

SUPPLEMENTARY INFORMATION

An effective Fe(II) doping strategy for stable and highly photoluminescent CsPbBr₂ nanocrystals

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Supplementary Discussion

Section 1

Herein, the experimental details related to Br-2 were discussed. During the purification process, it was found difficult to precipitate NCs from the crude solution only by increasing the rotation speed or prolonging the centrifugation time. Hence, the commonly used antisolvent ethyl acetate (EA) was added to the crude solution to precipitate NCs (See Experimental Section 2.5 for details). However, only a small number of PNCs was obtained, indicating that excessive iron precursors would decrease the yield of PNCs. Furthermore, ICP-MS showed that the actual Fe/Pb ratio of Br-2 was 2.7%, which was merely slightly higher than the Br-2.4%. The slight change in Fe²⁺ content, although not confirmed so far, was suspected to be the result of the self-purification effect,¹ which excluded excess Fe²⁺ within lattice and thus controlled the Fe²⁺ content at a low level.

The crystal information of Br-2 was also studied by XRD as shown in Fig. S5. Compared with Br-2.4%, both the (100) and (200) XRD peaks for Br-2 shifted to higher 2 θ , implying that further lattice contraction occurred. The broadening of the diffraction peak for Br-2 indicated the reduction in grain size, as confirmed by TEM image (Fig. S6a). Meanwhile, splitting of (200) XRD peak implied the existence of microstrain in the crystal,^{2,3} suggesting that a large amount of Fe²⁺ would reduce the symmetry of the cubic phase.

The XPS results of Br-2 revealed a Pb/X ratio of 1:2.484, indicating the increased content of crystal defects, which could be attributed to the destruction by ODE-EA system (discussed in Section 2) and lattice distortion induced by excessive Fe²⁺ doping. With the aid of the surface etching caused by ODE-EA system, the otherwise undetectable Fe signal was observed (Fig. S7f), indicating that Fe²⁺ was mainly distributed within the lattice instead of the surface of PNCs. In the HR-XPS spectra, the binding energies for Pb 4f, Br 3d, I 3d in Br-2 shifted to higher binding values (Fig. S7b-7d), which is consistent with the further contraction evidenced by XRD results. Interestingly, the binding energies for Cs 3d also increased in Br-2 (Fig. S7e), although Cs⁺ was not considered to interact directly with Pb²⁺/Fe²⁺. As we explained in Section 2, the ODE-EA system would increase the Br/I ratio, resulting in the increased average electronegativity of halides, and thus the Cs-X interaction was modified.

Furthermore, the Br-2 maintained orange emission at 630 nm, with PLQY of 59.8% (Fig. S8). The decline of PLQY may be attributed to the formation of defects resulted from the surface etching and lattice distortion induced by excessive Fe²⁺ doping.

As discussed above, the structure and luminescence properties of Br-2 and Br-2.4% showed significant differences. Apart from the difference in dopant concentration, the purification process of Br-2 and Br-2.4% were different. Hence, we also investigated the influence of the purification method, and a surface etching process caused by octadecene (ODE) and EA was conceived, as shown in Fig. S9 (See Supplementary Discussion Section 2 for studies).

Section 2

As a commonly used antisolvent, it is known that EA could promote the separation of NCs from unreacted precursors and ODE, while increasing the product yield during purification. However, an excessive amount of antisolvent will cause agglomeration or redissolution of perovskite, destroying the crystal structure. Besides, the damaging effect of solvent ODE on CsPbX₃, especially CsPbI₃, have been reported.^{4,5} By adding a mixture of ODE and EA to the dispersion of CsPbBrI₂ NCs in hexane, we observed the dramatical PL degradation process, confirming the destructive effect of ODE and EA on CsPbBrI₂ (Fig. S10). Herein, the influence of ODE and antisolvent EA on the structure and performance of PNCs was investigated.

To compare the differences between centrifugation method 1 and 2, a set of samples were obtained using centrifugation method 2, labeled Pri-EA, Br-EA, Ac-EA, and F-EA, collectively referred to as PNC-EA. The structure and luminescence performance of PNCs were carefully studied by using TEM, XRD, PL, TRPL measurements. It was found that, compared to their counterparts, PNC-EA retained a smaller average particle size, ranging from 11.3-15.2 nm (Fig. S11 and Fig. S12). We speculated that the mixture of ODE and EA would show the etching effect on the surface of CsPbBrI₂ NCs, resulting in the reduction of particle size. XRD patterns indicated that, compared with undoped CsPbBrI₂ NCs, the signals of (100) and (200) planes in Pri-EA were significantly weakened (Fig. S13), indicating that the crystallinity of corresponding planes became worse. We also observed the broadening of the characteristic diffraction peaks of Pri-EA, which could be attributed to the grain refinement as evidenced by TEM image. In addition, the XRD spectrum of the Pri-EA film showed random orientation of the powder characteristics, indicating that the assembly method between NCs and Si substrate had changed.^{6,7} These data indicated that the crystal structure of PNCs was changed during purification process. Furthermore, the additional diffraction peaks attributed to CsI and CsOH indicated that PNCs had undergone a humidity-induced decomposition process.⁸

