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Supplementary materials

Anion-assisted Yb^{3+} and Mn^{2+} doping of 0D and 2D lead halide perovskite nanostructures

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1 Chemicals

1-Octadecene (ODE, 90%, Merk), oleic acid (OA, 90%, Sigma-Aldrich), oleylamine (OlAm, 70%, Sigma-Aldrich), n-octylamine (OctAm, OXEA), ytterbium(III) chloride ($YbCl_3$, ≥99.9%, anhydrous, Sigma-Aldrich), ytterbium(III) chloride hexahydrate ($YbCl_3 \cdot 5H_2O$, ≥99.9%, Sigma-Aldrich), ytterbium(II) iodide (YbI_2, ≥99.9%, Sigma-Aldrich), lead(II) acetate trihydrate ($Pb(CH_3COO)_2 \cdot 3H_2O$, ≥99.9%, Sigma-Aldrich), manganese(II) chloride ($MnCl_2$, ≥98%, anhydrous, Sigma-Aldrich), cesium carbonate (Cs_2CO_3, 99.9%, Sigma-Aldrich), lead(II) bromide ($PbBr_2$, ≥99.999%, Sigma-Aldrich), lead(II) chloride ($PbCl_2$, ≥99.999%, Sigma-Aldrich), formamidinium bromide (FABr, ≥98%, Sigma-Aldrich), ytterbium(III) acetate tetrahydrate ($Yb(CH_3COO)_3 \cdot 3H_2O$, ≥99.9%, Sigma-Aldrich), ytterbium(III) nitrate pentahydrate ($Yb(NO_3) \cdot 5H_2O$, ≥99.9%, Sigma-Aldrich), toluene (Vekton), ethyl acetate (EtOAc, anhydrous, ≥99.5%, Sigma-Aldrich), N,N-Dimethylformamide (DMF, anhydrous, 99.8%, Sigma-Aldrich), acetonitrile (ACN, anhydrous, 99.8%, Sigma-Aldrich). All chemicals were used as received.

2 Synthesis of lead-halide perovskite (LHP) nanostructures

2.1 $CsPbBr_3$ NCs

$CsPbBr_3$ NCs were synthesized according to previously published procedure.[1] Preparation of Cs-Oleate (Cs-OA) solution. To prepare Cs-OA solution, 0.814 g of Cs_2CO_3, 2.5 mL of dried OA and 40 mL of ODE were added into a 50 ml three-neck flask. The mixture was degassed under vacuum at 120 °C for 30 min, and then the temperature was increased to 150 °C under N_2 atmosphere. After the solid phase was completely dissolved, the temperature was set back to 120 C for further use.

138 mg (0.376 mmol) of $PbBr_2$ was added into a 50 mL three-neck flask containing 1 mL of OA, 1 mL of OlAm and 10 mL of ODE. The mixture was degassed under vacuum at 120 °C for 20 min and then changed to inert atmosphere. When the $PbBr_2$ was completely dissolved, the solution was heated up to 180 °C. Subsequently, 0.8 mL of hot Cs-OA was injected into the solution. After 5 s the reaction was quenched by an ice-water bath. Obtained NCs were centrifuged at 5000 rpm for 10 min. Then precipitation was dissolved in hexane, mixed with ethyl acetate, and centrifuged at 10000 for 10 minutes. The obtained $CsPbBr_3$ NCs were dissolved in toluene and centrifuged at 10000 for 10 minutes to take supernatant.

2.2 $CsPbBr_3$ NPls

$CsPbBr_3$ NPls were synthesized and purified according to the previous reports.[2,3] To prepare Cs-OA solution, 0.16 g of Cs_2CO_3, 0.5 mL of dried OA and 8 mL of ODE were added into a 50-mL three-neck flask. The mixture was degassed at 120 ºC for 30 min. After complete dissolution at 150 ºC under N_2 atmosphere, the temperature was lowered down to 120 ºC.

0.069 mg (0.188 mmol) of $PbBr_2$ was added into a 50 mL three-neck flask along with 0.5 mL of OA, 0.5 mL of OlAm and 5 mL of ODE. The mixture was degassed at 120 ºC for 20 min and then changed to N_2 atmosphere. After complete dissolution, the temperature was lowered down to 25 °C. 0.4 mL of Cs-OA was injected into the solution. The mixture was then heated up, and the reaction was quenched by an ice-water bath when the temperature reached 180 ºC. Obtained NPls were centrifuged at 8000 rpm for 5 min. Then precipitation was dissolved in hexane and centrifuged at 3000 for 5 minutes to take supernatant.

2.3 $FAPbBr_3$ NCs and NPls

Synthesis of $FAPbBr_3$ NCs was adopted from the previous report work.[4] 0.1 mmol of FABr and $PbBr_2$ were dissolved in 1 ml of DMF, after that 200 µL of oleic acid and 40 µL of oleylamine were added. 100 µL of the prepared precursor was swiftly injected into 3 mL of chloroform under vigorous stirring. For purification, 3 ml of the 1-to-1 mixture of toluene and acetonitrile was added followed by centrifugation at 8000 rpm for 5 minutes. The precipitate was dissolved in toluene and centrifuged 1 more time at 8 000 rpm for 5 minutes to take supernatant.

To produce $FAPbBr_3$ NPls, a new synthetic protocol was developed as follows: 20 µL of oleic acid and 15 µL of n-octylamine were added to 100 µL of 0.1 mmol FABr+$PbBr_2$ DMF solution. This mixture was injected into 3 mL of chloroform. For purification, 3 ml of the 1-to-1 mixture of toluene and acetonitrile was added followed by centrifugation at 3000 rpm for 5 minutes. The precipitate was dissolved in toluene and centrifuged 1 more time at 5 000 rpm for 5 minutes to take supernatant.

2.4 $CsPbCl_3$ NCs

$CsPbCl_3$ NCs were synthesized according to previously published procedure.[1] To prepare Cs-OA solution, 0.814 g of Cs_2CO_3, 2.5 mL of dried OA and 30 mL of ODE were added into a 50 ml three-neck flask. The mixture was degassed under vacuum at 120 °C for 30 min, and then the temperature was increased to 150 °C under inert atmosphere. After the complete dissolution of cesium carbonate, the temperature was set back to 110 °C for further use.

104.6 mg of $PbCl_2$ (0.376 mmol), 1ml of OA, 1 mL OlAm and were mixed with 10 mL of ODE in 100-mL three-neck round bottom flask and dried under vacuum at 110 °C for 1 h. Then the flask was switched to inert atmosphere and heated up to 180 °C. 0.8 mL of Cs-oleate was swiftly injected and after 5 s the reaction was quenched by colling down with ice-bath. Obtained NCs were mixed with hexane and centrifuged at 5000 rpm for 10 min. Then precipitation was dissolved in hexane, mixed with ethyl acetate, and centrifuged at 12000 for 10 minutes. Obtained $CsPbCl_3$ NCs were dissolved in toluene for further use.

2.5 Yb^{3+}:$CsPbCl_3$ NCs

Yb^{3+}:$CsPbCl_3$ NCs were synthesized and purified according to Zhang et al.[5] with minor modifications. To prepare Cs-OA solution, 0.814 g of Cs_2CO_3, 2.5 mL of dried OA and 30 mL of ODE were added into a 50-mL three-neck flask. The mixture was degassed under vacuum at 120 C for 30 min, and then the temperature was increased to 150 °C under inert atmosphere. After the complete dissolution of cesium carbonate, the temperature was set back to 110 °C for further use.

46.6 mg of $Pb(CH_3COO)_2·3H_2O$ (0.123 mmol), 96.6 mg of $YbCl_3·6H_2O$ (0.246 mmol), 1 mL of OA, 1 mL OlAm and were mixed with 10 mL of ODE in 100-mL three-neck round bottom flask and dried under vacuum at 110 °C for 1 h. Then the flask was switched to inert atmosphere and heated up to 260 °C. 0.8 mL of Cs-oleate was swiftly injected and after 10 s the reaction was quenched by colling down with ice-bath. Obtained nanocrystals were mixed with hexane and centrifuged at 5000 rpm for 10 min. Then precipitation was dissolved in hexane and centrifuged at 12000 for 10 minutes. Obtained Yb^{3+}:$CsPbCl_3$ NCs were dissolved in hexane and centrifuged at 3000 rpm for 3 minutes. After that supernatant was discarded for further use.

