Electronic Supporting Information

Metal Co-doped Cesium Manganese Chlorines Nanocrystals with Highly Efficiency and Tunable Red Emission

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Experimental Section

Materials: Cesium carbonate (Cs_2CO_3, 99%, Aladdin), Manganese chloride tetrahydrate ($MnCl_2{\cdot}4H_2O$, 99.99%, Macklin), Thulium chloride hexahydrate ($TmCl_3{\cdot}6H_2O$, 99.99%, Aladdin), Ytterbium chloride hexahydrate ($YbCl_3{\cdot}6H_2O$, 99.99%, Aladdin), Erbium chloride hexahydrate ($ErCl_3{\cdot}6H_2O$, 99.99%, Macklin) 1-octadecene (ODE, ≥90%, Macklin), oleic acid (OA, 85%, Aladdin), oleylamine (OAm, 80-90%, Aladdin), ethyl acetate ($C_4H_8O_2$, Shanghai test, 99.5%), n-octane (C_8H_{18}, 96%, Macklin). All chemicals were used without further purification.

Preparation of Cesium oleate precursors: Cs_2CO_3 (0.36 g, 1.1 mmoL), octadecene (15 mL), and oleic acid (1.5 mL) were added into 100 mL 3-neck flask, exhausted for half an hour at 120°C, and then heated to 150°C under Ar atmosphere until all Cs_2CO_3 reacted with OA. The solution was kept at 120°C to avoid solidification before injection.

Synthesis of $CsMnCl_3$ NCs: $MnCl_2{\cdot}4H_2O$ (0.0744 g, 0.376 mmol), OA (1.5 mL), OAm (0.5 mL), and ODE (10 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The temperature was increased to 140°C under Ar atmosphere. The preheated Cs-oleate solution (0.8 mL, 0.035 mmoL) was swiftly injected into the transparent precursor solution. After 5 seconds, the reaction mixture was cooled down using an ice bath.

Purification of the $CsMnCl_3$ NCs: Ethyl acetate was added into the crude solution at a volume ratio of 1:3 and the mixture were centrifuged for 1 min at 8000 rpm. The precipitate was dispersed into 1.5 mL of hexane to obtain a clear solution.

Synthesis of Tm^{3+}-$CsMnCl_3$ NCs: $MnCl_2{\cdot}4H_2O$ (0.072-0.065 g, 0.365-0.327 mmol), $TmCl_3{\cdot}6H_2O$ (0.004-0.019 g, 0.011-0.049 mmoL), OA (1.5 mL), OAm (0.5 mL), and ODE (10 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The other procedures were the same as for the synthesis of the $CsMnCl_3$ NCs.

Synthesis of Yb^{3+}-$CsMnCl_3$ NCs: $MnCl_2{\cdot}4H_2O$ (0.072-0.065 g, 0.365-0.327 mmol), $YbCl_3{\cdot}6H_2O$ (0.004-0.022g,0.011-0.056mmoL), OA (1.5 mL), OAm (0.5 mL), and ODE (10 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The other procedures were the same as for the synthesis of the $CsMnCl_3$ NCs.

Synthesis of Er^{3+}-$CsMnCl_3$ NCs: $MnCl_2{\cdot}4H_2O$ (0.072-0.065 g, 0.365-0.327 mmol), $ErCl_3{\cdot}6H_2O$ (0.004-0.021 g, 0.011-0.056 mmoL), OA (1.5 mL), OAm (0.5 mL), and ODE (10 mL) were loaded into a 100 mL 3-neck flask and degassed for half an hour at 120°C under Ar flow. The other procedures were the same as for the synthesis of the $CsMnCl_3$ NCs.

Characterizations: The transmission electron microscopy (TEM) images were taken on a transmission electron microscope (Tecnai 12). The HR-TEM images and EDS elemental mappings were taken on a field emission transmission electron microscope (Tecnai G2 F30 S-TWIN). Steady-state PL spectra were measured by the F-7000 fluorescence spectrometer 2014XHTM158. Ultraviolet-visible (UV-vis) absorption spectra were carried out with LAMBDA 650 spectrometer (PerkinElmer, USA). The X-ray

diffraction (XRD) was performed on a D8 ADVANCE diffractometer. The absolute PLQY of NCs solution was determined using a Quantaurus-QY absolute photoluminescence quantum yield spectrometer (C11347-11, Hamamatsu Photonics, Japan). The time-resolved decay data were performed on an Edinburgh FLS1000 fluorescence spectrometer.

