Electronic Supporting Information

Efficient Energy Transfer in $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ Layered Perovskites and Anomalously Responsive Photodetectors

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Experimental method and characterization

Chemicals

Cesium chloride (CsCl; Macklin, 99.99%), cadmium chloride ($CdCl_2$; Aladdin, 99%), manganese (II) chloride ($MnCl_2$; 9dingchem, 99%), antimony chloride ($SbCl_3$; Aladdin, 99%), hydrochloric acid (HCl; ChengDu Chron Chemicals Co,.Ltd, AR, 37 wt% in water), hypophoaphoeous acid (H_3PO_2; Macklin, AR, 50 wt% in water) and ethanol (EtOH; Guangdong Guanghua Sci-Tech Co,.Ltd, AR) were used without any purification.

Synthesis of $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ microcrystals with Mn/(Mn+Cd) feed ratio = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1)

$Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ microcrystals were synthesis by a solvent thermal method. 2 mmol CsCl, 1 mmol $SbCl_3$, variable ratio of $CdCl_2$ and $MnCl_2$ while keeping the whole amount of $CdCl_2$ and

$MnCl_2$ to be 0.5 mmol, 8 mL HCl and 0.2 mL H_3PO_2 were added in the 25 mL stainless steel autoclave. The mixture solution was heated at 160 ℃ for 12 h and then cooled slowly to room temperature. The precipitated $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ microcrystals were washed with ethanol and were dried at 80 ℃ for 8 h.

Synthesis of $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$ single crystals

$Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$ single crystals was synthesis by solvent thermal method. 2 mmol CsCl, 1 mmol $SbCl_3$, 0.375 mmol $CdCl_2$, 0.125mmol $MnCl_2$, 8 mL HCl and 0.2 mL H_3PO_2 were added in the 25 mL stainless steel autoclave. The mixture solution was heated at 160 ℃ for 12 h and then cooled slowly to room temperature at a rate of 1℃ per hour. Finally, the obtained $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ single crystals were washed with ethanol and was dried at 80 ℃ for 8 h.

Fabrication of LED and Photodetector

LED device was fabricated by combining a UV-LED chip (365 nm). The $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$ powders were thoroughly mixed with the epoxy resin. Then, the mixture was coated on the surface of the LED chip. Finally, the LED device cured under the UV light. For photodetector fabrication, the vacuum evaporation method was used to deposit a certain thickness of low melting metal electrode on the surface of single crystal.

Material characterization

A SMARTLAB 3KW X-ray diffractometer with Cu Kα radiation (λ= 1.54059 Å) was used to collect the powder X-ray diffraction data in the 2θ range of 10°-70°. The scanning electron microscopy (SEM, Hitachi SU8020) was used to observe the morphology. The energy-dispersive spectrometry (EDS, Oxford X-Max Aztec) was used to collect the element composition and distribution. The Raman spectrum was characterized by WITec alpha300R Raman fluorescence spectrometer with a 532 nm laser as an excitation source. The photoluminescence (PL), PL excitation (PLE) spectrum, time-resolved photoluminescence (TRPL), photoluminescence quantum yields (PLQYs), temperature-dependent PL spectra, and temperature-dependent PL decay curve were obtained on the Edinburgh FLS-1000 spectrofluorometer and Horiba Jobin Yvon Fluorolog-3 spectrometer. The Lambda 750 ultraviolet-visible spectrophotometer was used to measure the absorption spectrum. The magnetic property was analyzed by a Lake Shore 7404

vibrating sample magnetometer (VSM). The photoelectric properties of the as-fabricated LED device, including the emission spectra, correlated color temperature (CCT), and Commission Internationale de L'Eclairage (CIE) chromaticity coordinate were obtained on an ATA-1000 (Everfine, China) optoelectronic analyzer.

Computational Details

The projector-augmented wave[1] method is used to calculate the band structure, as implemented in the Vienna Ab initio simulation package (VASP)[2]. The generalized gradient approximation of the Perdew-burke-Ernzerhof[3] parameterization is used for the exchange and correlation functional. The kinetic energy cutoff of 500 eV and a 4×4×4 Monkhorst-Pack k-mesh for the wavefunction basis set is used. The energy convergence criterion is set as 1.0×10^{-6} eV for structure relaxations.

Table S1. Elements content of $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ from the EDS data.

Mn/(Mn+Cd) feed ratio	Cs	Mn	Cd	Sb	Cl	Mn Occupancy	Cd Occupancy
0.0	23.63	-	5.68	11.37	59.32	-	1.00
0.1	22.07	0.59	5.07	11.35	60.91	0.10	0.89
0.2	22.67	0.79	4.70	11.49	60.35	0.16	0.84
0.3	20.97	1.33	3.90	11.06	62.73	0.25	0.75
0.4	23.14	2.11	3.4	11.77	59.58	0.38	0.62
0.5	21.83	2.56	3.66	11.25	60.70	0.41	0.59
0.6	22.90	3.43	2.37	11.48	59.82	0.59	0.41
0.7	22.59	3.19	1.57	11.41	61.25	0.67	0.33
0.8	23.08	3.69	1.02	11.59	60.62	0.78	0.22
0.9	22.47	4.86	0.78	11.54	60.35	0.86	0.14
1.0	22.44	5.89	-	11.36	60.32	1.00	-