3 Doping

To dope the pre-synthesized LHP nanostructures, $YbCl_3$ and $MnCl_2$ precursors were prepared as follows: 0.1 mmol of anhydrous $YbCl_3$ ($MnCl_2$) and 15 μL of OlAm were dissolved in 2 mL of toluene by stirring during 3 hours at 100 °C and then stirring overnight at 70 °C. Then the specified amount of precursor was added to diluted LHP toluene solutions under stirring. The reaction of doping takes less than 1 minute. All doping reactions were performed inside a glovebox. For optical characterization, the obtained solutions were used as obtained. For the XPS measurements, the doped nanostructures were additionally washed in a 1-to-1 mixture of toluene/ethyl acetate followed by precipitation and re-dispersion in toluene. For comparative experiments, $Yb(CH_3COO)_3$ and $Yb(NO_3)_3$ precursors were prepared in a similar way but with an additional degassing step.

4 Characterization

Absorption spectra were taken using a Shimadzu UV-3600 spectrophotometer. PL spectra in the VIS were taken on a Jasco FP-8200 spectrofluorimeter. PL decays in the VIS were taken on a MicroTime 100 confocal microscope (PicoQuant). PL spectra in the VIS-NIR were taken using a purpose-built setup based on an Acton SP-2500i monochromator (Princeton Instruments), Andor iDus 401A CCD camera (Andor Technology Ltd.), and OXXIUS 375-nm cw laser. To measure PL QY in the NIR, PL spectra of Yb^{3+}-doped LHP and PbS QDs were registered with an InGaAs G5852-21 photodiode (Hamamatsu). PL decays in the NIR were taken using a purpose-built setup based on avalanche InGaAs/InP photodiode (MicroPhotonDevices) with DPC-230 photon correlator (B&H), Acton SP-2150 monochromator (Princeton Instruments), and 351-nm pulsed laser DTL-339QT (Laser-Export).[6,7] XPS measurements were performed on an Escalab 250Xi photoelectron spectrometer (Thermo Fisher Scientific). TEM and HAADF-STEM measurements were made on a Zeiss Libra 200FE microscope. STEM measurements were made using a Zeiss

Merlin microscope. HR-TEM images were made on a JEOL 2100F microscope. XRD analysis was performed by using an Ultima IV Rigaku diffractometer with Cu Kα radiation (λ = 1.5418 Å).

5 Results

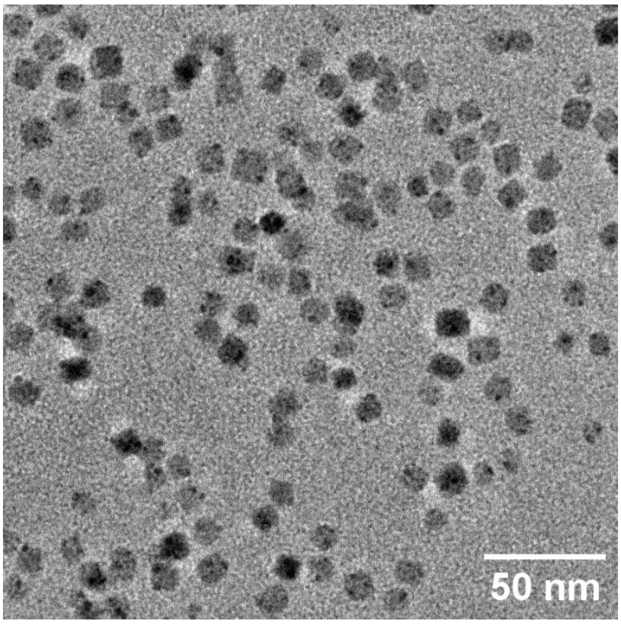

Fig.S1 Typical TEM image of the pristine $CsPbBr_3$ NCs

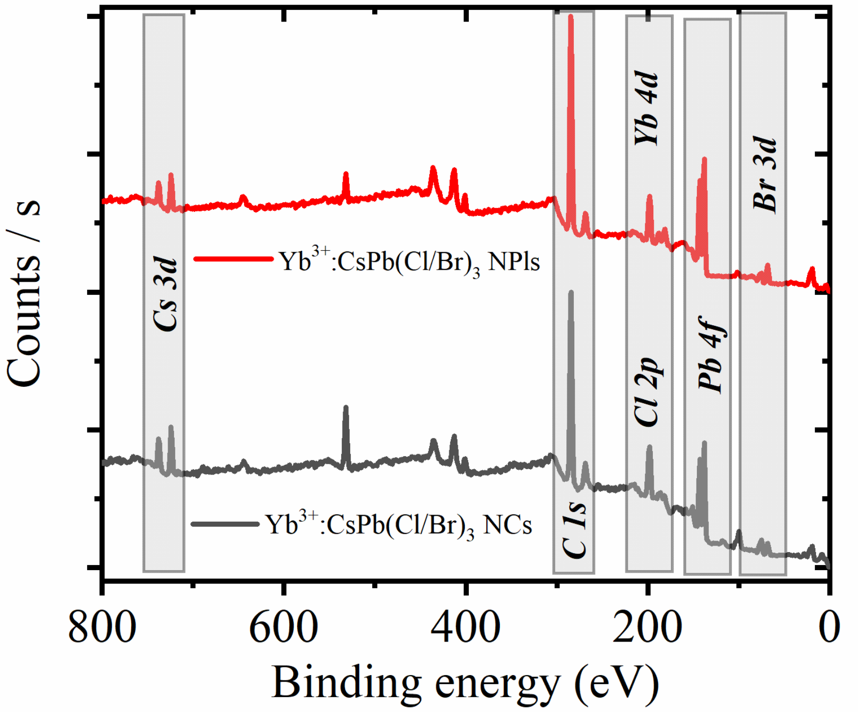

Fig.S2 XPS surveys for the Yb^{3+} doped $CsPbCl_xBr_{3-x}$ NCs (black line) and NPls (red line).

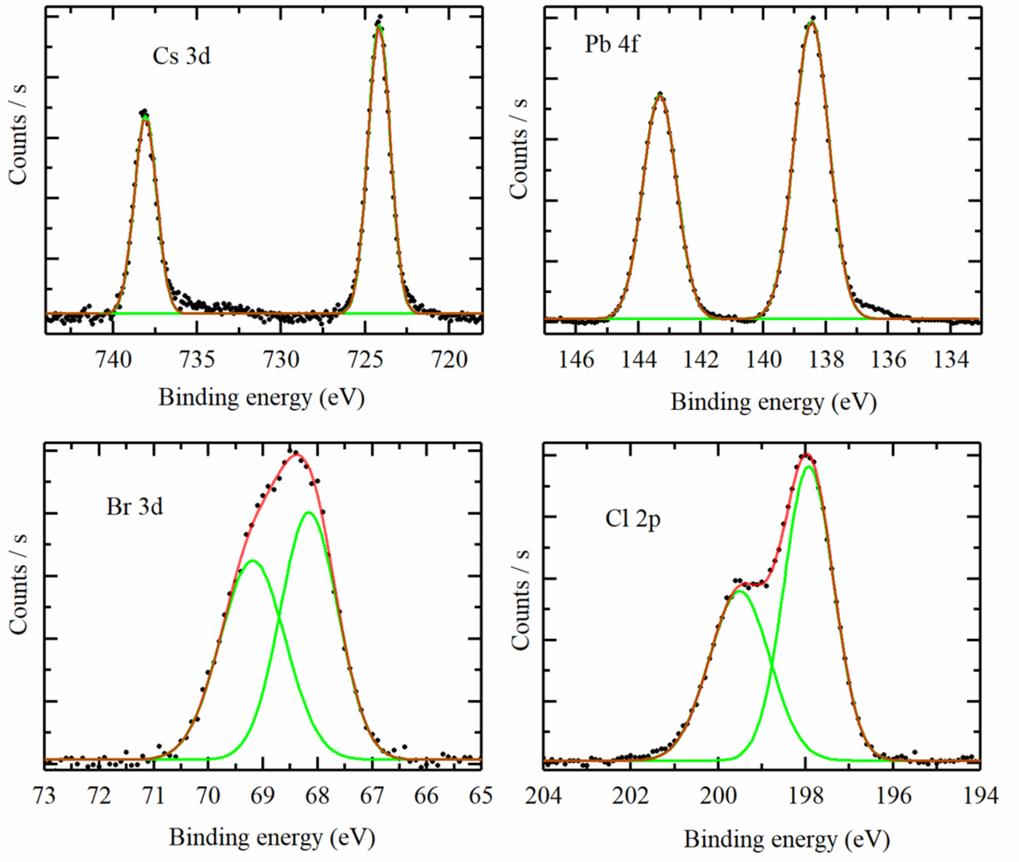

Fig.S3 High-resolution XPS spectra obtained for the Yb^{3+} doped $CsPbCl_xBr_{3-x}$ NCs.