The PL spectrum showed that the PL peak of PNC-EA exhibited a blueshift of 5-19 nm compared to their counterparts (Fig. S14a and Table S4). It is reported that adding the antisolvent isopropanol to the crude solution of CsPbBr₃ NCs would cause the agglomeration, resulting in a redshift of the PL emission peak.⁶ In our experiments, the existence of surface ligands in PNC-EA maintained the existence of NCs (Fig. S3). To figure out the cause of the PL peak shift, the contribution of quantum confinement effects to band gap was estimated using Equation 1. The decreased average size of Pri-EA from 20.2 to 14.1 nm would result a reduction of band gap $\sim 4.8 \times 10^{-3}$ eV. The mismatch between calculated value and observed PL emission peak shift indicated the existence of other factors that caused the band gap to decrease. Based on the high angle shift of XRD diffraction peaks and the decreased lattice constant in HR-TEM (Fig. S11 and Fig. S13), we considered that the etching process caused by ODE and EA changed the halide composition of PNCs, which contributes to the increase of band gap. The weaker interactions between I⁻ and oleylammonium / Pb²⁺ made the iodide components more vulnerable compared to

the cases in bromide components,^{5,6} resulting in the increased Br/I ratio after purification. The PLQYs and PL lifetimes were shown in Fig. S14b and 14c and Table S4. The decreased PL lifetimes could be attributed to the increased exciton binding energy induced by the increased Br/I ratio and decreased particle size. In addition, it was found that K_r did not change significantly but K_{nr} increased significantly in PNC-EA, indicating that a large number of defects were generated during the etching process, which accelerated the nonradiative recombination rate and resulted in decreased PLQYs.

The above results disclosed the changes in structure and luminescence performance of CsPbBrI₂ NCs with and without etching and provided support for our understanding of this process. The CsPbX₃ perovskites were endowed with the properties of the large ionic mobilities within the lattice and dynamic surface. Nonetheless, the ion exchange process becomes slow and uneven in systems with high viscosity, such as gels.⁹ This novel phenomenon inspired us to understand the observed experimental phenomena. In the hexane-EA system, despite the ligand desorption process, the rapid ligand resorption process makes the exposed surface passivated in time. Nevertheless, both processes were greatly slowed down in ODE-EA system due to the relatively high viscosity of ODE, resulting in the exposure of the NCs surface. The exposed surface of CsPbBrI₂ was destroyed by ODE and EA, resulting in structure collapse, which caused changes in crystal structure and luminescence properties. In both systems, the antisolvent EA weakens the binding strength between ligands and perovskite and promotes the ligand desorption process, leading to the production of Cs-oleate, X-oleylammonium or Pb-oleate species.⁴⁻⁶

The structure and performance changes of CsPbBrI₂ NCs in the ODE-EA system reflect its lattice instability, which is related to the intrinsic ionic nature of perovskite. We have summarized the variations of average particle size, PL peak position and PLQYs of samples obtained using centrifugation methods 1 and 2, as shown in Table S5. We found that Fe²⁺ doped PNCs is affected much weaker than undoped sample, which implies the higher lattice stability of Fe²⁺ doped samples against ODE and EA.

As far as we know, pyridine etching and ion gun etching have been used to detect the distribution of impurity metal,^{10,11} and thiocyanate etching has been used to remove surface Pb species of CsPbBr₃ NCs to improve performance,¹² and acetone etching has been used to partially remove the surface iodine of CsPb(Br_xI_{1-x})₃ NCs to form a stable bromine-rich surface.¹³ Herein, the etching process caused by ODE and EA was used to evaluate the purification stability of CsPbBrI₂ NCs, providing an intuitive and convenient method for characterizing the stability of the perovskite. Nevertheless, many obscure issues in the etching process are remaining, including the mechanism of the etching process, the influence of the antisolvent type and volume, whether the etching process will occur in CsPbX₃ (X=Cl or Br). Our research on the etching process highlights the important role of ODE and antisolvent EA, which could be used to modify and investigate the structure and evaluate the purification stability of PNCs.

