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Supporting information

Lanthanide ions doping enabling highly sensitive and stable all-inorganic $CsPbI_2Br$ perovskite photodetectors

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Experimental section

Chemicals: $YbCl_3$H2O • $6H_2O$(99%), N, N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (99.8%), lead iodide were all purchased from Sigma-Aldrich Lead iodide (PbI_2, 99.999%), lead bromide ($PbBr_2$, 99.999%), cesium iodide (CsI), 2,2′,7,7′-tetrakis (N, N p-dimethoxy-phenylamino)-9,9′-spirobifluorene (Spiro-OMeTAD, 99.8%),4-tert-butylpyridine (4-TBP, 96%), Lithium bis (trifluoromethanesulfonyl) imide (Li-TFSI, 98%) were obtained from Xi'an Polymer Light Technology Corporation.

Preparation of PbI_2 and $PbBr_2$: 0.5 g PbI_2 or $PbBr_2$ was dissolved in 10 mL dimethylsulfoxide (DMSO) with heating and stirring at 60 °C. Then 10 mL toluene was slowly added into the PbI_2 or $PbBr_2$ solution, and a white precipitate was formed. After the precipitate was completely produced, it was filtered and then dried in a vacuum oven for 24 h to yield white PbI_2 and $PbBr_2$ adducts.

Device Fabrication: First, place the FTO substrate in deionized water and ethanol. Acetone, isopropanol for cleaning in order. Before use, put in UV/ozone environment for 15 minutes. SnO_2 layers were deposited by spin coating a solution of tin (IV) oxide (1ml) in ultrapure water (1mL) at a speed of 5000 rpm and annealing in air at 150 °C for 30 min. Then, continue to put into the ozone environment for 5 minutes. To prepare a $CsPbI_2Br:xLn^{3+}$ inorganic perovskite solution with DMSO adducts, 0.2338 g CsI, 0.2426 g PbI_2, and 0.2003 g $PbBr_2$ were dissolved into 1 mL mixed solvent of N, N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (3:2, v/v) to form a 0.9 m solution. Adjust the doping concentration according to the molar ratio of Pb and Ln3+. Spin-coat the prepared solution at 1000 rpm for 10 seconds, 4000 rpm for 40 seconds, and drop 0.2ml of chlorobenzene at the 20th second. Then, anneal at 150 °C for 15 minutes. Next, spin-coat 0.06ml Spiro-OMeTAD on the perovskite and spin at 3000rpm for 30 seconds. At last, on top of the Spiro-OMeTAD layer, a 100 nm Ag electrode was thermally evaporated and the active area was limited to 0.1 cm^2 by the metal mask.

Characterization: The current-voltage curves were tested by a solar simulator (ABET Sun 2000) and a Keithley 2400 source-meter under AM 1.5 G in ambient conditions from +1 V to −1 V. The light source was calibrated by a certified reference solar cell (RERA Solutions RR-1002) for the intensity of 1 kW m–2 illumination. SEM was carried out by a SIRION field-emission scanning electron microscope at 5 kV. The UV– vis absorption spectra were recorded by a UV-3600 (Shimadzu, Japan) spectrophotometer. Photoluminescence and excitation spectra were measured by RF-6000 (Shimadzu, Japan). Powder XRD was obtained on Rigaku D/max 2550 X-ray diffractometer with Kα radiation of Cu at a scanning speed of 15° min-1 and operated at 8 Kw. EIS measurement was recorded with AMETEK Versa STAT 4 at a frequency of 0.1 Hz–0.1 MHz in the dark. The external quantum efficiencies (EQE) were carried out on a Crowntech Qtest Station 1000 AD measurement system. Keithley 2601 source-measure unit was used to obtain density–voltage (*J–V*) curves of fabricated devices in the dark. The response speed of devices was performed with the transient photocurrent method (TPC). In order to minimize the adverse external effects of the electrical signal during transmission, the gold probe was used for TPC measurements. A femtosecond laser was used to generate a pulsed light source with an emission wavelength of 400 nm. The photodetector collected the pulse signal and then recorded the current pulse with a 1 GHz oscilloscope at a 5 GHz sampling rate and generated a corresponding TPC curve. The photocurrent decay time from a peak drop to approximately 1/*e* after a single exponential fitting of the TPC curve is defined as the response time. After that, the TPC curve is calculated to obtain the response time of the device. The measurement conditions were maintained at room temperature and measurements were made without any other illumination. The noise current was carried out on a proplus 9812D wafer-level 1/*f* noise characterization system.