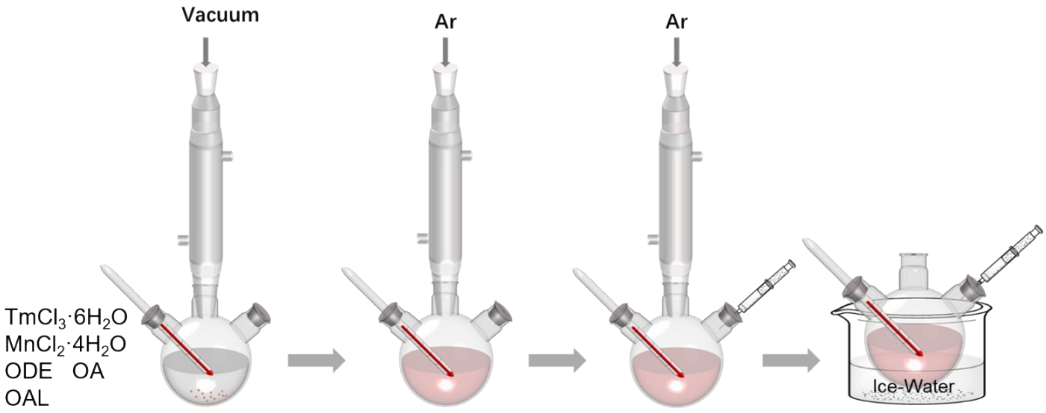

Figure S1. Synthesis of undoped and Tm-doped $CsMnCl_3$ using hot-injection method.

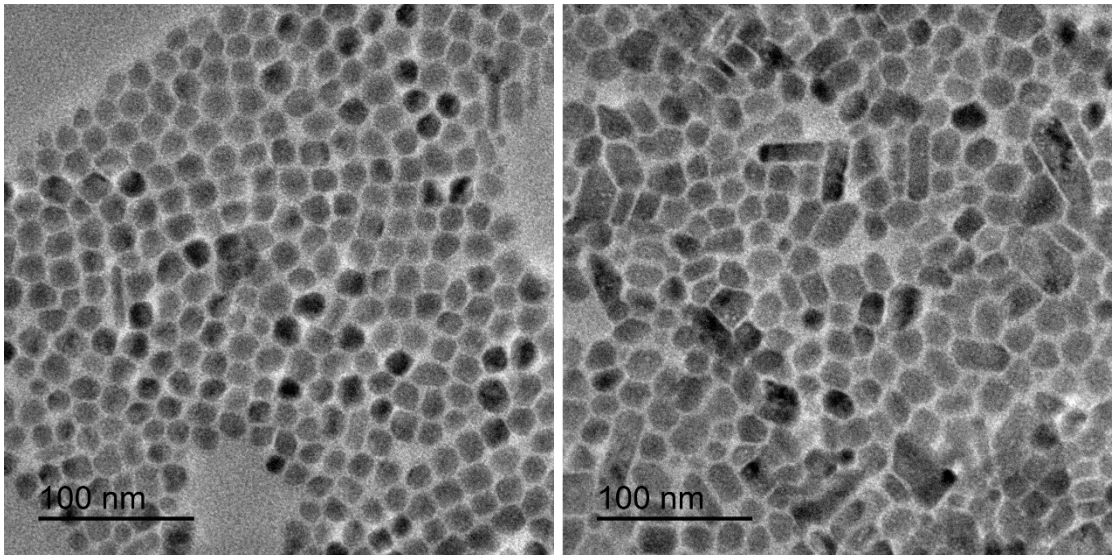

Figure S2. TEM images of $CsMnCl_3$ NCs dispersed in octane (left) and tetradecane (right).