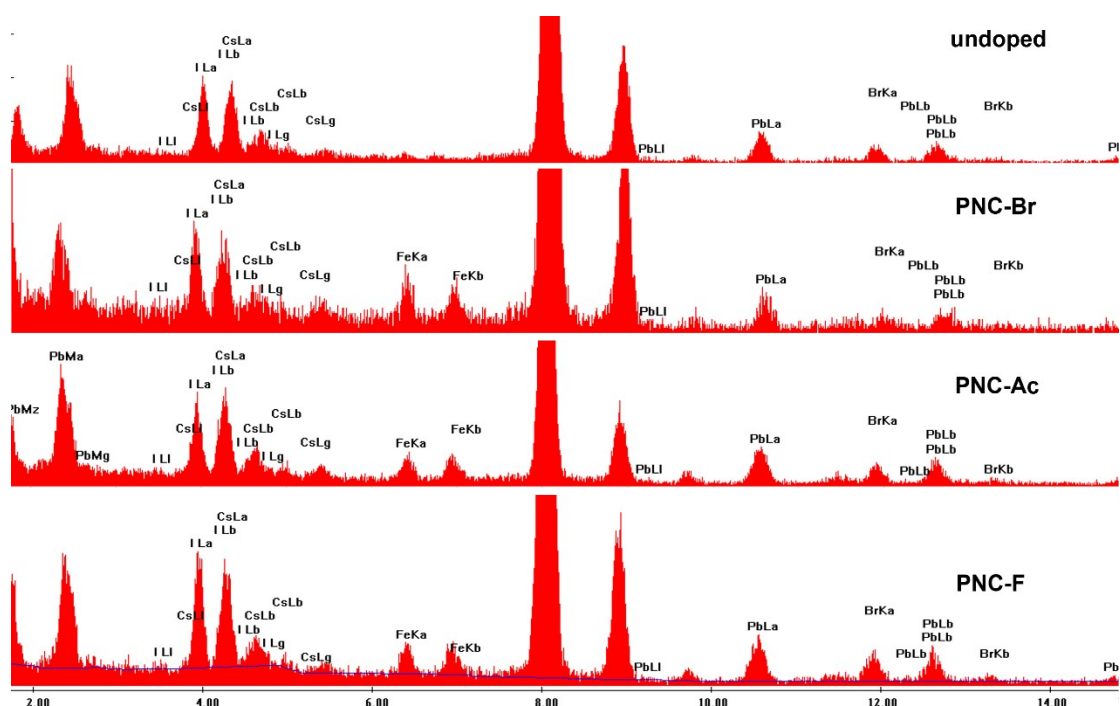


Fig. S1 Energy dispersive X-ray spectroscopy (EDS) of undoped and Fe^{2+} doped CsPbBr_2 NCs.

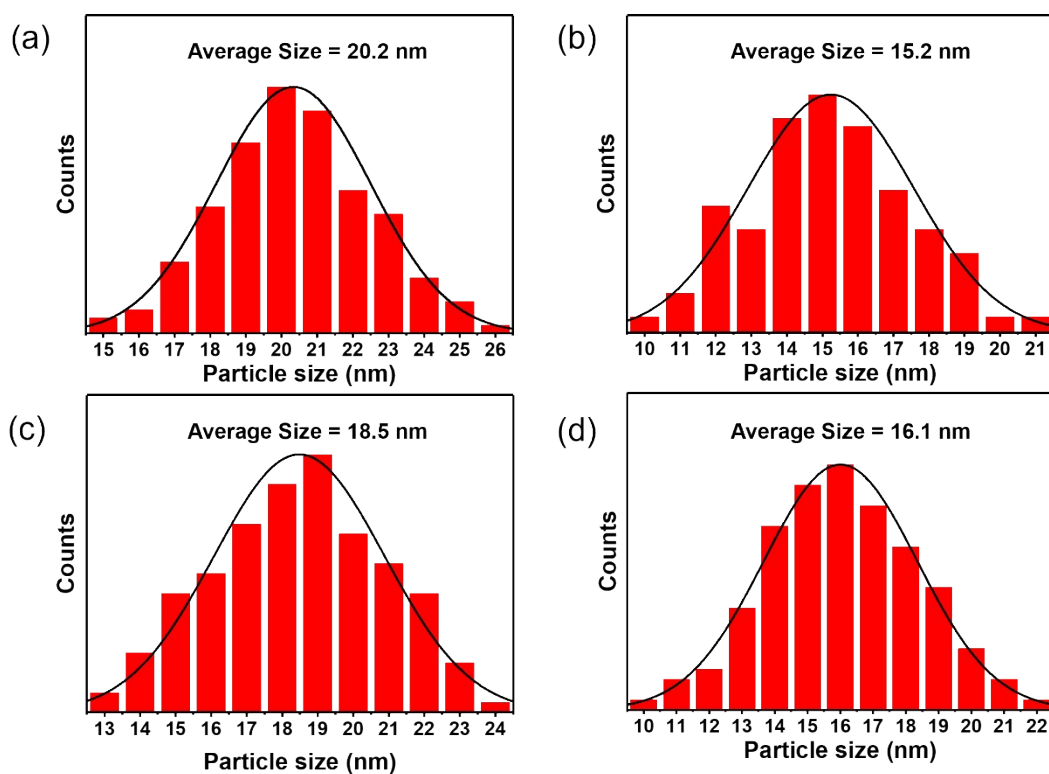


Fig. S2 Particle size statistical charts of (a) undoped CsPbBr_2 NCs, (b) Br-2.4%, (c) Ac-2.1%, (d) F-1.7%.