Supplementary Figures

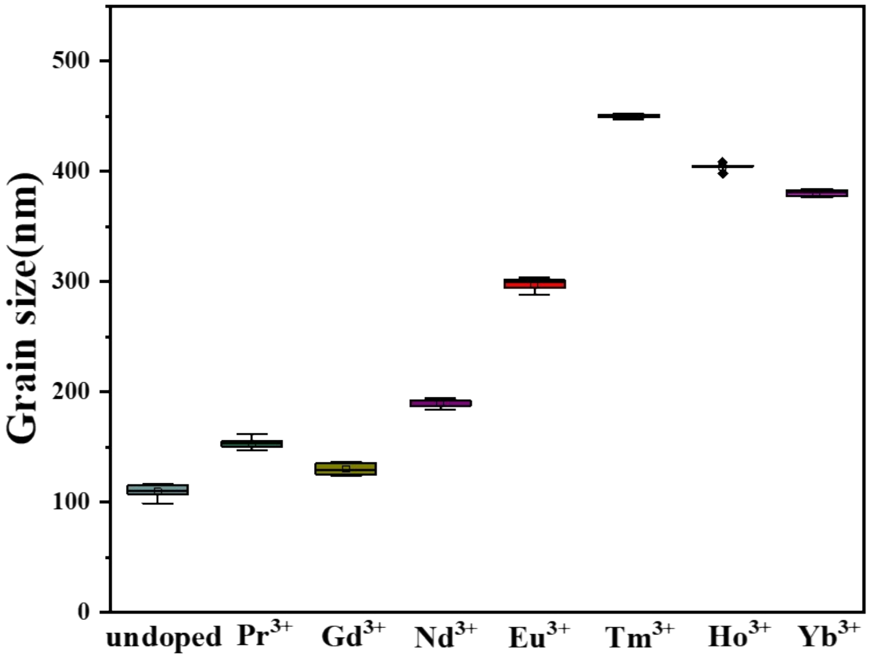

Figure S1. The average grain sizes of $CsPbI_2Br:Ln^{3+}$ (Ln^{3+}= Pr^{3+}, Gd^{3+}, Nd^{3+}, Eu^{3+}, Tm^{3+}, Ho^{3+}, Yb^{3+}) films.

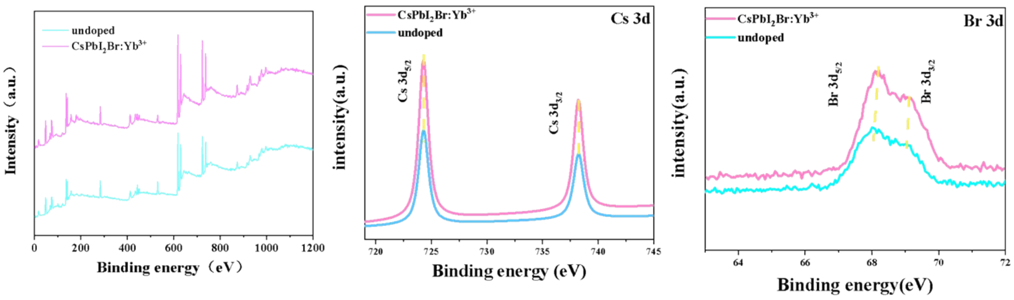

Figure S2. HR-XPS spectra of Cs^+ and Br^- in $CsPbI_2Br$ and Yb^{3+} doped $CsPbI_2Br$ films.