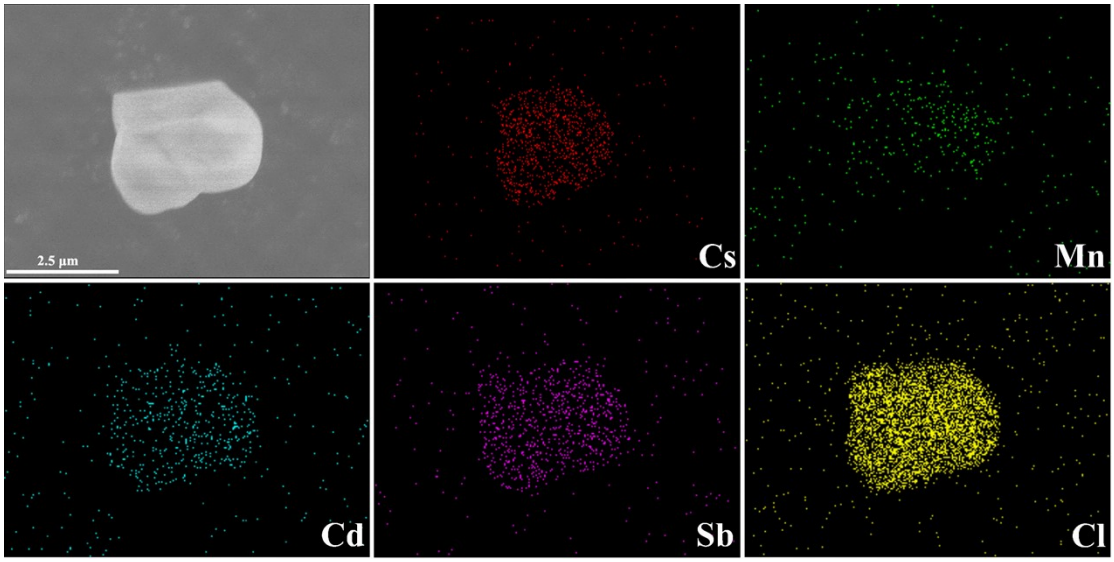

Fig. S1 SEM image of the microcrystal and the corresponding mapping elements distribution in $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$.

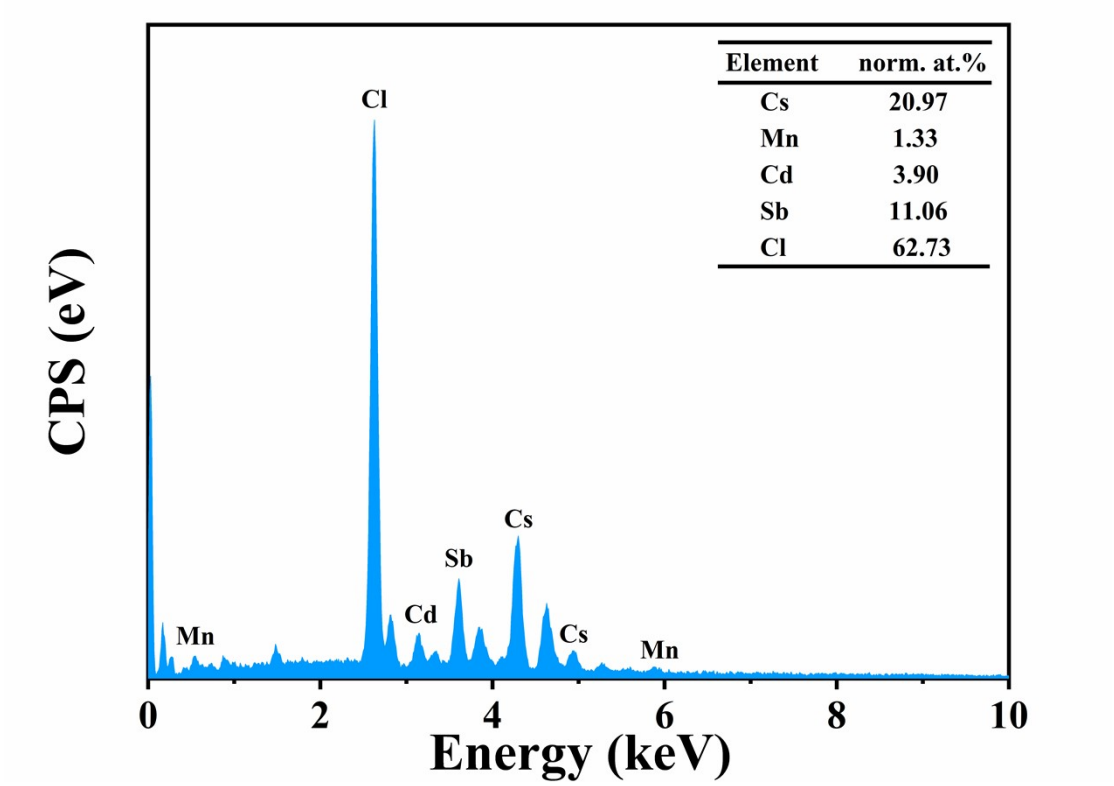

Fig. S2 Energy disperse spectrum of $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$.