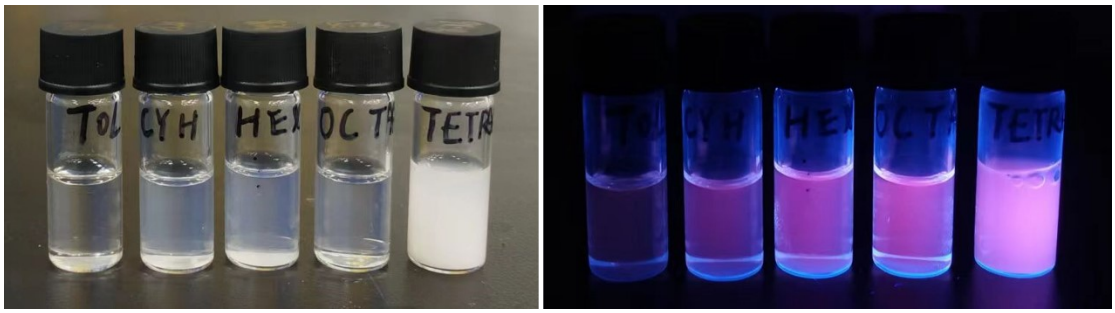

Figure S3. The photographs of toluene, cyclohexane, n-hexane, octane, tetradecane solution of $CsMnCl_3$ NCs under natural light (left) and 365 nm UV lamps (right), respectively.

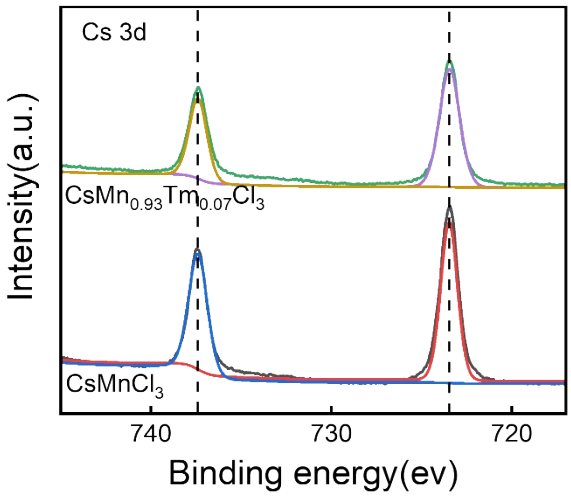

Figure S4. XPS data of Cs 3d for Tm^{3+}-$CsMnCl_3$ and $CsMnCl_3$ NCs.

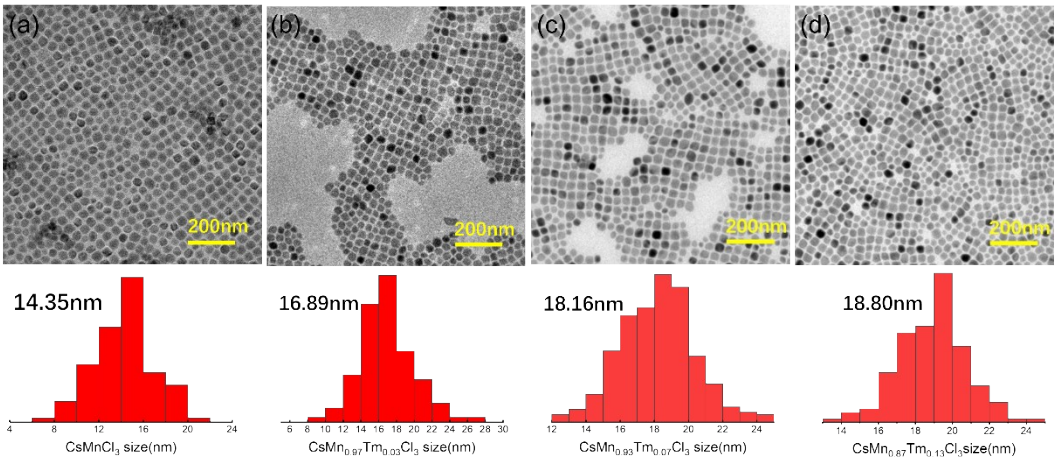

Figure S5. TEM images (above) and corresponding size distributions (below) of (a) 0%, (b) 3%, (c) 7%, and (d) 13% Tm doing of $CsMnCl_3$ NCs.