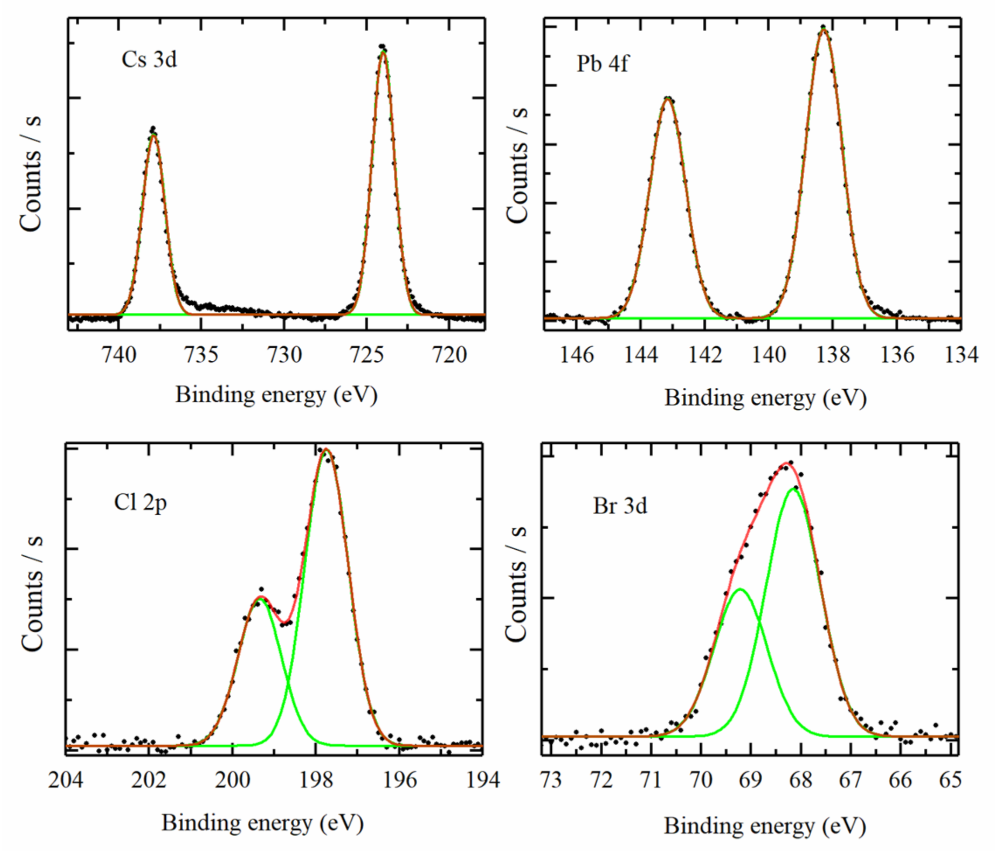

Fig.S4 High-resolution XPS spectra obtained for the referent $CsPbCl_xBr_{3-x}$ NCs.

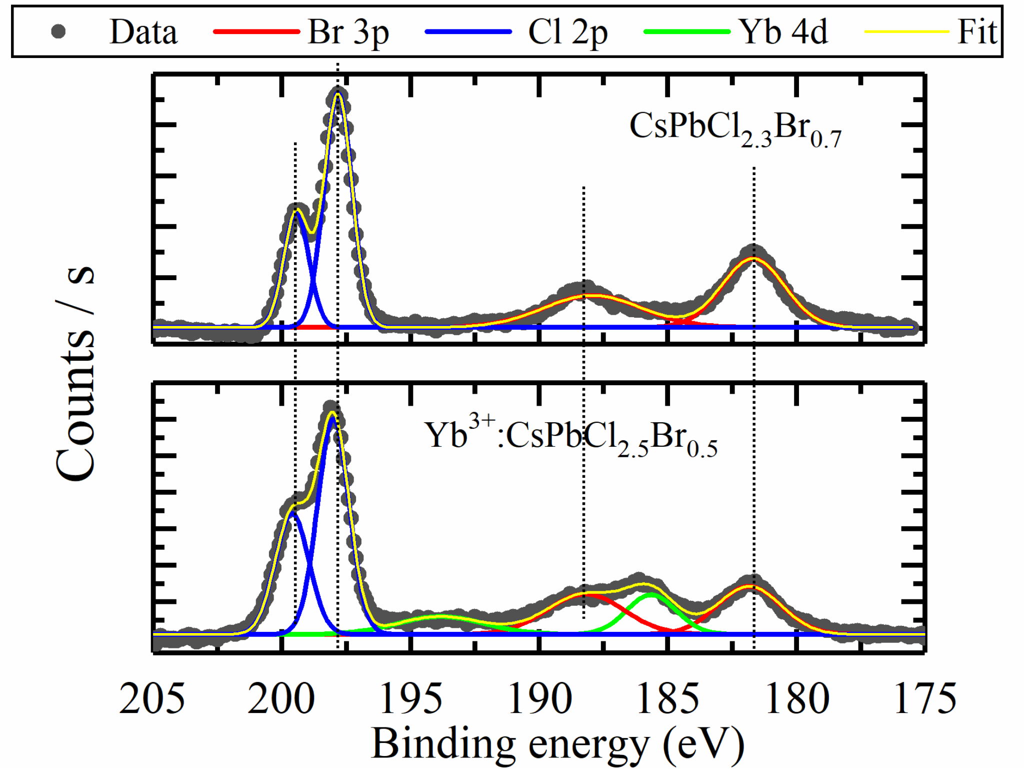

Fig.S5 XPS spectra obtained for the referent (upper panel) and Yb^{3+} doped (lower panel) $CsPbCl_xBr_{3-x}$ NCs. A new peak at ~ 186 eV is clearly observed when Yb^{3+} ions are introduced into the perovskite matrix.