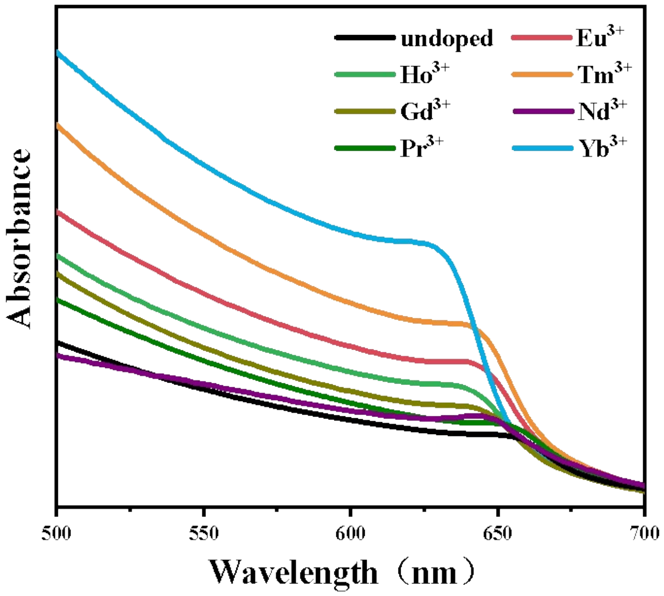

Figure S3. The absorbance spectra of $CsPbI_2Br:Ln^{3+}$ ($Ln^{3+}= Pr^{3+}, Gd^{3+}, Nd^{3+}, Eu^{3+}, Tm^{3+}, Ho^{3+}, Yb^{3+}$) films.

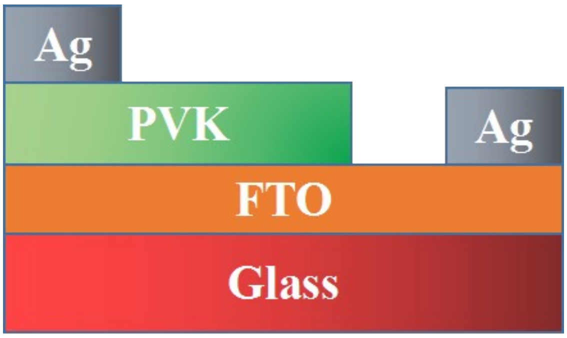

Figure S4. The structure of FTO/ $CsPbI_2Br:Ln^{3+}$/Ag.

