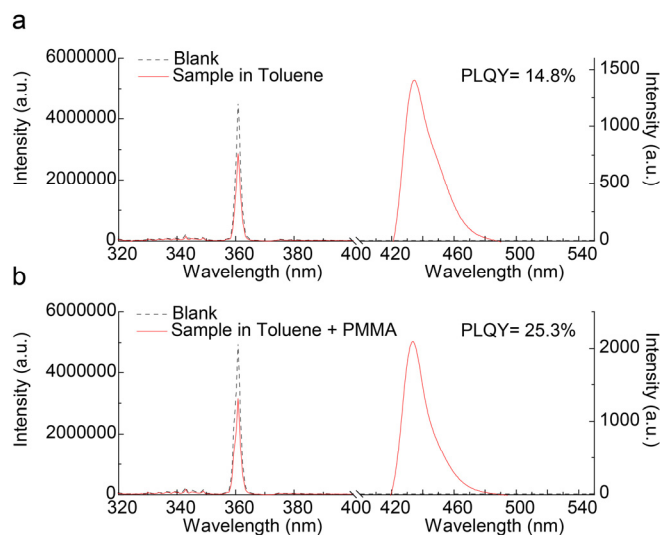


Figure S12 PLQY for (a) the 2 ML CsPbBr₃:Lu³⁺ nanoplalelets in pure toluene and (b) the 2 ML CsPbBr₃:Lu³⁺ nanoplalelets in toluene with the addition of PMMA.

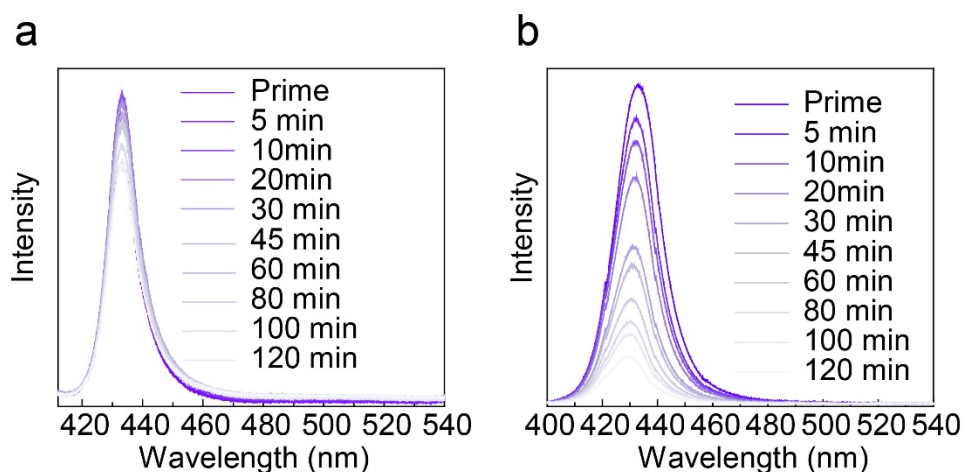


Figure S13. PL evolution of PMMA/toluene suspensions of (a) 2 ML CsPbBr₃:Lu³⁺ nanoplatelets and (b) CsPb(Br_{0.25}Cl_{0.75})₃ mixed-halide nanocrystals in ambient condition under continuous light injection (10 W cm⁻²) at 360 nm.

Table S1 Transient absorption decay lifetime fitting of 2 ML CsPbBr₃: Ln³⁺ (Ln=Nd, Gd, Lu) at 431 nm under 360nm laser excitation.

	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)	τ_A (ps)
2ML-CsPbBr ₃ :Nd ³⁺	3.0(0.5%)	41.7(6.1%)	836.3(93.3%)	783.1
2ML-CsPbBr ₃ :Gd ³⁺	1.6(0.6%)	39.7(11.3%)	478.7(88.0%)	425.8
2ML-CsPbBr ₃ :Lu ³⁺	2.9(0.21%)	54.9(3.5%)	962.8(96.2%)	928.0

Table S2 PL decay time fitting of 2 ML CsPbBr₃: Ln³⁺ (Ln=Nd, Gd, Lu) at 431 nm under 360nm laser excitation.

	τ_1 (ps)	τ_2 (ps)	τ_A (ps)
2ML-CsPbBr ₃ :Nd ³⁺	1.0(41%)	4.3(59%)	3.0
2ML-CsPbBr ₃ :Gd ³⁺	1.0(35%)	4.3(65%)	3.1
2ML-CsPbBr ₃ :Lu ³⁺	0.9(51%)	4.8(49%)	2.8

Table S3 The chemical compositions of the as-synthesized CsPbBr₃ nanoplatelets measured by EDS from different Lu(NO₃)₃:PbBr₂ ratios in reactions.

Lu(NO ₃) ₃ : PbBr ₂ [*]	Cs ^{**}	Pb ^{**}	Lu ^{**}	Br ^{**}	Lu/(Pb+Lu) ^{**}
0.33: 1	17.8%	24.9%	2.5%	54.8%	9.1%
0.4: 1	20.0%	23.3%	3.1%	53.6%	11.7%
0.5: 1	23.6%	18.7%	3.3%	54.4%	15.0%

*: The mole ratio in reactants.

** : The mole ratio in CsPbBr₃:Lu³⁺ samples measured by EDS.

References

1.L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh, M. V. Kovalenko. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* 2015, **15**(6), 3692-3696.