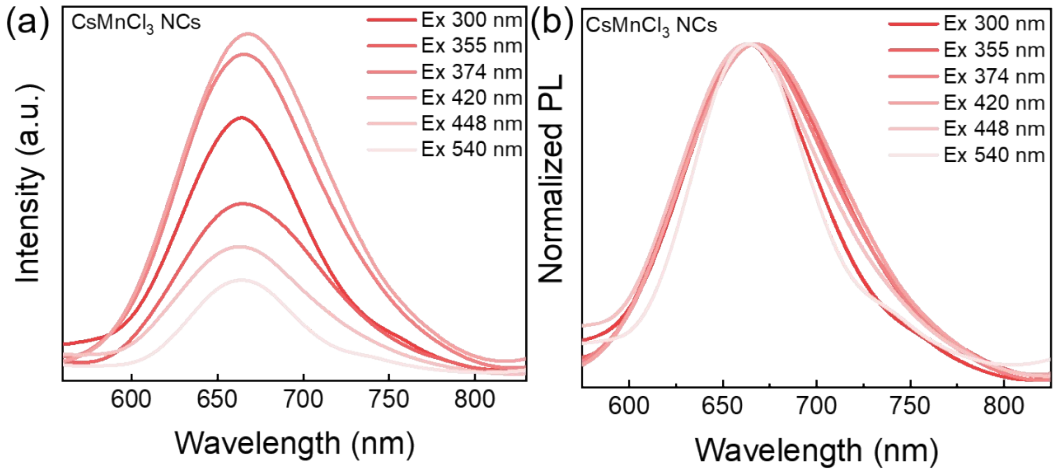

Figure S6. The PL (a) and normalized PL (b) emission spectra of undoped $CsMnCl_3$ NCs after illuminations at the six different excitation wavelengths.

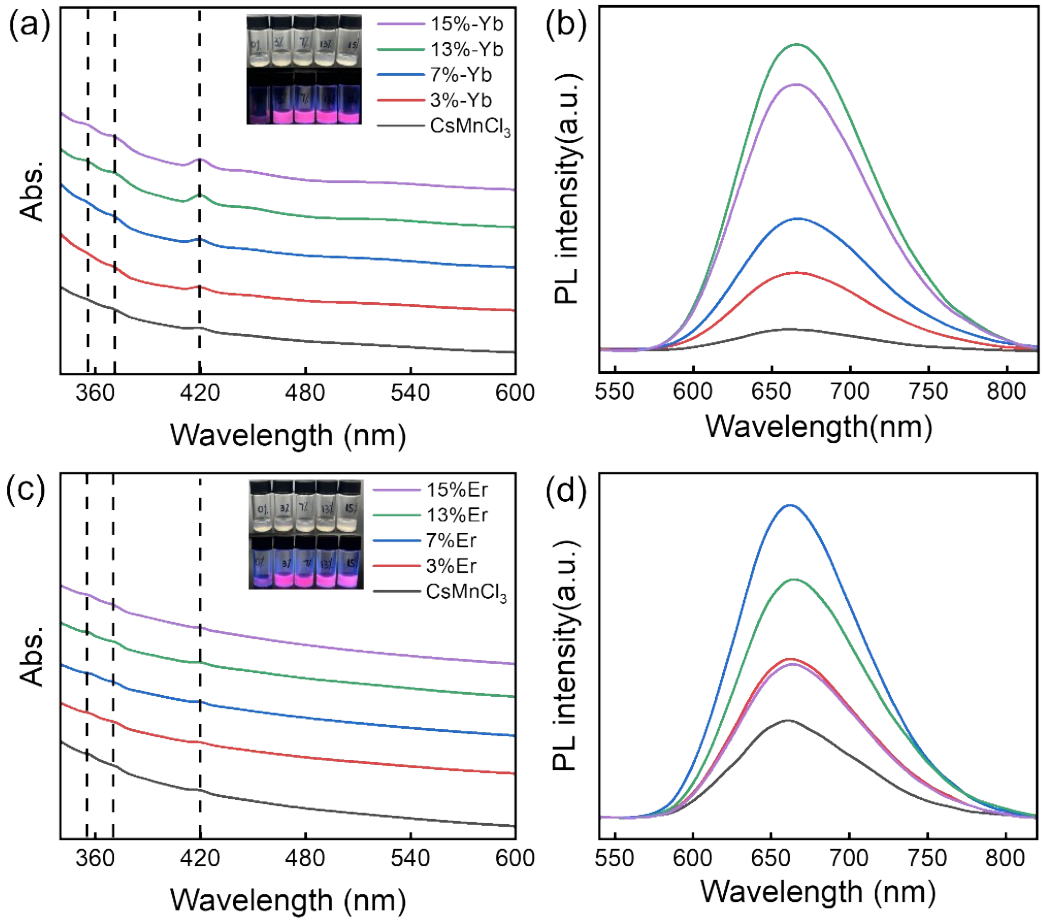

Figure S7. UV-vis of Er^{3+}-$CsMnCl_3$ NCs (a) and Yb^{3+}-$CsMnCl_3$ NCs (b). The insets are luminescence photographs of Er^{3+}-$CsMnCl_3$ NCs (a) and Yb^{3+}-$CsMnCl_3$ NCs (b) under a 365 nm UV lamp. PL spectra of Er^{3+}-$CsMnCl_3$ NCs (c) and Yb^{3+}-$CsMnCl_3$ NCs (d).