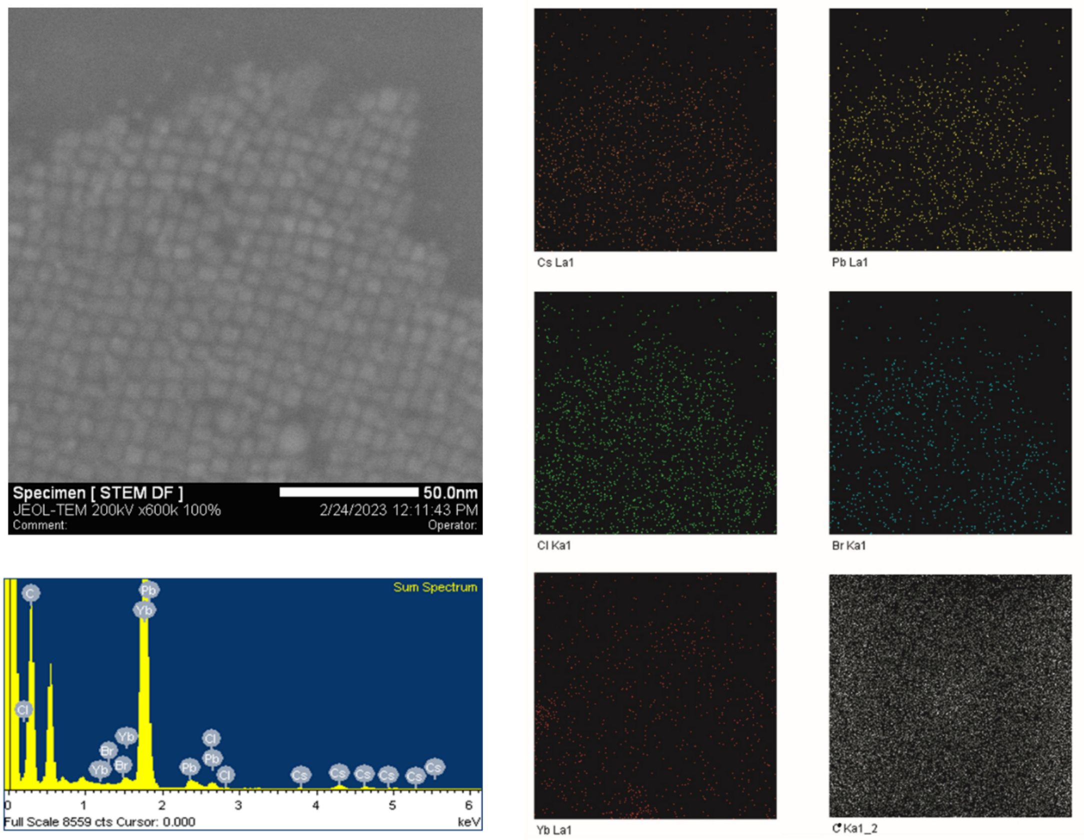

Fig.S6 EDX analysis of Yb^{3+} doped $CsPbCl_xBr_{3-x}$ NCs confirming the existence of all Cs, Pb, Cl, Br, and Yb elements.

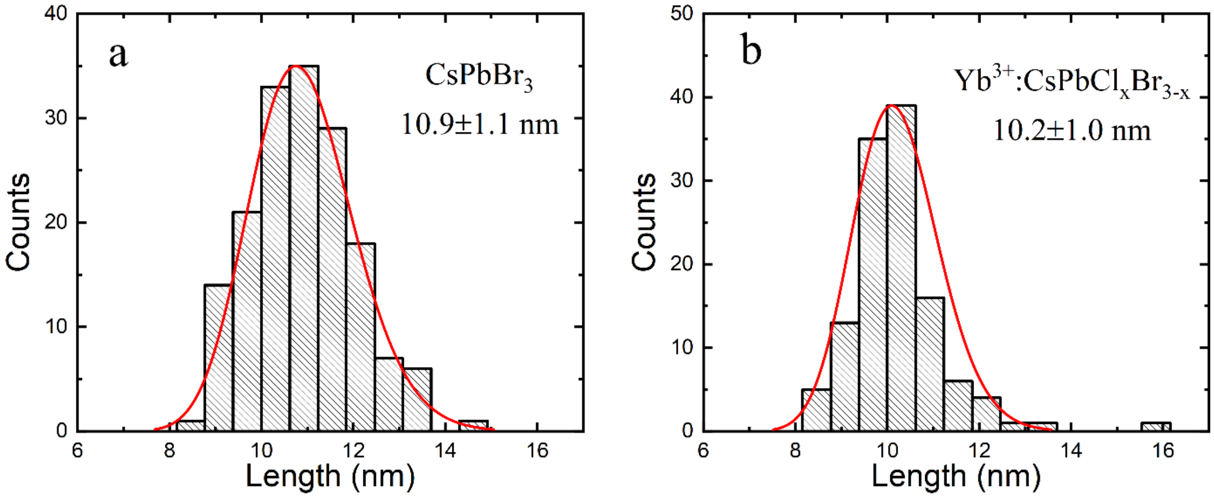

Fig.S7 Size distributions estimated for the (a) pristine CsPbBr3 NCs and (b) Yb^{3+} doped CsPbCl$_x$Br$_{3-x}$ NCs.

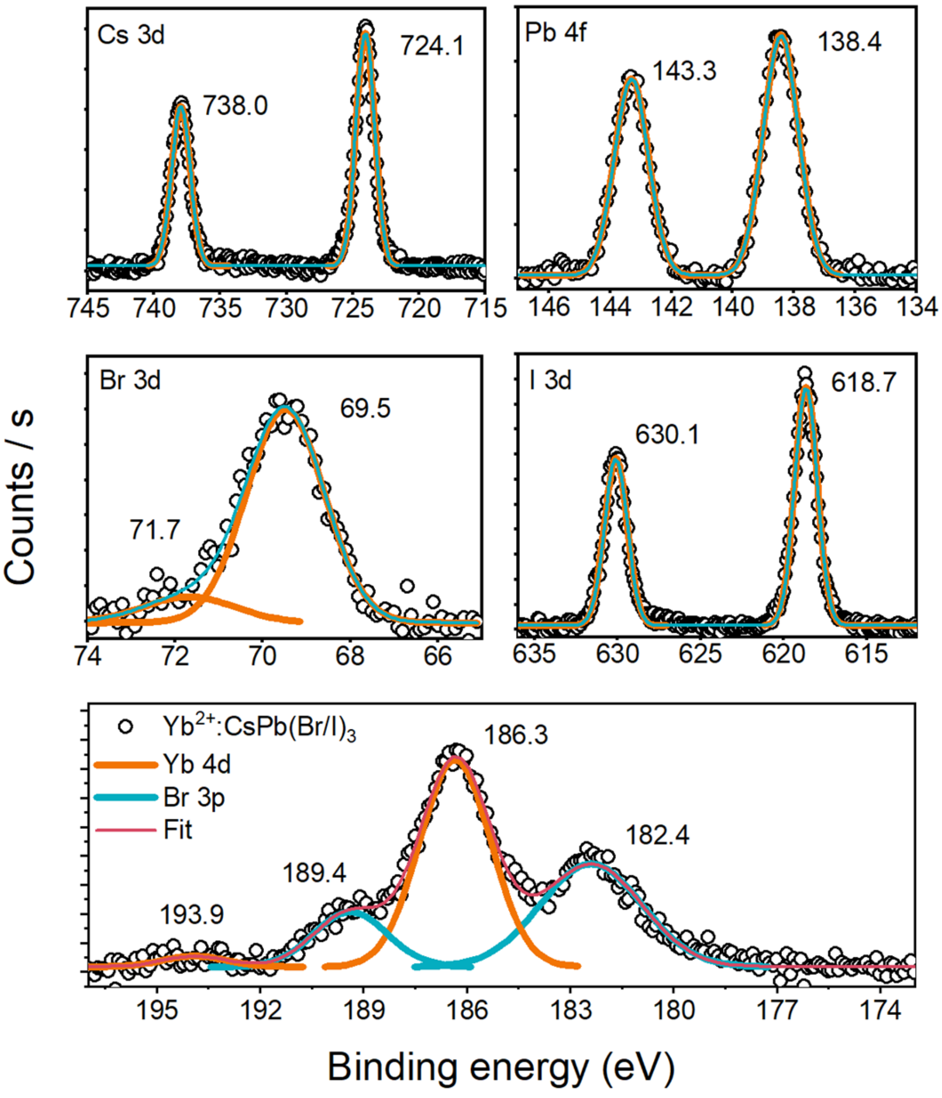

Fig.S8 High-resolution XPS spectra obtained for the Yb^{2+} doped CsPbBr$_x$I$_{3-x}$ NCs.