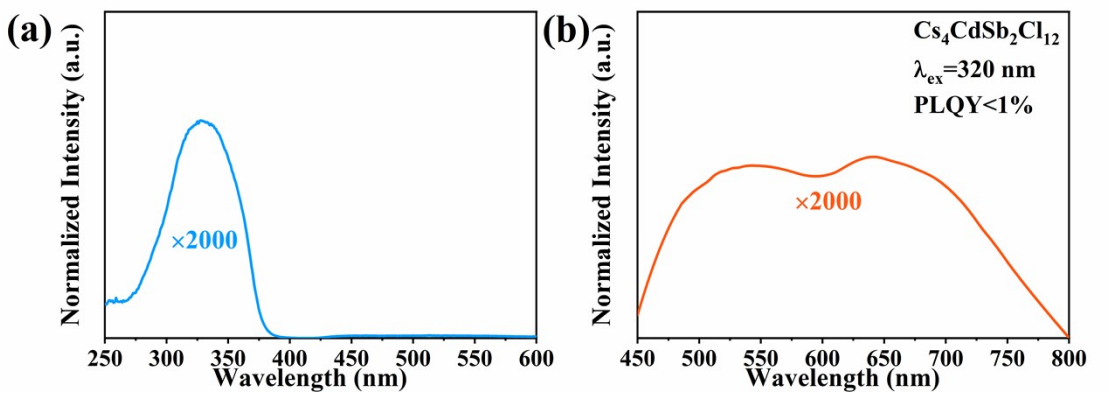

Fig. S3 The (a) excitation and (b) emission spectra of $Cs_4CdSb_2Cl_{12}$.

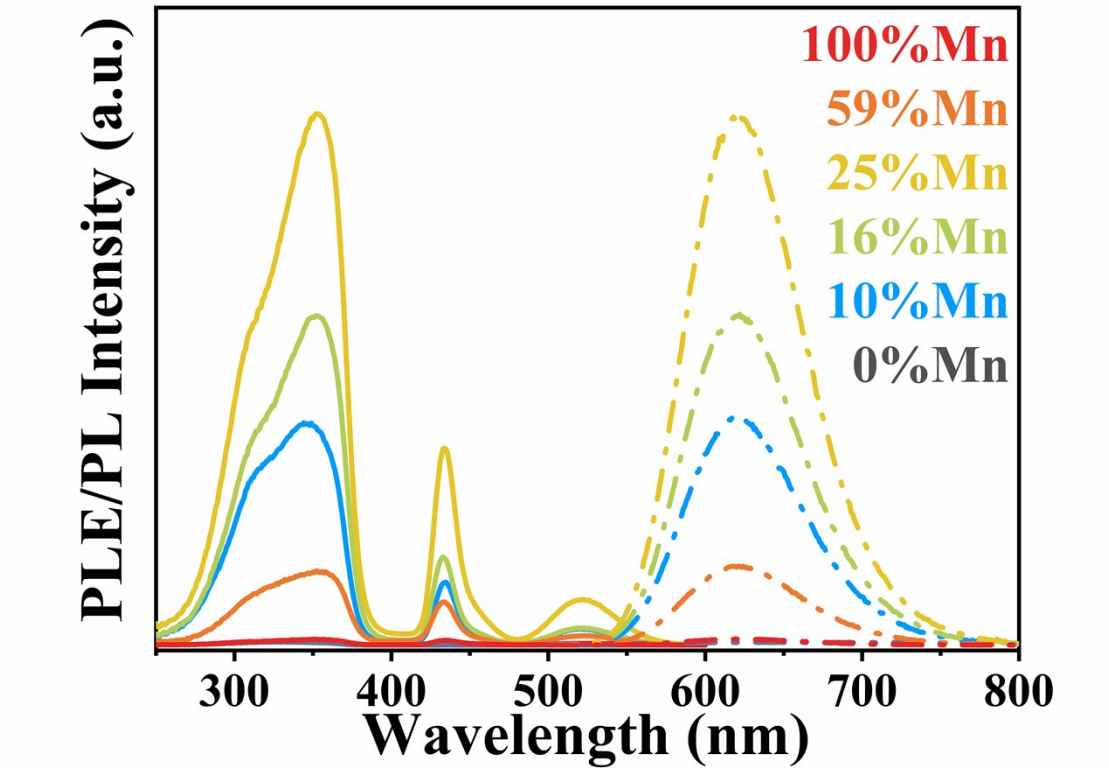

Fig. S4 PLE/PL spectrum of $Cs_4CdSb_2Cl_{12}$ with different Mn^{2+} concentration.