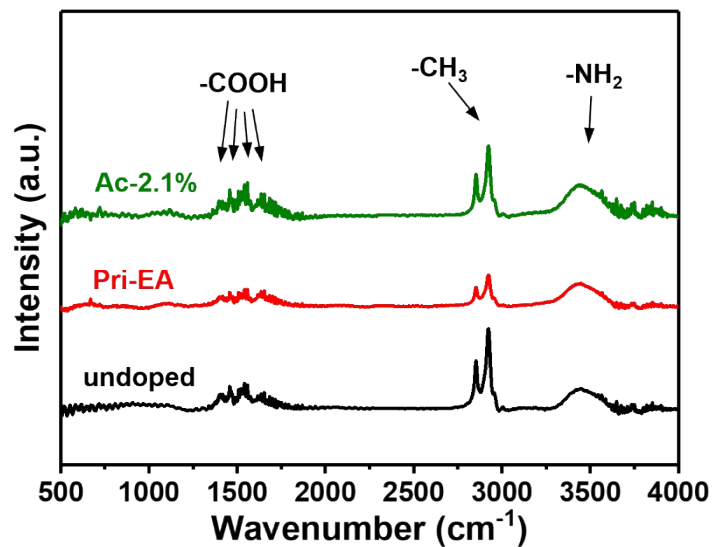


Fig. S3 FTIR of undoped CsPbBr₂ NCs, Pri-EA and Ac-2.1%.

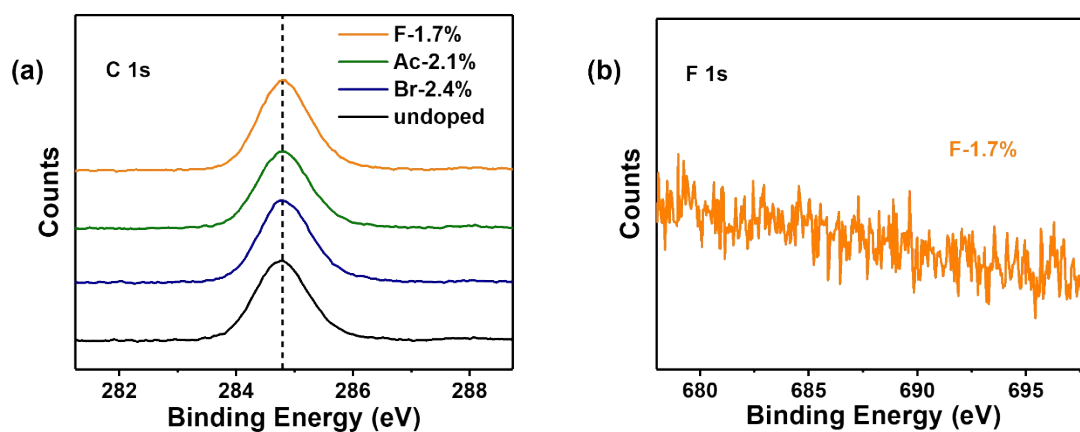


Fig. S4 (a) XPS C 1s spectra of corresponding samples after peak calibration at 284.80 eV. (b) XPS F 1s spectra of F-1.7%.

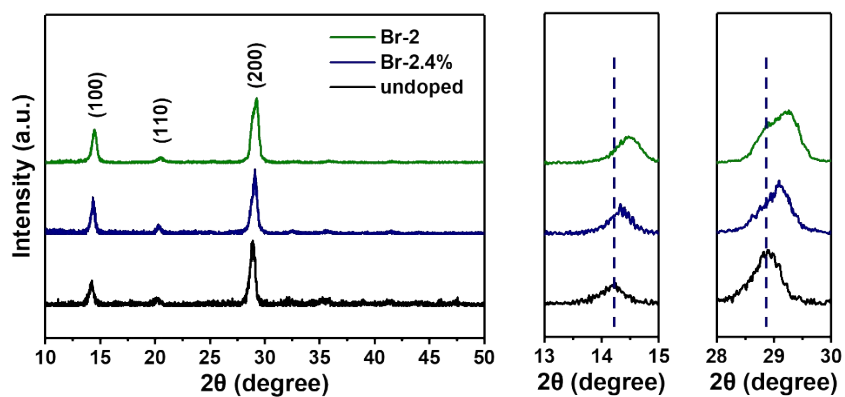


Fig. S5 XRD pattern of undoped CsPbBr₂ NCs, Br-2.4%, and Br-2. Enlarged XRD patterns show a systematic shift in peak position of (100) and (200) planes with the increasing of Fe²⁺ content.