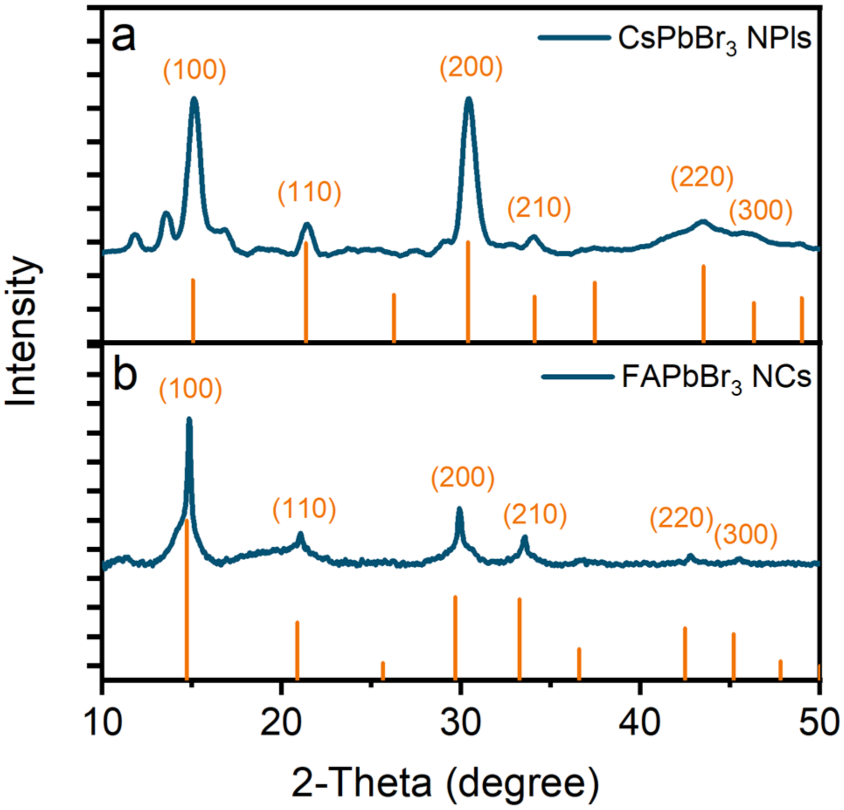

Fig.S9 XRD patterns obtained for (a) $CsPbBr_3$ NPls and (b) $FAPbBr_3$ NCs. The are compared to a standard cubic phase of $CsPbBr_3$ (PDF #01-075-0412) and cubic phase of $FAPbBr_3$ (Cif available from Ref.[8])

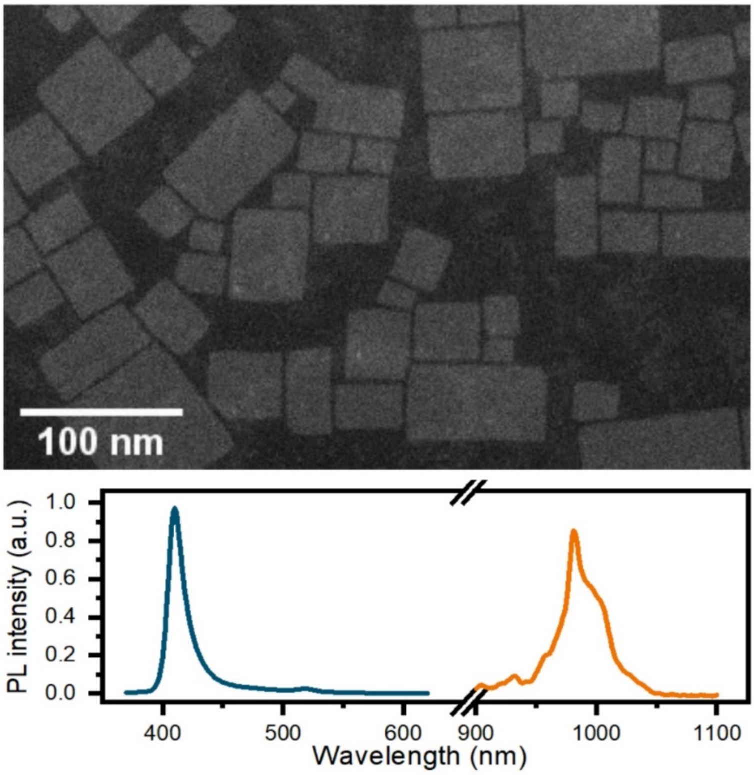

Fig.S10 HAADF-STEM image (upper panel) of the Yb^{3+}-doped $CsPbCl_xBr_{3-x}$ NPls emitting at 410 nm and 980 nm and their PL spectrum (lower panel).

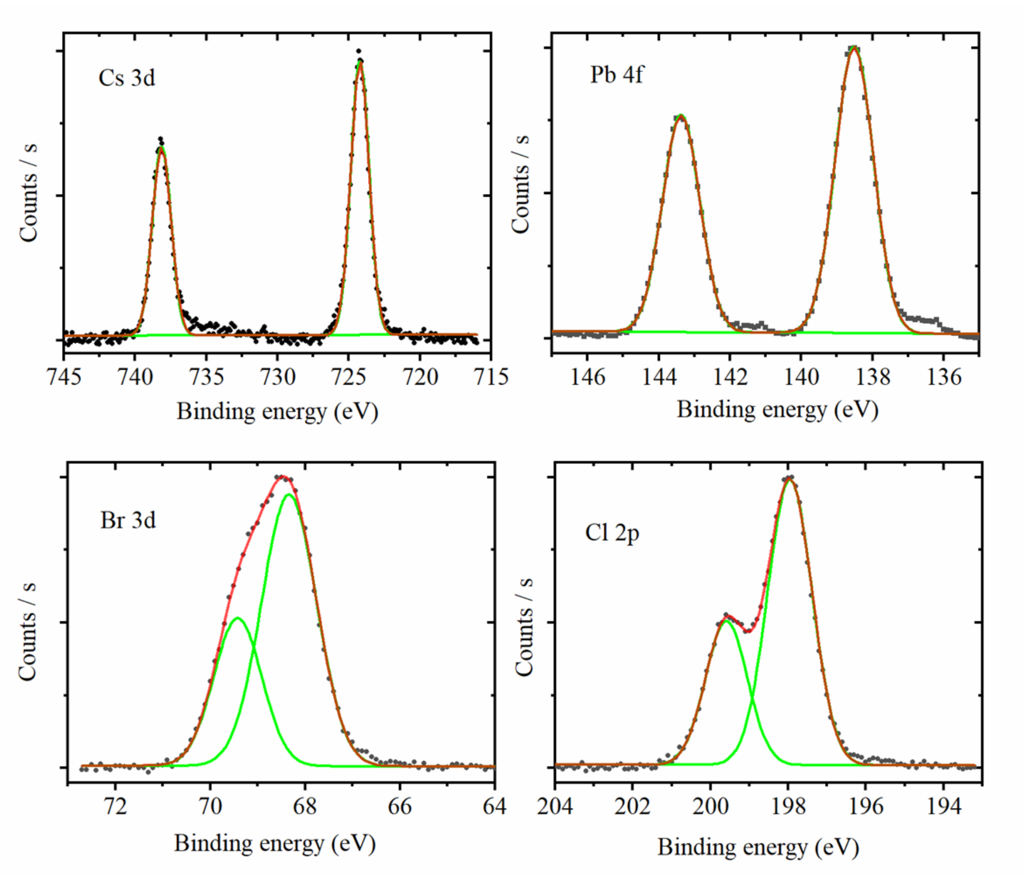

Fig.S11 High-resolution XPS spectra obtained for the Yb^{3+} doped $CsPbCl_xBr_{3-x}$ NPls.

Table S1 Estimated XPS peak positions for the Yb^{3+} doped and reference $CsPbCl_xBr_{3-x}$ samples.