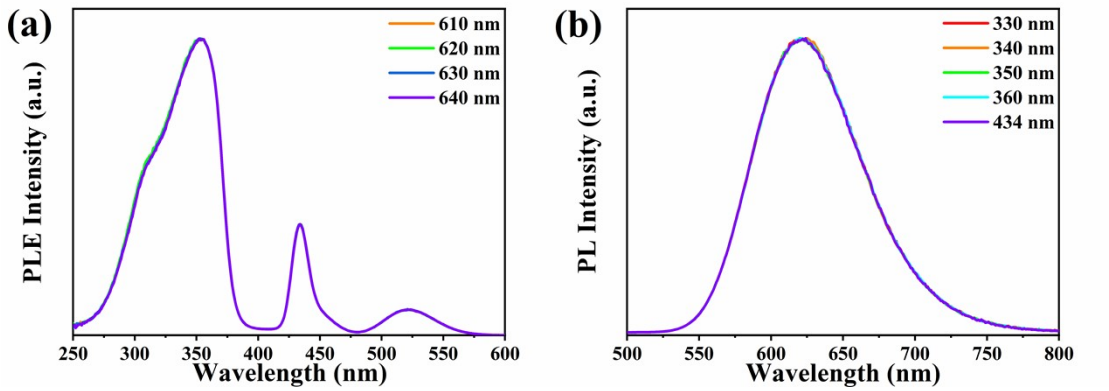

Fig. S5 (a) The excitation spectra at emission wavelengths of 610 nm, 620 nm, 630 nm, 640 nm

and (b) PL spectra under 330 nm, 340 nm, 350 nm, 360nm and 434 nm excitation of $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$, respectively.

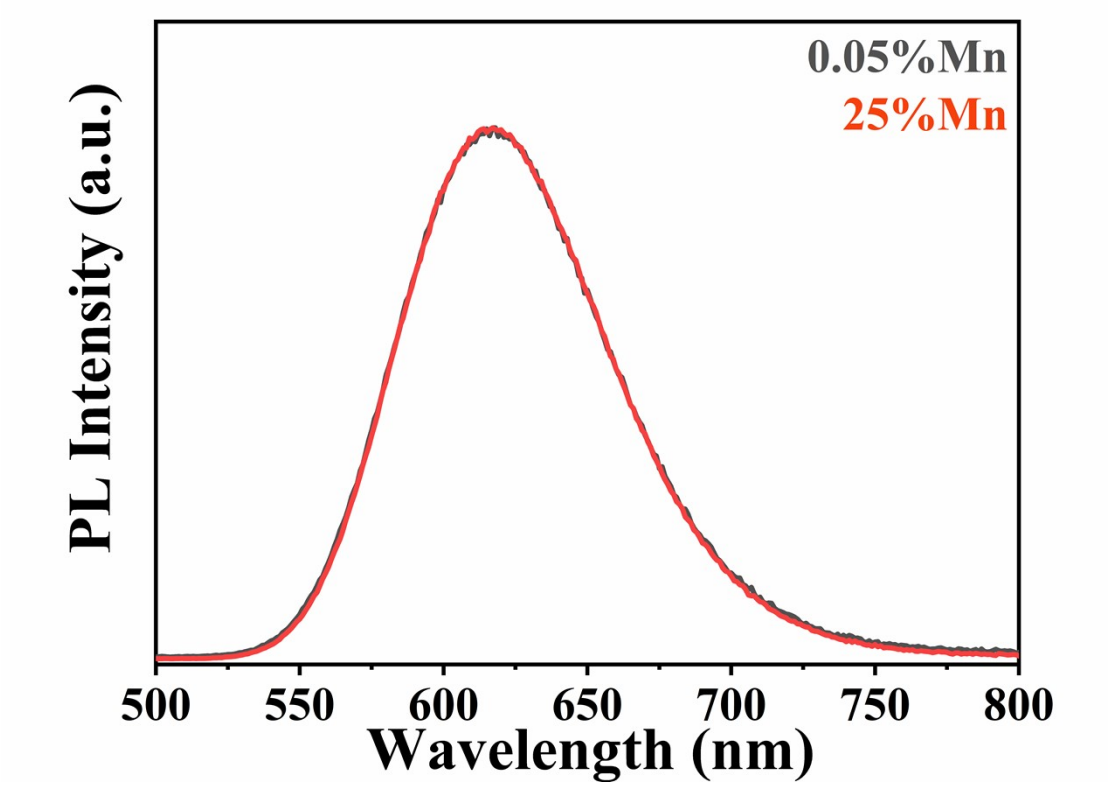

Fig. S6 The normalized PL spectrum of $Cs_4CdSb_2Cl_{12}$ with Mn content x=0.05% and x=25%.