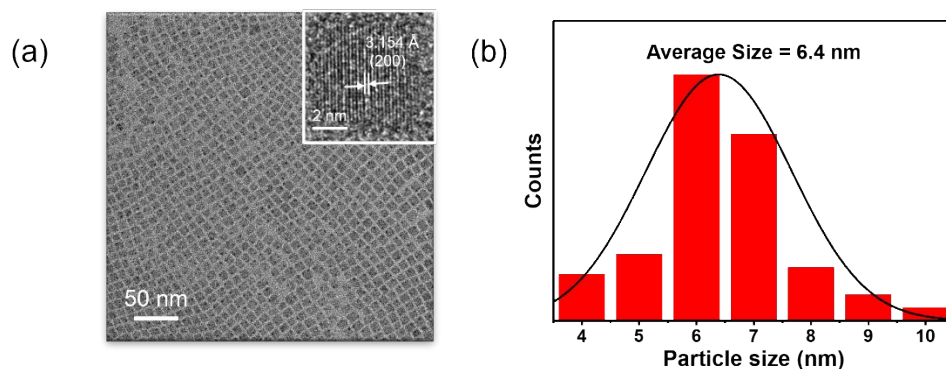


Fig. S6 (a) TEM and HR-TEM images of Br-2, and (b) corresponding particle size statistical chart. (c) Steady state absorption (dotted line) and PL (solid line) spectra of Br-2. Inset shows the photographs of Br-2 in hexane under UV-light (365 nm) irradiation.

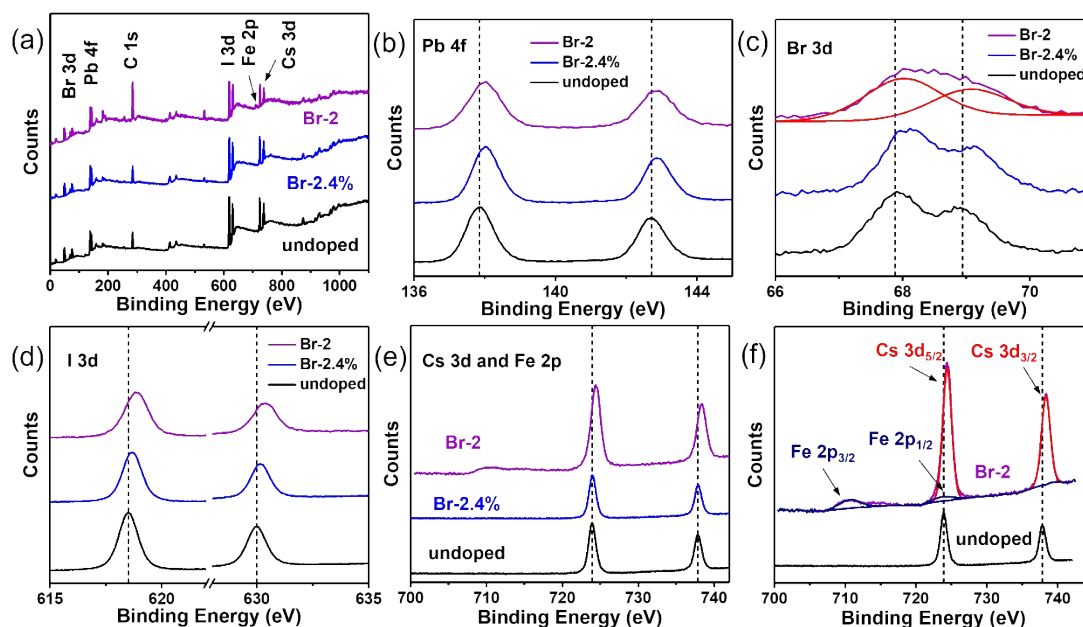


Fig. S7 (a) Survey XPS spectra and (b-e) HR-XPS spectrum of Pb, Br I, Cs and Fe for undoped CsPbBr₂ NCs, Br-2.4% and Br-2. (f) Fitting curves of HR-XPS spectrum of Cs 3d and Fe 2p for Br-2.

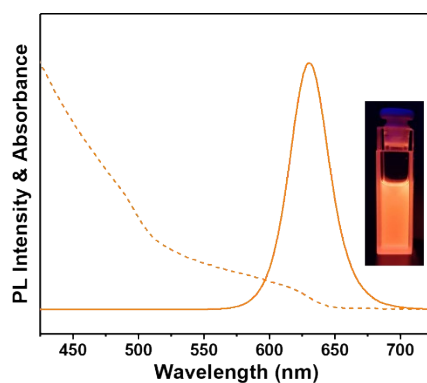


Fig. S8 Steady state absorption (dotted line) and PL (solid line) spectra of Br-2. Inset shows the photographs of Br-2 in hexane under UV-light (365 nm) irradiation.

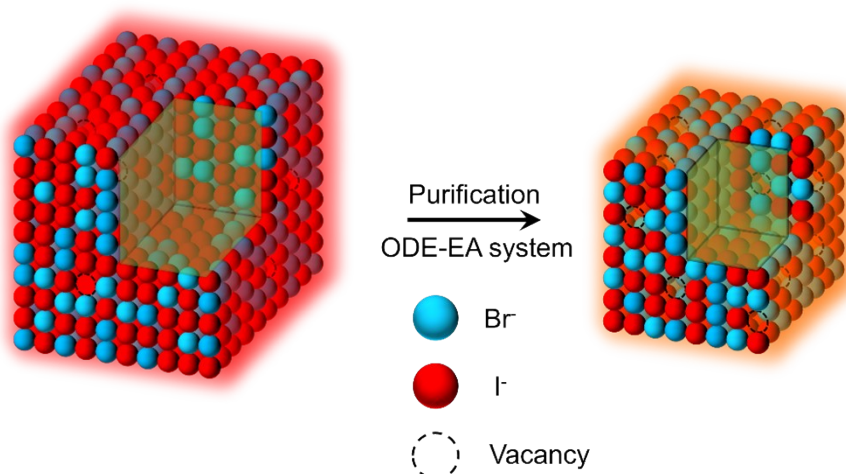


Fig. S9 Schematic illustration showing the structural changes after the surface etching process. The surface structure of PNC is destroyed by ODE and EA, and halide ion vacancies are generated during this process.