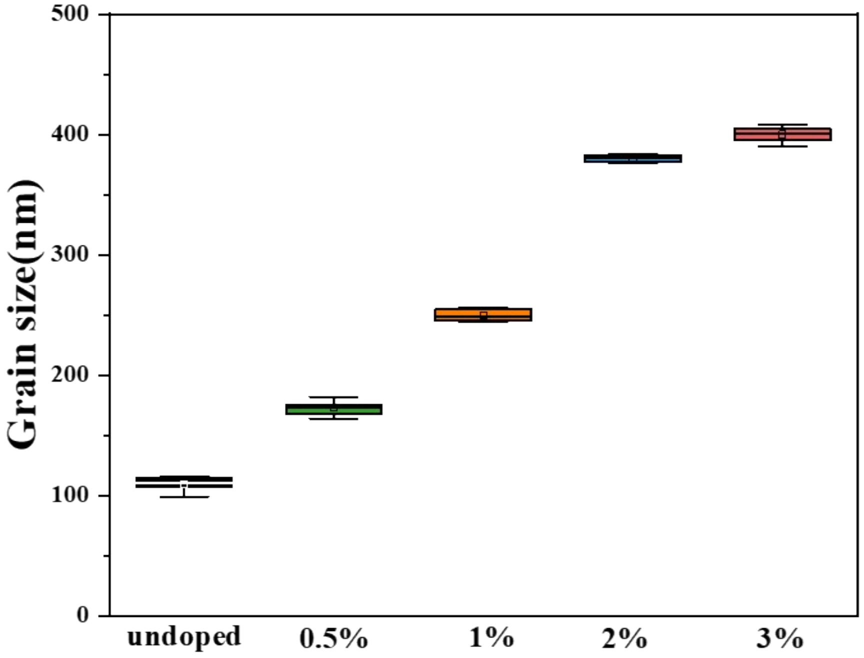

Figure S5. Absorption spectra of $CsPbI_2Br:xYb^{3+}$ (x=0, 0.5, 1, 2 and 3%) films.

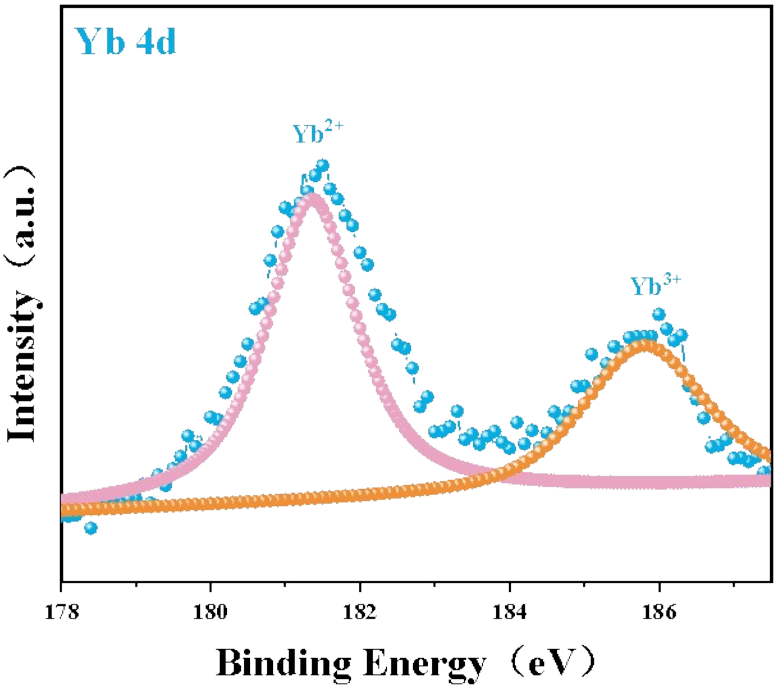

Figure S6. HR-XPS spectra of Yb^{2+} and Yb^{3+} in the $CsPbI_2Br$:Yb^{3+} film.

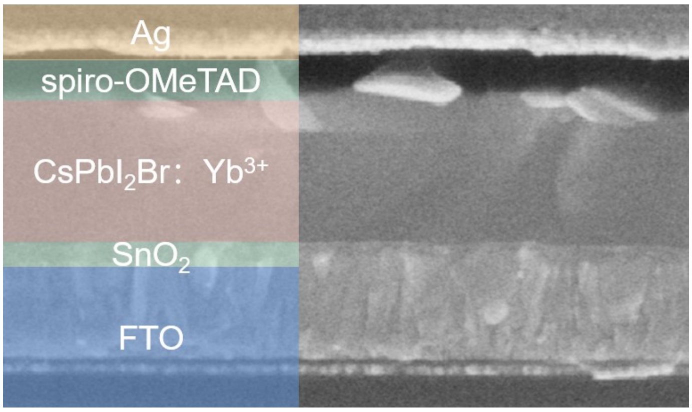

Figure S7. The cross-sectional scanning electron microscopy (SEM) image of photodetector .