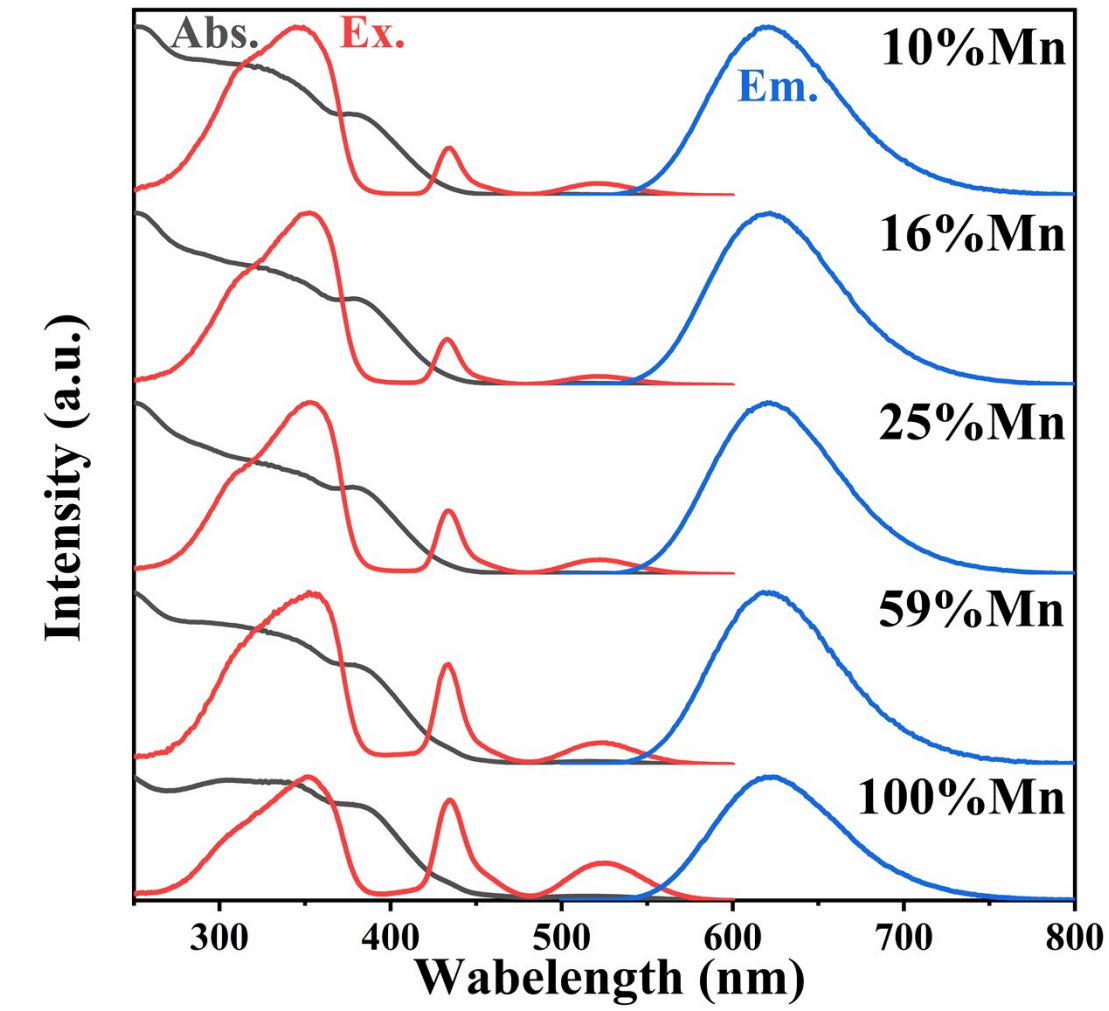

Fig. S7 Absorbance (dark gray), excitation (red) and emission (blue) spectrum with different Mn concentration.