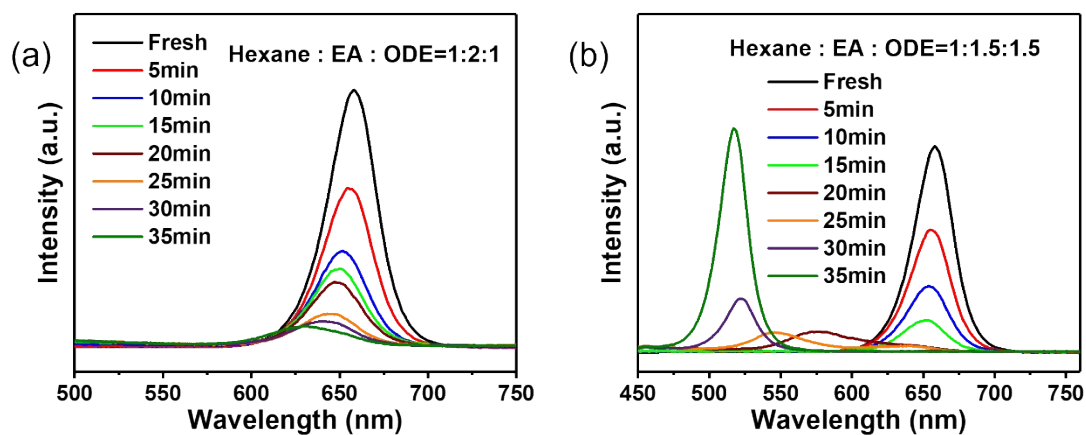


Fig. S10 The time-dependent PL spectrum of CsPbBr₂ NCs solution by adding mixed solvent (3 mL) containing ODE and EA with a volume ratio of (a) 1:2 and (b) 1:1 to 1 mL NCs suspension (in hexane).

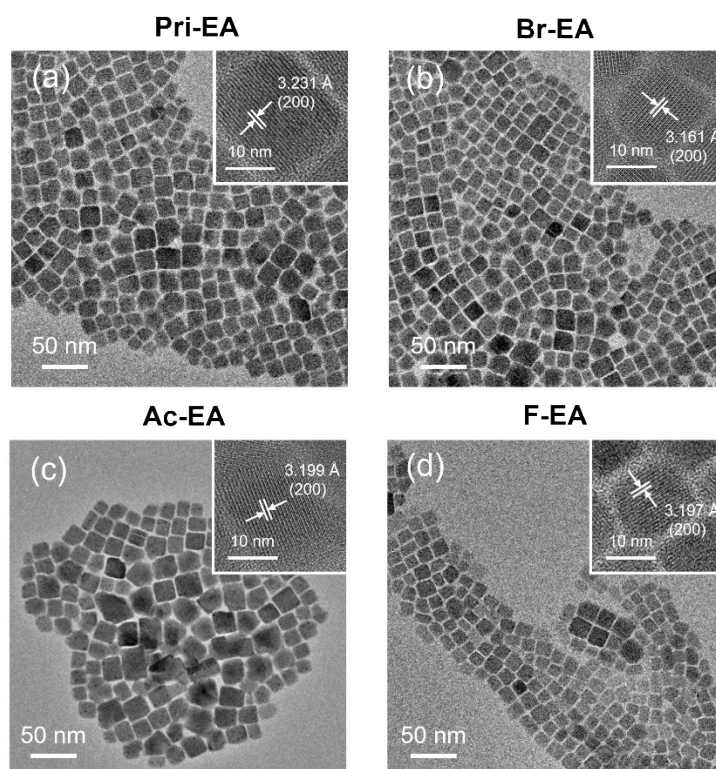


Fig. S11 TEM and HR-TEM images of Pri-EA (a), Br-EA (b), Ac-EA (c), F-EA (d).