Element	Yb^{3+}:$CsPbCl_{2.5}Br_{0.5}$ NCs	Yb^{3+}:$CsPbCl_{2.2}Br_{0.8}$ NPls	$CsPbCl_{2.3}Br_{0.7}$ NCs
Cs 3d	724.12±0.01	724.22±0.01	724.00±0.01
	738.07±0.01	738.14±0.01	737.89±0.01
Pb 4f	138.45±0.01	138.51±0.01	138.29±0.01
	143.32±0.01	143.37±0.01	143.15±0.01
Cl 2p	197.93±0.01	197.96±0.01	197.75±0.01
	199.51±0.01	199.60±0.01	199.35±0.02
Br 3d	68.16±0.05	68.34±0.02	68.16±0.05
	69.19±0.06	69.42±0.04	69.22±0.08

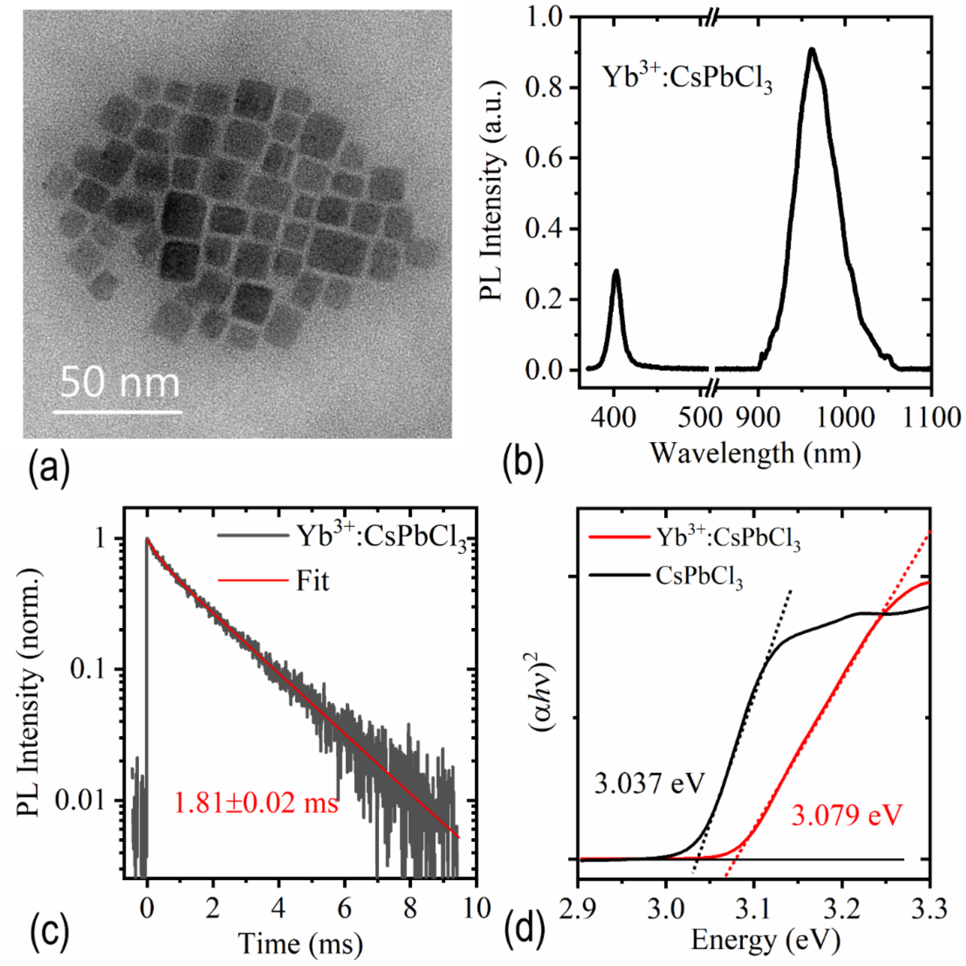

Fig.S12 (a) TEM image, (b) PL spectrum, and (c) NIR PL decay from the Yb^{3+}:$CsPbCl_3$ NCs obtained by a hot-injection method. (d) Tauc plot for Yb^{3+}:$CsPbCl_3$ (red line) and pristine $CsPbCl_3$ (black line) NCs obtained by a hot-injection method.

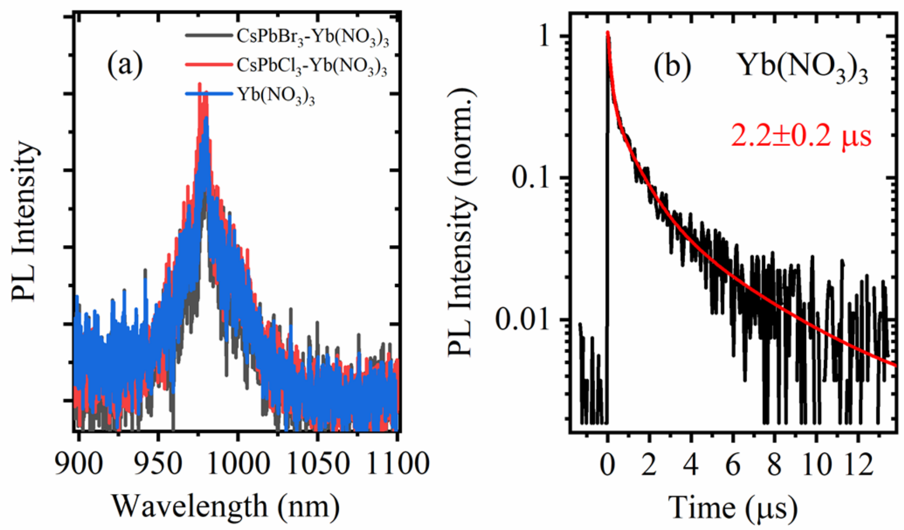

Fig.S13 (a) PL spectra in the NIR spectral region obtained for the $Yb(NO_3)_3$-treated $CsPbBr_3$ (black line) and $CsPbCl_3$ (red line) NCs and the $Yb(NO_3)_3$-OlAm solution with the same amount of ytterbium nitrate. (b) PL decay curve recorded from the concentrated $Yb(NO_3)_3$-OlAm solution.

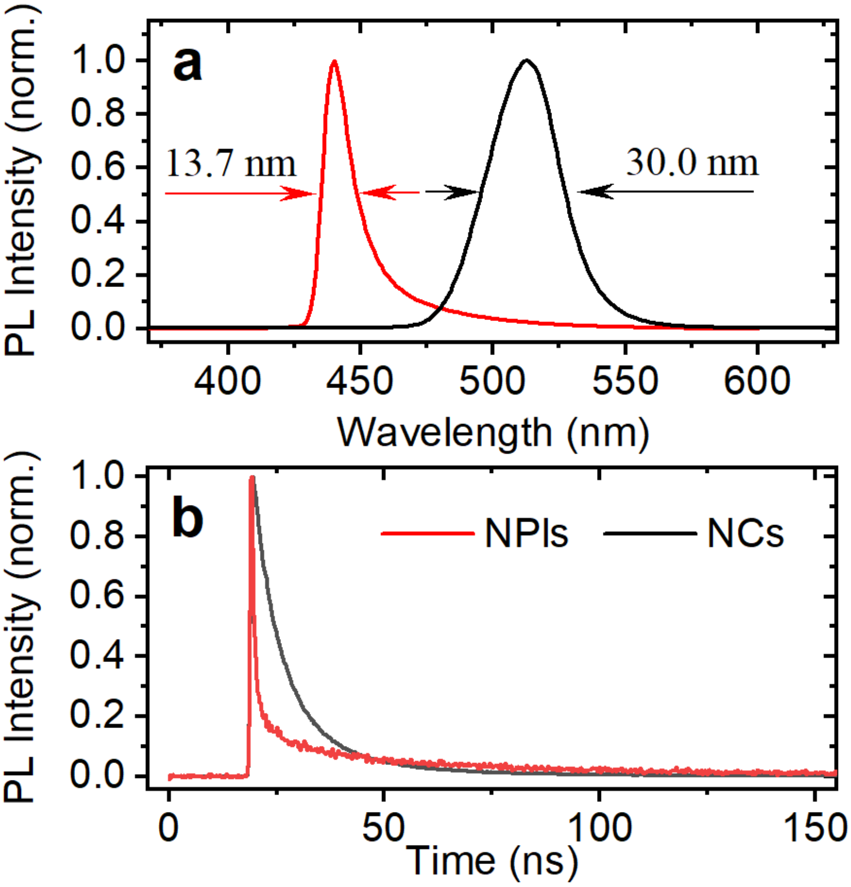

Fig.S14 PL spectra (a) and PL decay curves (b) recorded for the $FAPbBr_3$ NCs (black lines) and NPls (red lines).