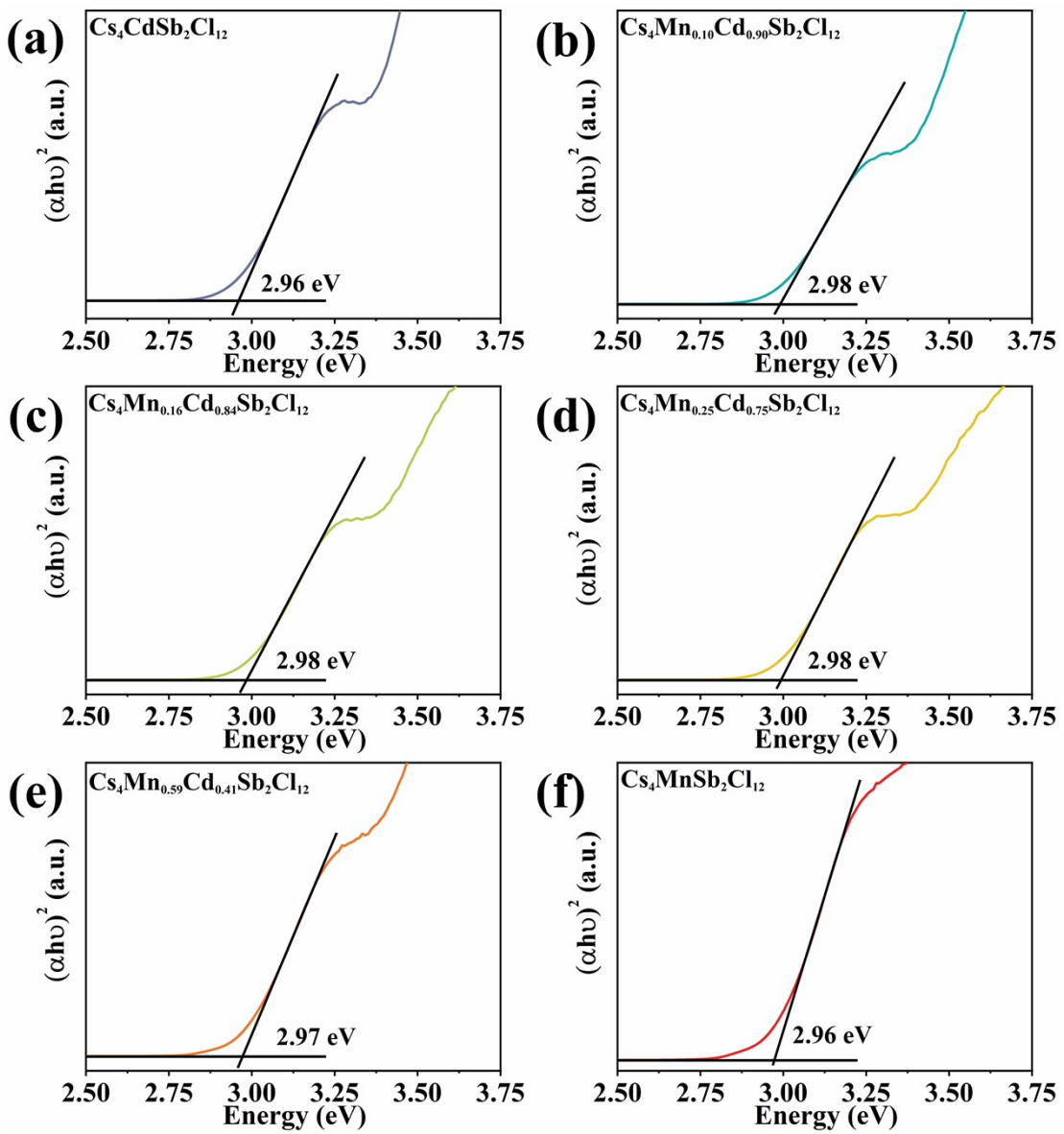

Fig. S8 The Tauc plots of $Cs_4Mn_xCd_{1-x}Sb_2Cl_{12}$ with different Mn concentration.

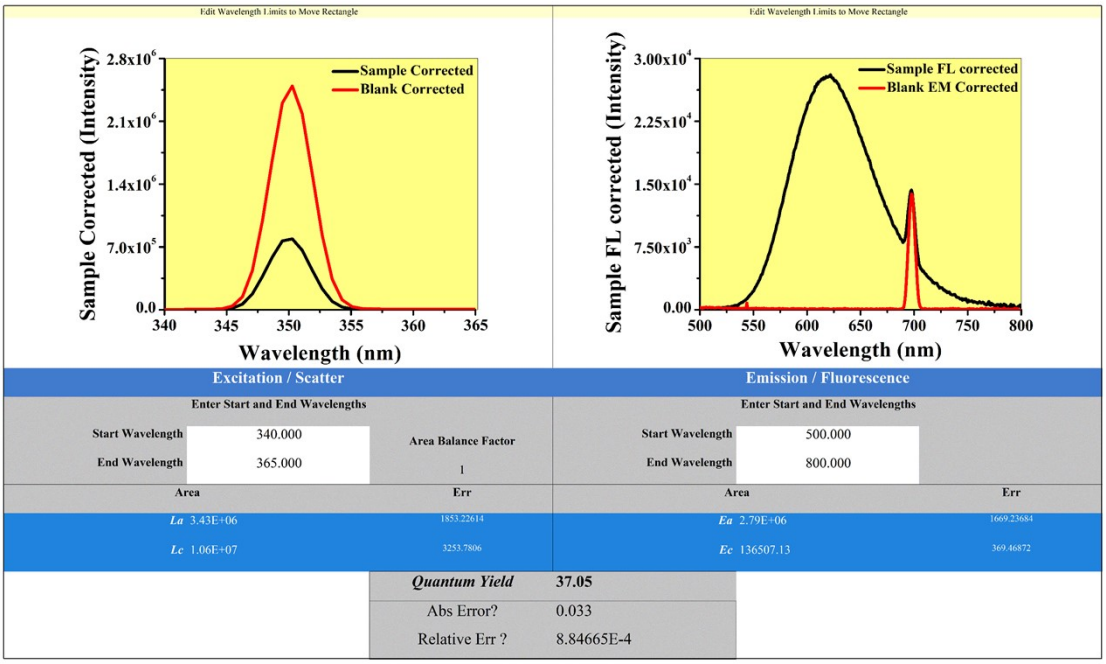

Fig. S9 The PLQY measurement view of $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$ sample (the black curve) shows that the PLQY is as high as 37.05%. The excitation wavelength was 350 nm. The red curve is the reference view of the blank. The peak at 700 nm of the emission spectrum on the right panel is the second diffraction of the excitation wavelength.

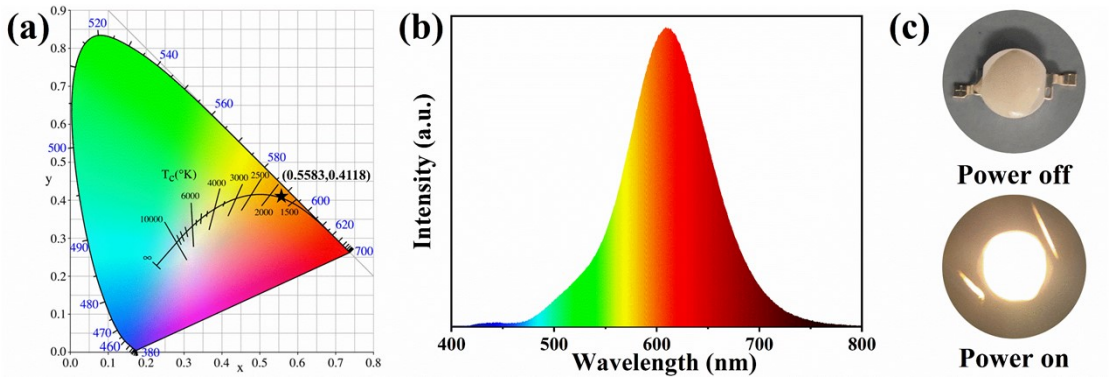

Fig. S10 (a) CIE chromaticity diagram corresponding to emission spectrum. (b) The emission spectrum of the LED based on $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$. (c) Packaging of LED device and effects of power on/off.