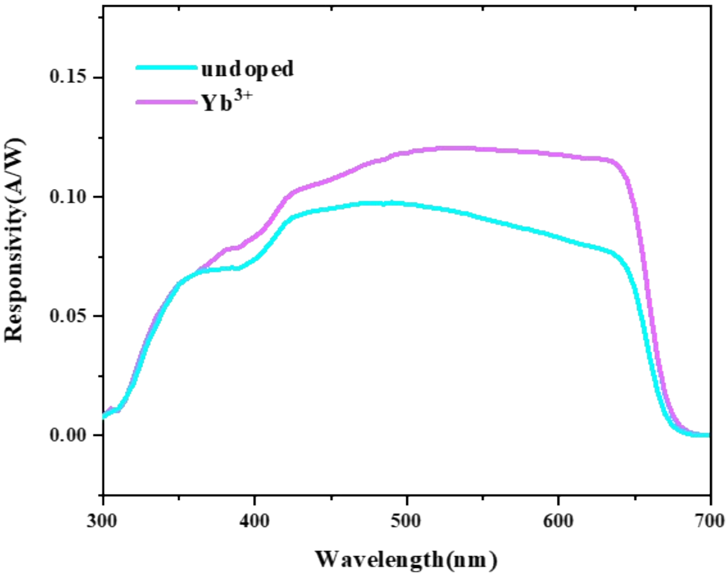

Figure S8. The Responsivity (R*) of undoped and Yb^{3+} doped films.

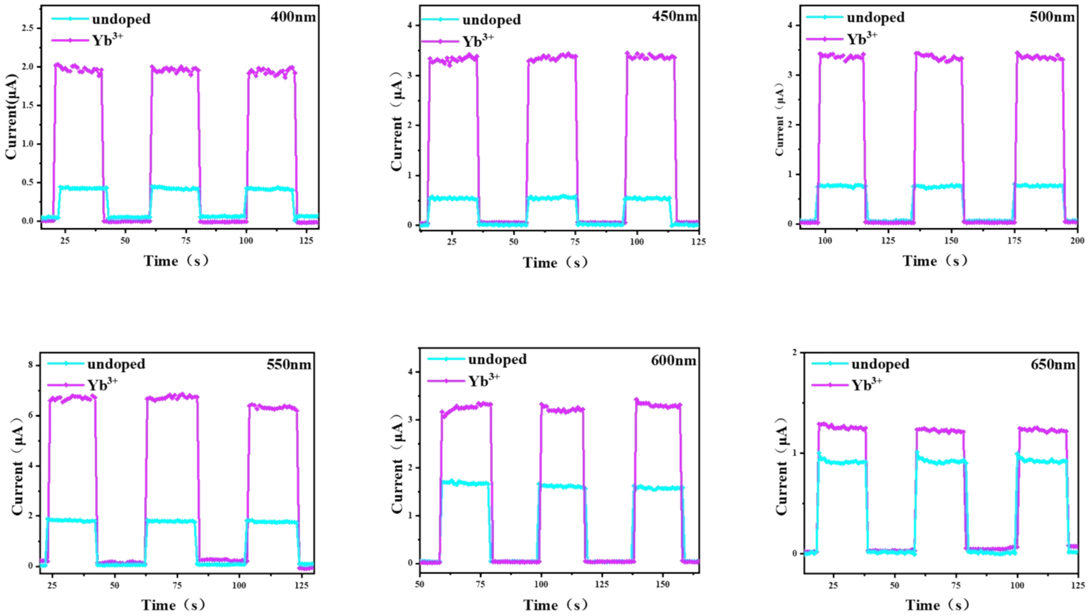

Figure S9. The photocurrents at different wavelengths (400, 450, 500, 550, 600, 650nm) of the devices before and after doping.