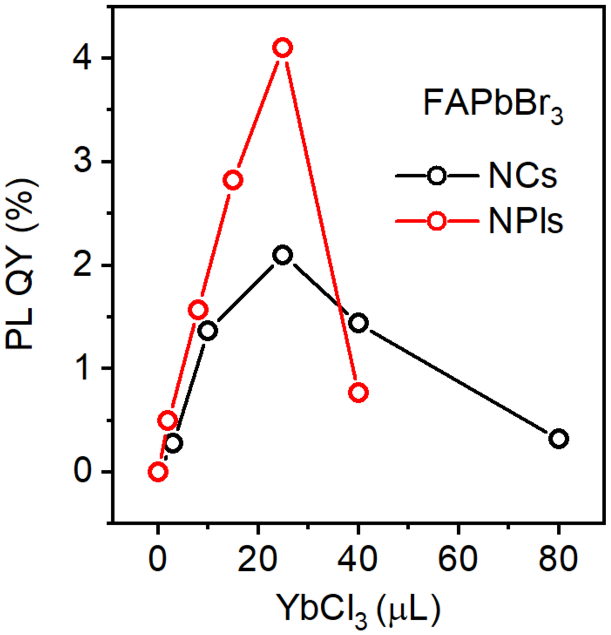

Fig.S15 PL QY of the Yb-related NIR photoluminescence from $FAPbBr_3$ NCs (black circles) and NPls (red circles) under the addition of different amounts of $YbCl_3$ precursor (in microliters).

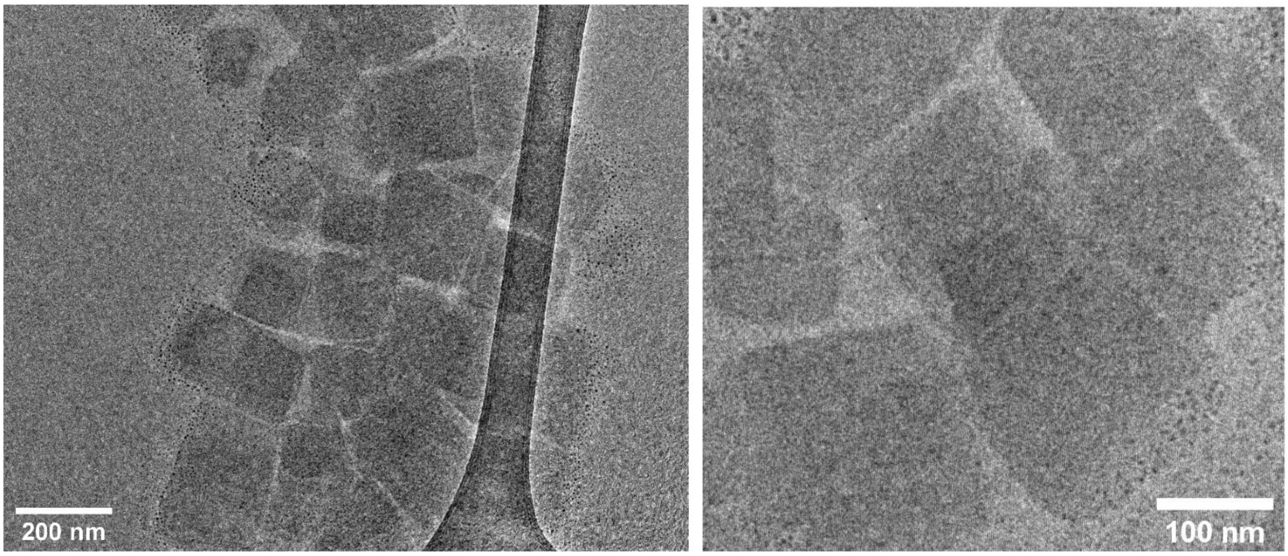

Fig.S16 TEM images of the doped Yb^{3+}:FAPbCl$_x$Br$_{3-x}$ NPls.

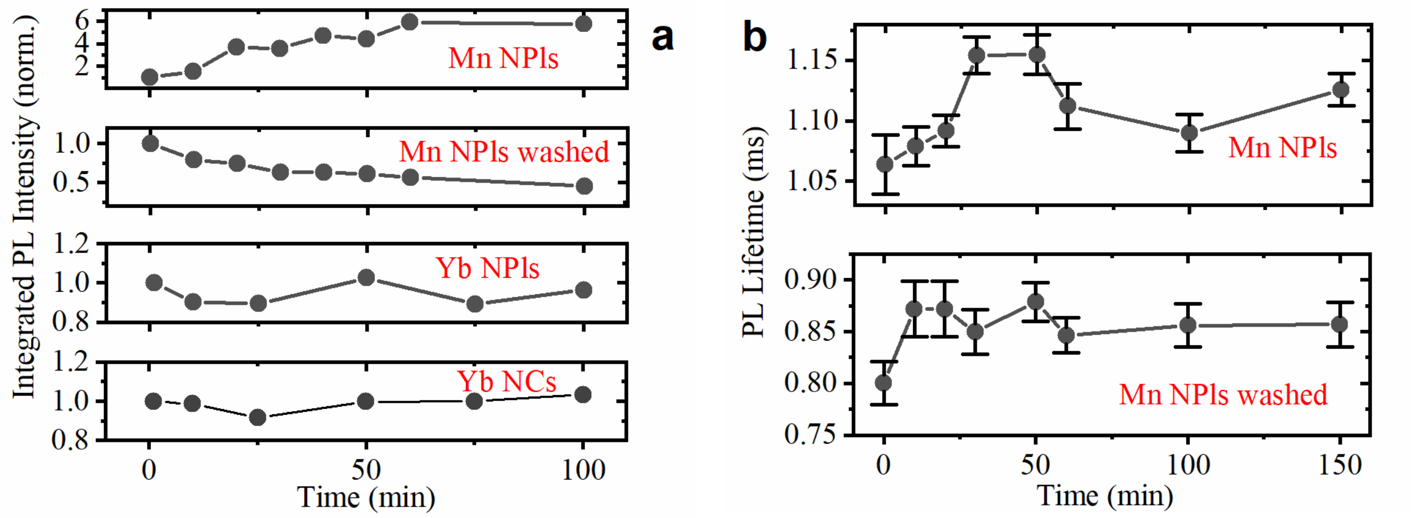

Fig.S17 (a) The time dependencies of the integrated intensity of the dopant-related PL for unwashed and washed Mn^{2+}-doped NPls and unwashed Yb^{3+}-doped NPls and NCs. (b) The time dependencies of Mn^{2+}-related PL lifetimes for unwashed and washed Mn^{2+}-doped NPls.

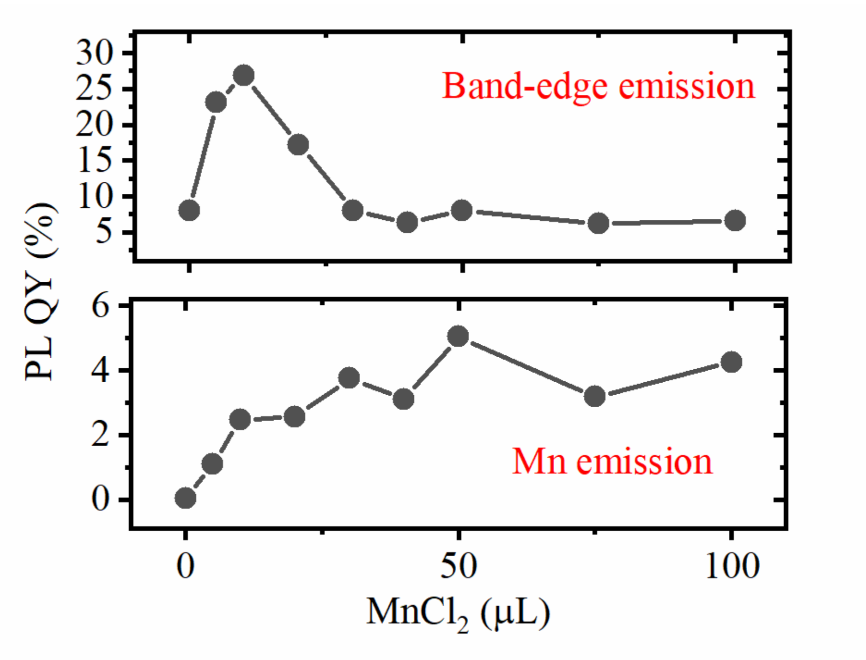

Fig.S18 The dependencies of the PLQY for the band-edge and Mn^{2+}-related emissions on the amount of $MnCl_2$ precursor obtained for the samples washed after the doping.