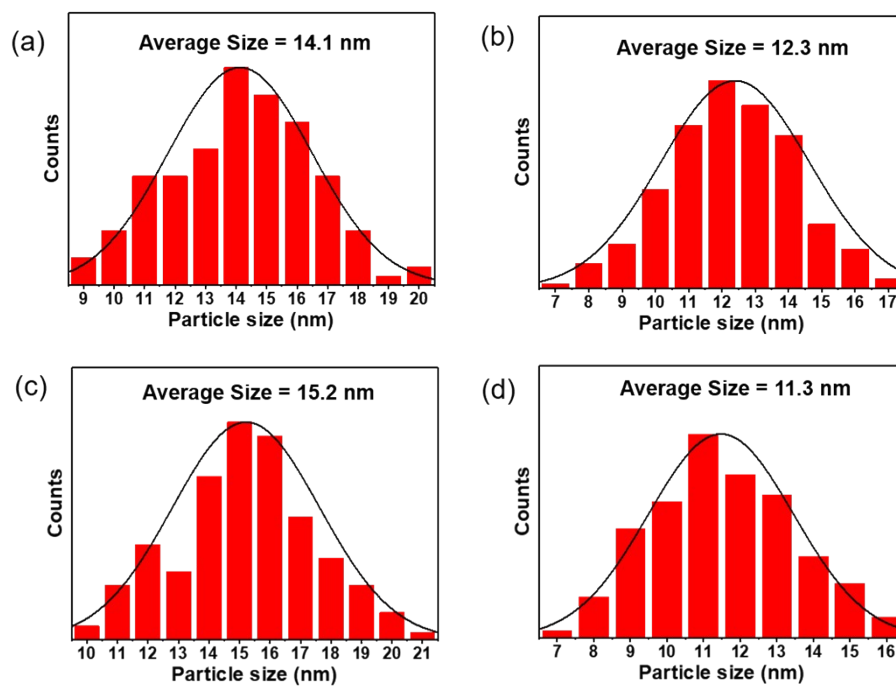


Fig. S12 Particle size statistical charts of Pri-EA (a), Br-EA (b), Ac-EA (c), F-EA (d).

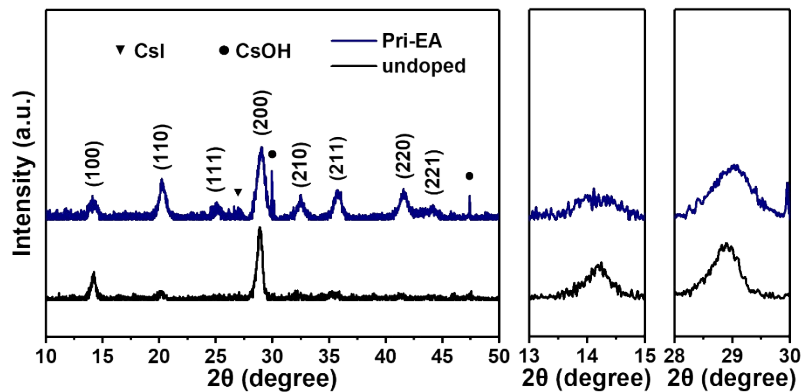


Fig. S13 XRD pattern of undoped CsPbBr₂ NCs and Pri-EA film.