Table S2. The PL lifetime fitting result of $Cs_4CdSb_2Cl_{12}$ with different Mn concentration.

Mn concentration	A_1	τ_1	A_2	τ_2
0%	1.12856	1.66 μs	-	-
10%	0.87008	3.39 ms	-	-
16%	0.94655	3.24 ms	-	-
25%	0.94816	3.02 ms	-	-
38%	0.90732	2.45 ms	-	-
41%	0.45892	1.80 ms	0.47896	242.11 μs
59%	0.30306	835.32 μs	0.71814	117.16 μs
67%	0.38177	275.95 μs	0.60365	74.04 μs
78%	0.21080	126.20 μs	0.81293	44.87 μs
86%	1.0527	42.40 μs	-	-
100%	0.91808	20.03 μs	-	-

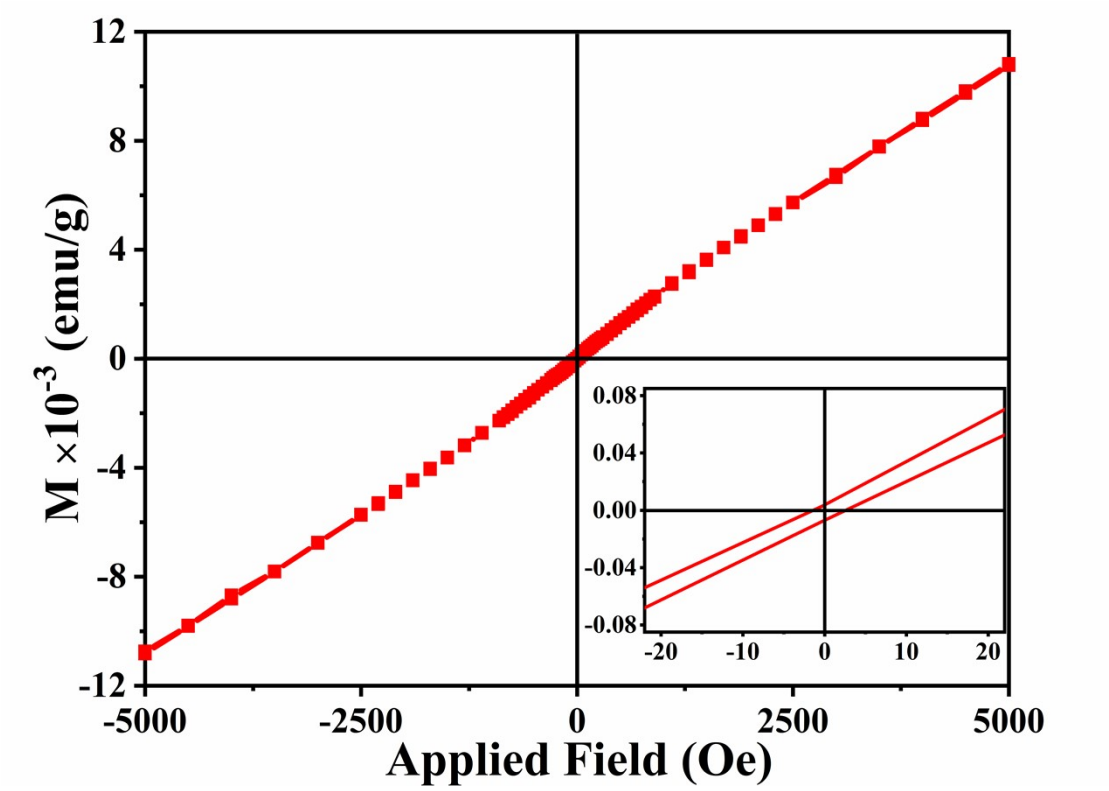

Fig. S11 Magnetic hysteresis loop of $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$ at room temperature. Insert: Magnetic hysteresis loop near zero field.

Table S3. The temperature-dependent PL lifetime fitting result of $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$.