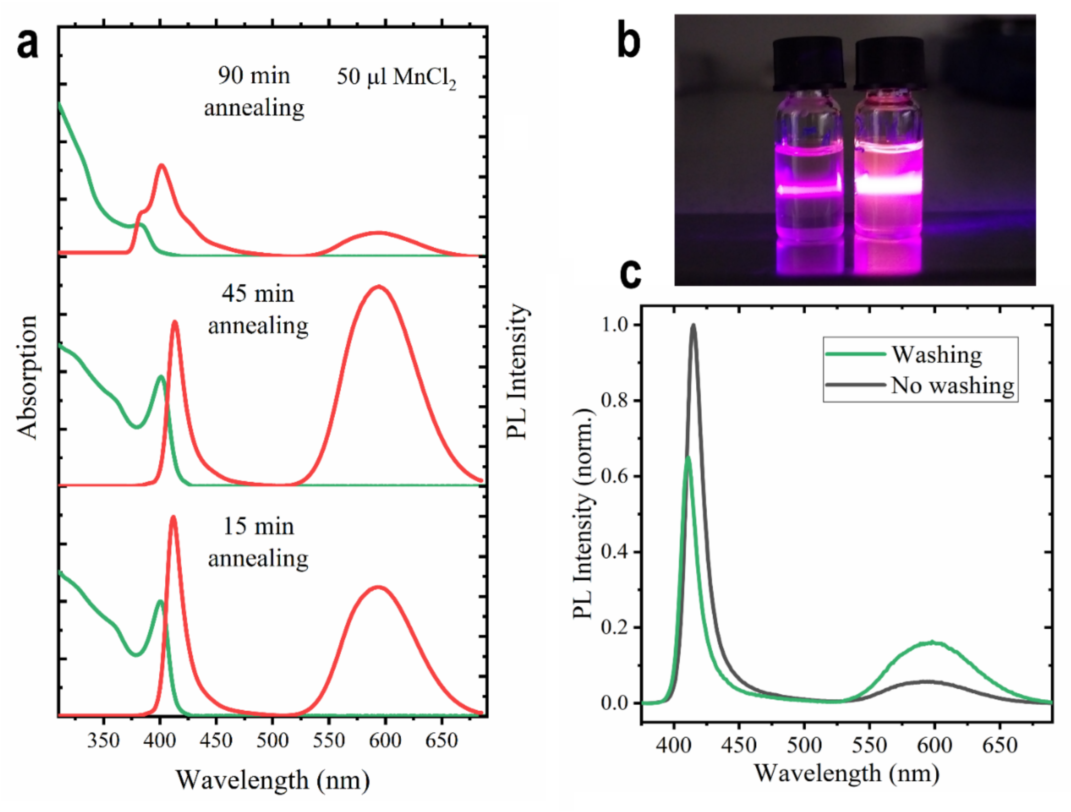

Fig.S19 (a) Absorption and PL spectra obtained for the Mn^{2+}:$CsPbCl_xBr_{3-x}$ NPls after different annealing times at a temperature of 60° C. (b) The photograph of colloidal solutions of as prepared and annealed Mn^{2+}:$CsPbCl_xBr_{3-x}$ NPls under illumination with a UV laser pointer. (c) PL spectra for Mn^{2+}:$CsPbCl_xBr_{3-x}$ NPls obtained *via* doping with and without preliminary washing with ethyl acetate.

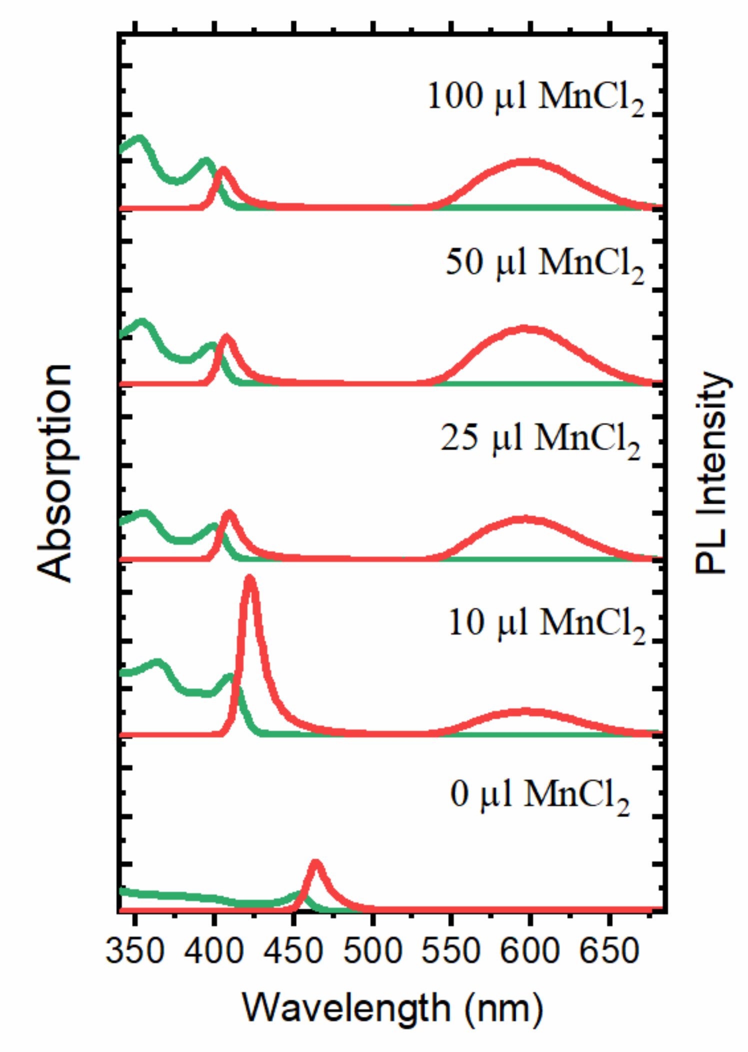

Fig.S20 Absorption and PL spectra taken for $CsPbBr_3$ NPls treated with different during the optimized doping procedure.

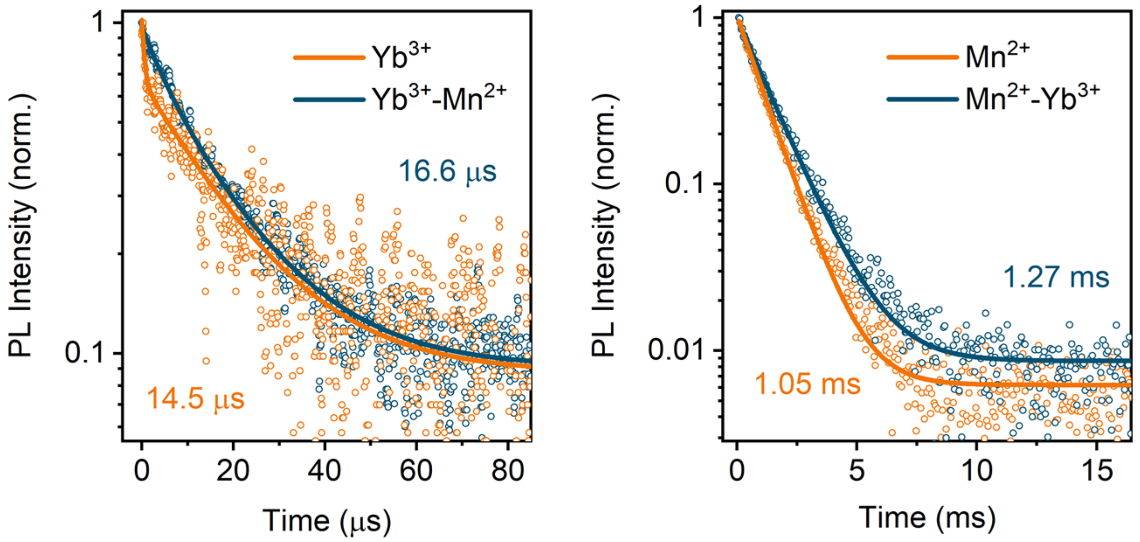

Fig.S21 PL decay curves for Yb^{3+} (left) and Mn^{2+} (right) ions in doped and co-doped $CsPbCl_xBr_{3-x}$ NPls.

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