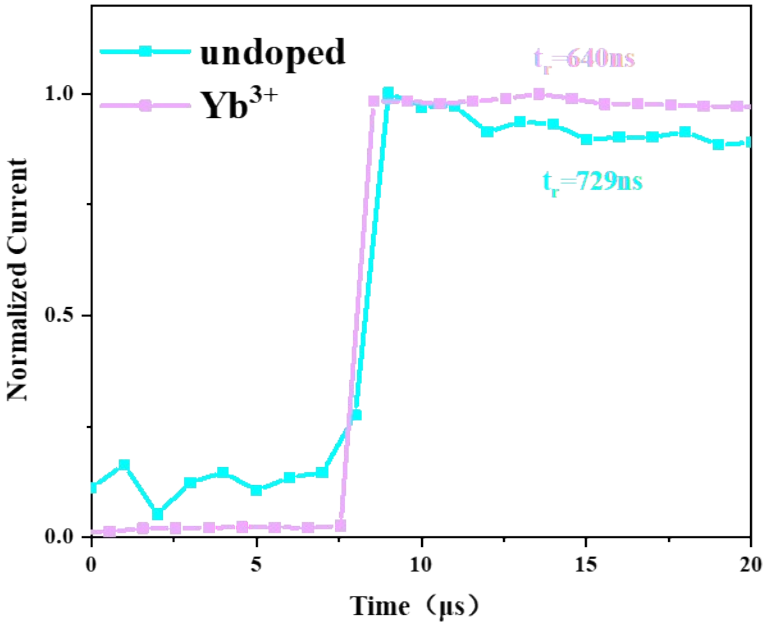

Figure S10. The rise response time of the devices before and after doping.

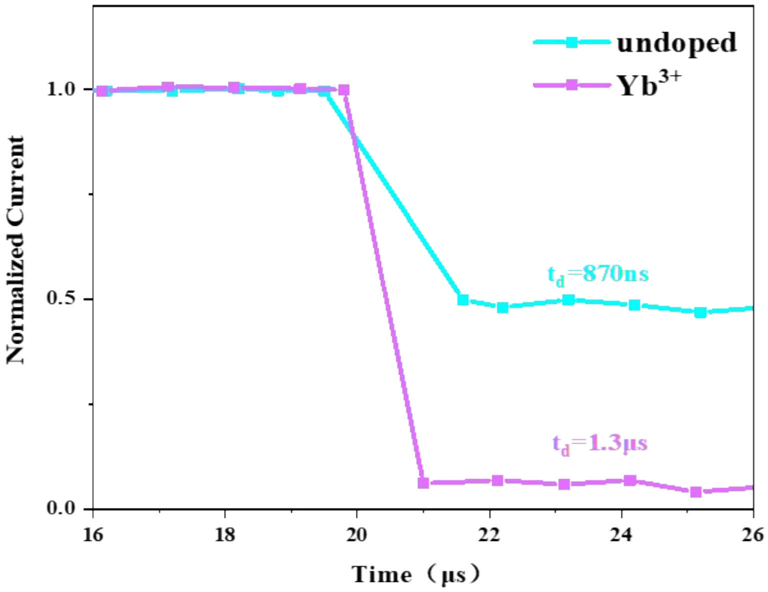

Figure S11. The drop response time of the devices before and after doping.

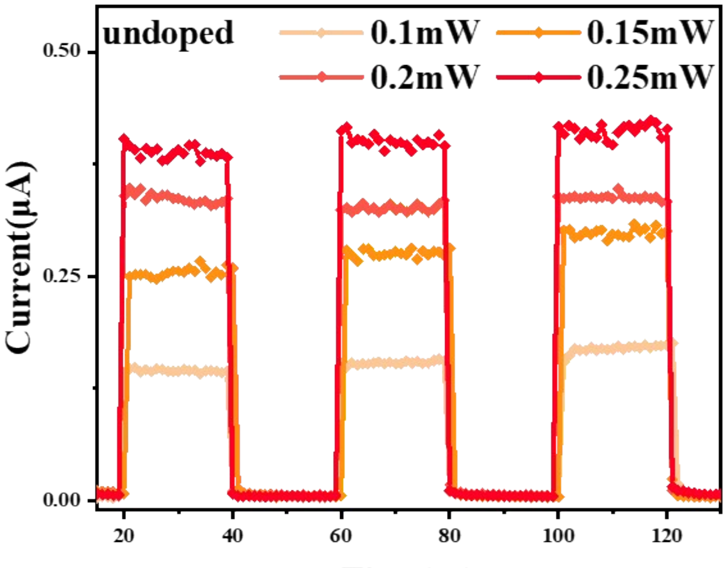

Figure S12. The photo currents at different optical power density of the devices before doping.