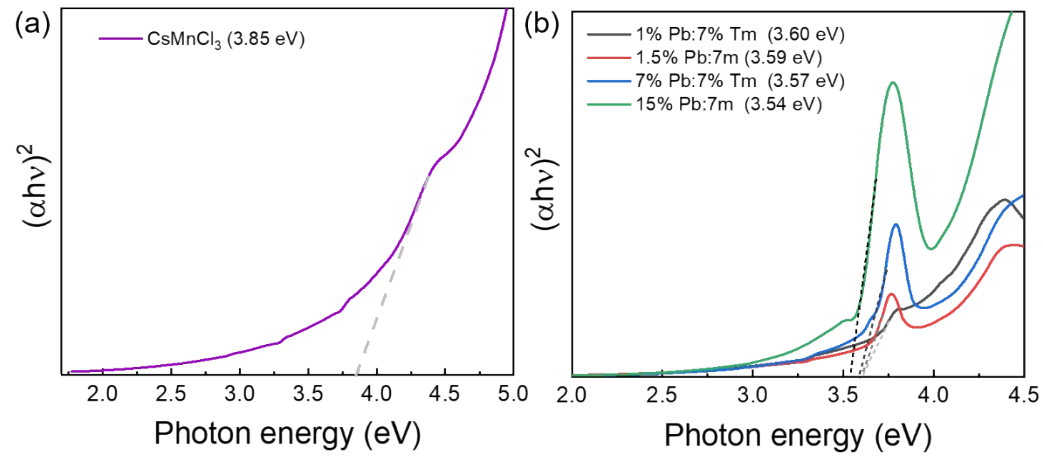

Figure S8. Tauc plot analysis of $CsMnCl_3$ NCs and Pb/Tm co-doped $CsMnC_{l3}$ NCs. (a) The bandgap of $CsMnCl_3$ NCs 3.85 eV could be estimated. (b) The bandgap of Pb/Tm co-doped $CsMnCl_3$ NCs is 3.60 eV, 3.59 eV, 3.57 eV and 3.54 eV, respectively.

Table S1. The parameters of PL decay lifetimes of undoped, 7% Tm^{3+} and Pb/Tm co-doped $CsMnCl_3$ NCs.

Samples	A_1	A_2	A_3	τ_1 (μs)	τ_2 (μs)	τ_3 (μs)	τ (μs)
$CsMnCl_3$	0.22	0.42	0.35	3.60	52.53	198.50	162.10
7%Tm^{3+}-$CsMnCl_3$	0.19	0.68	0.12	82.89	298.84	533.08	340.82
15%Pb:7%Tm- $CsMnCl_3$	0.47	0.34	0.18	16.30	140.65	467.64	330.93