Temperature (K)	PL Lifetime (ms)	Temperature (K)	PL Lifetime (ms)
80	5.85	260	3.40
100	6.10	280	3.13
120	5.78	300	2.85
140	5.38	320	2.6
160	4.97	340	2.18
180	4.59	360	1.93
200	4.26	380	1.90
220	3.97	400	1.51
240	3.67	-	-

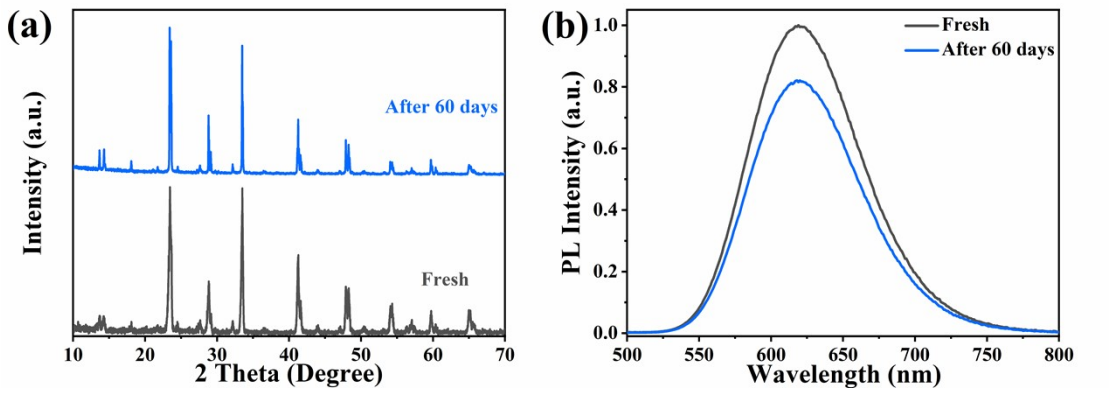

Fig. S12 (a) XDR of fresh and aged $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$. (b) PL intensity of fresh and aged $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$.

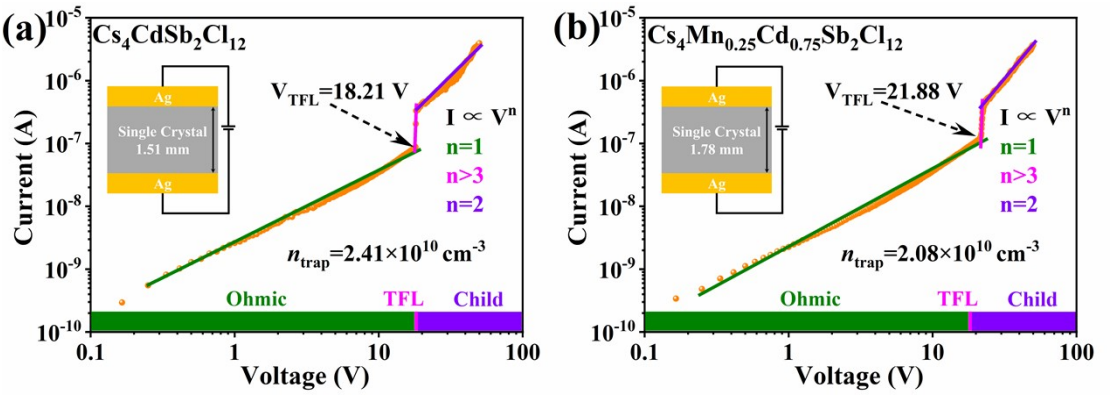

Fig. S13 I-V curve to derive the trap density of the (a) $Cs_4CdSb_2Cl_{12}$ and (b)

$Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$ single crystals.

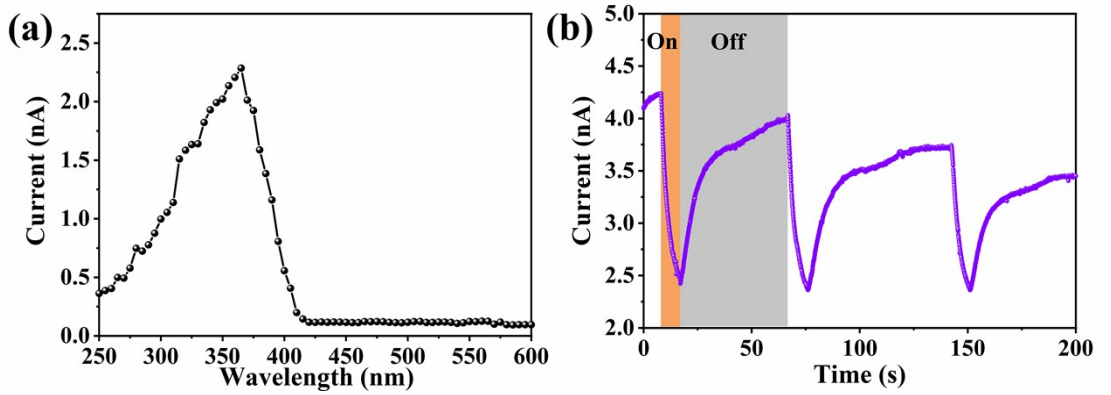

Fig. S14 (a) Photoresponse spectrum and (b) on-off curve of multiple switching cycles and photoresponse spectrum of $Cs_4Mn_{0.25}Cd_{0.75}Sb_2Cl_{12}$ SC device.

REFERENCES

[1]Blochl, P. E., Projector augmented-wave method. *Phys Rev B Condens Matter* **1994,** *50* (24), 17953-17979.

[2]Kresse, G.; Furthmuller, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B* **1996,** *54* (16), 11169-11186.

[3]Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized gradient approximation made simple. *Physical Review Letters* **1996,** *77* (18), 3865-3868.