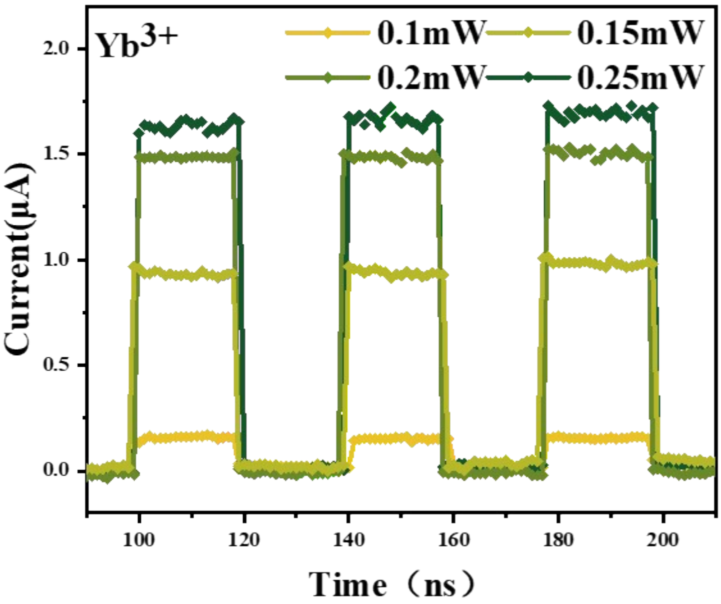

Figure S13. The photo currents at different optical power density of the devices after doping.

Supplementary Tables

$CsPbI_2Br:Ln^{3+}$	unoped	Eu^{3+}	Ho^{3+}	Tm^{3+}	Gd^{3+}	Nd^{3+}	Pr^{3+}	Yb^{3+}
hv（eV)	1.76	1.8	1.79	1.82	1.78	1.77	1.77	1.87

Table S1. The data of hν (eV) in $CsPbI_2Br:Ln^{3+}$ films.

$CsPbI_2Br:Ln^{3+}$	unoped	Eu^{3+}	Ho^{3+}	Tm^{3+}	Gd^{3+}	Nd^{3+}	Pr^{3+}	Yb^{3+}
Conductivity(10^{-4}S cm^{-1})	5.64	6.85	6.9	7.61	7.37	7.42	7.48	7.81
Rrec(Ω)	780.9	790.8	1116.1	1201.5	909.7	1137.9	857.7	1235.9
V_{TFL} electron(V)	0.46	0.41	0.35	0.35	0.38	0.38	0.35	0.32
Electron defect intensity (10^{15} cm^{-3})	5.835	5.239	4.406	4.425	4.761	4.763	4.430	4.059
V_{TFL} hole(V)	1.24	1.01	0.91	0.83	1.08	0.74	0.94	0.62
Hole defect intensity (10^{16} cm^{-3})	1.548	1.214	1.107	1.000	1.346	0.929	1.179	0.774

Table S2.The conductivity, Rrec, electron-defect intensity and hole-defect intensity $CsPbI_2Br:Ln^{3+}$ films.

$CsPbI_2Br:xYb^{3+}$x=	**0**	**0.5%**	**1%**	**2%**	**3%**
FWHM(degree)	**0.48**	**0.42**	**0.34**	**0.2**	**0.33**

Table S3. The FWHM of $CsPbI_2Br:xYb^{3+}$ (x = 0, 0.5, 1, 2, 3%).