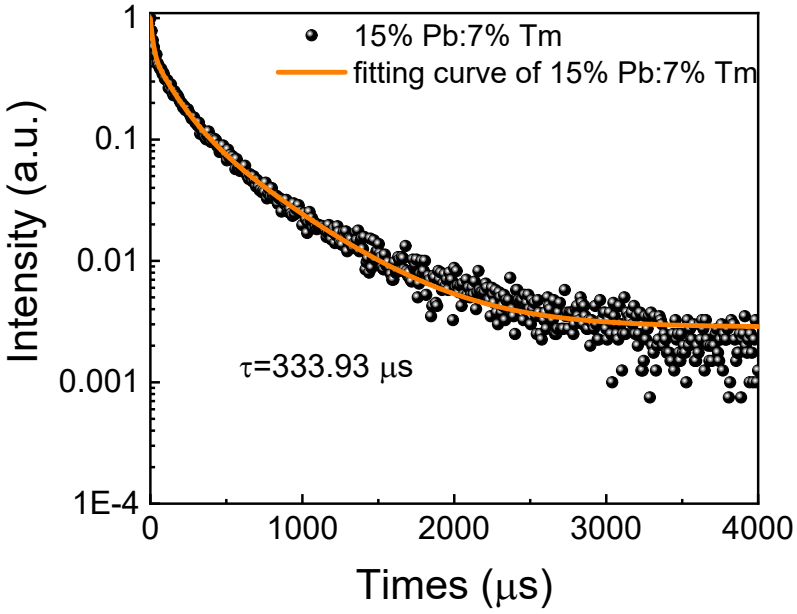

Figure S9. PL decay curves of Pb/Tm co-doped $CsMnCl_3$ NCs.

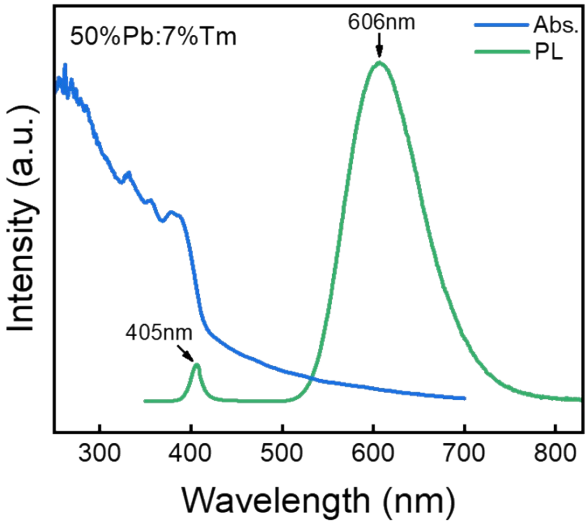

Figure S10. UV-vis and PL spectra of NCs with 50% Pb and 7% Tm doping.

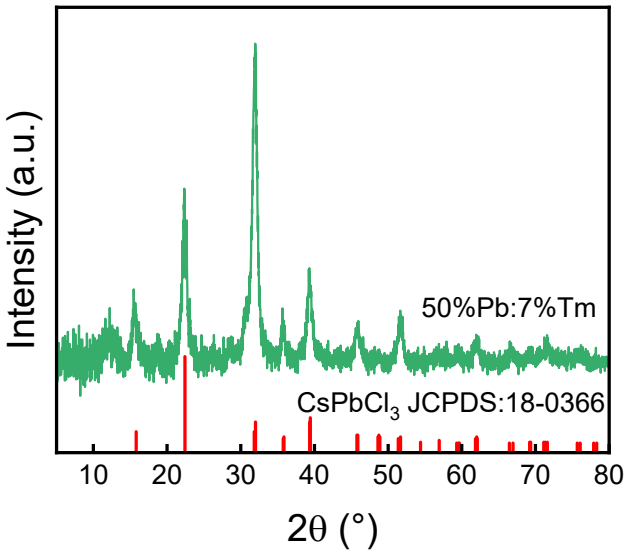

Figure S11. XRD pattern of NCs with 50% Pb and 7% Tm doping.

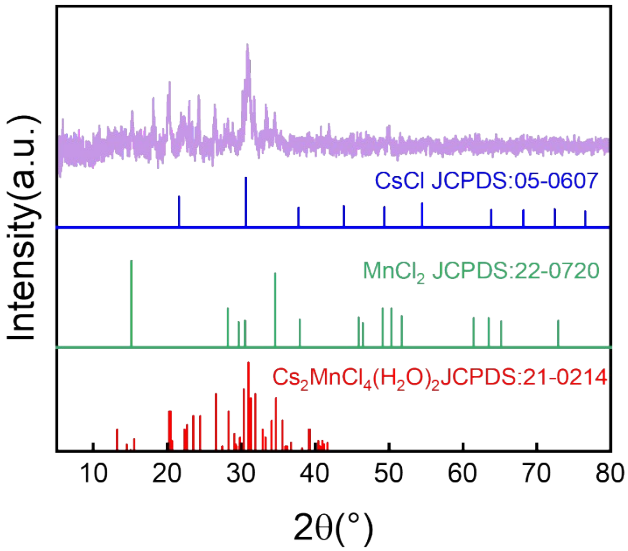

Figure S12. XRD pattern of $CsMnCl_3$ film after 15 days in air.