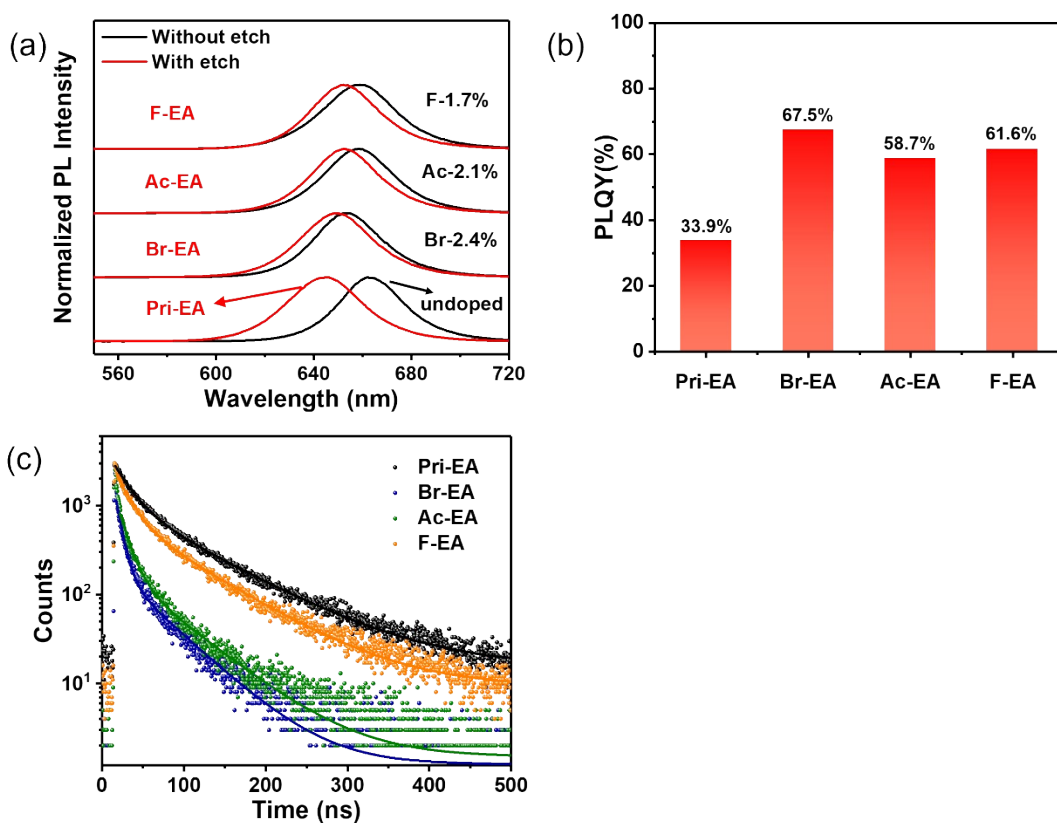


Fig. S14 (a) The PL spectrum of obtained PNCs using different centrifugal method. The black and red lines correspond to the samples obtained using centrifugal method 1 and 2, respectively. (b) The PLQY values of Pri-EA, Br-EA, Ac-EA, F-EA. (c) Time-resolved photoluminescence decays for excitonic luminescence of PNC-EA upon excitation by a 375-nm pulsed laser.

Table S1. Amounts of PbBr₂, PbI₂ and iron precursor added for undoped CsPbBrI₂ NCs and Fe²⁺ doped CsPbBrI₂ NCs.

Sample	PbBr ₂	PbI ₂	Iron precursor
undoped	48.8 mg (0.133mmol)	123.6 mg (0.267 mmol)	
PNC-Br		185.2 mg (0.4 mmol)	FeBr ₂ (43.1 mg, 0.2 mmol)
PNC-Ac	0.133mmol	0.267 mmol	FeAc ₂ (34.8 mg, 0.2 mmol)
PNC-F	0.133mmol	0.267 mmol	FeF ₂ (18.8 mg, 0.2 mmol)
Br-2	0.133mmol	0.267 mmol	FeBr ₂ (57.6 mg, 0.267 mmol) FeI ₂ (165.0 mg, 0.533 mmol)

Table S2. The calculated values of quantum confinement energy (ΔE), quantum confinement energy difference (ΔE_{cal}), PL energy difference (ΔE_{PL}).

Sample	ΔE ($\times 10^{-3}$ eV)	ΔE_{cal} ($\times 10^{-3}$ eV)	ΔE_{PL} ($\times 10^{-3}$ eV)
undoped	6.19		
Br-2.4%	10.96	4.77	22.33
Ac-2.1%	7.39	1.20	10.82
F-1.7%	9.79	3.60	9.67

Table S3. The table encloses PL lifetimes, PLQY values, radiative (K_r) and nonradiative (K_{nr}) decay rates of undoped PNCs, Br-2.4%, Ac-2.1%, F-1.7%. The values in the parentheses of τ_1 and τ_2 represent the statistical weights of the corresponding lifetime components.

Samples	undoped	Br-2.4%	Ac-2.1%	F-1.7%
τ_1 (ns)	31.5 (24.5%)	24.0 (65.5%)	26.2 (54.7%)	28.1 (31.6%)
τ_2 (ns)	152.2 (75.5%)	89.5 (34.5%)	87.5 (45.3%)	100.5 (68.4%)

τ_{av} (ns)	144.6	67.4	71.2	92.2
PLQY (%)	69.2	92.1	89.3	87.6
K_r ($\times 10^6$ s $^{-1}$)	4.784	13.65	12.53	9.499
K_{nr} ($\times 10^6$ s $^{-1}$)	2.129	1.171	1.502	1.345

Table S4. The table encloses the PL peak position (λ_{PL}), PL lifetimes, PLQY values, radiative (K_r) and nonradiative (K_{nr}) decay rates of Pri-EA, Br-EA, Ac-EA, F-EA. The values in the parentheses of τ_1 and τ_2 represent the statistical weights of the corresponding lifetime components.

Samples	Pri-EA	Br-EA	Ac-EA	F-EA
λ_{PL} (nm)	642.9	649.5	653.0	652.9
τ_1 (ns)	20.4 (28.4%)	7.4 (46.3%)	11.7 (43.0%)	17.0 (32.7%)
τ_2 (ns)	86.4 (71.6%)	50.9 (53.7%)	59.7 (57.0%)	76.6 (67.3%)
τ_{av} (ns)	80.7	46.0	53.5	70.8
PLQY (%)	33.9	67.5	58.7	61.6
K_r ($\times 10^6$ s $^{-1}$)	4.198	14.65	10.97	8.696
K_{nr} ($\times 10^6$ s $^{-1}$)	8.185	7.056	7.719	5.421

Table S5. The size change, shift of PL peak position, and PLQYs of the synthesized PNCs using centrifugation methods 1 and 2. PLQY-1 and PLQY-2 represent the PLQY values of the samples obtained using centrifugation methods 1 and 2, respectively.

Samples	Pri-EA	Br-EA	Ac-EA	F-EA
$ \Delta \text{size} $ (nm)	6.1	2.9	3.3	4.8

$ \Delta \lambda_{PL} $ (nm)	19.1	4.8	5.4	5.6
PLQY-1	69.2%	92.1%	89.3%	87.6%
PLQY-2	33.9%	67.5%	58.7%	61.6%

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