Cyan-rich Sunlight-like Spectra from Mn^{2+}-doped $CsCd(Cl_{1-y}Br_y)_3$ Perovskites with Dual Tunable Emissions and High Stability

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Methods

Materials: CsCl (99.99% metals basis), $CdCl_2$ (anhydrous, 99.99% metals basis), $MnCl_2 \cdot 5H_2O$ (99.99% metals basis) and CsBr (99.99% metals basis) were all purchased from Aladdin. No further purifications were conducted to prepare the product.

Preparation of precursors: 1mmol (16.84 mg) $CdCl_2$ was dissolved in 500uL ultrapure water as the precipitant, and 1mmol (18.83 mg) CsCl was dissolved in 500 μL ultrapure water as CsCl precursor.

Synthesis: The $CdCl_2$ precipitant was swiftly injected in CsCl precursor, and immediately the white precipitation of $CsCdCl_3$ would form in water. To obtain composite samples, the amount of Br^- ought to hold in 0.06 mmol (2.13 mg) - 0.50 mmol (10.63 mg), and Mn^{2+} is 0.1 mmol (1.79 mg) - 1.0 mmol (17.97 mg), added to CsCl precursor. Then leaved the precipitant saturating in the water for 30 minutes to ensure a fully ion exchange. No washing was needed in the process, and all the precipitations were dried at 50℃ for 6 hours.

Characterization: X-ray diffraction was performed on the German Bruker D8 Advance X-ray diffractometer with Cu Kα radiation. Scanning electron microscope was performed on Czechoslovakia Tescan MIRA LMS. The photoluminescence (PL) spectra collections were measured us a fluoresce spectrophotometer (F-4600 fluoresce spectrophotometer, Japan). The luminescence decay curves were obtained using Edinburgh FLS1000 fluoresce spectrophotometer. The luminous flux, luminous efficiencies, Ra of WLEDs were measured using a LED automatic temperature control photoelectric analysis and measurement system. (ATA-500, EVERFINE)

Optical properties

Rich cyan light in white light spectra of $CsCd_{1-x}(Cl_{1-y}Br_y)_3$: xMn^{2+} making it more close to sunlight in the range 380-500nm (Fig. S1) compared with the previous works [1] [2] [3] [4]

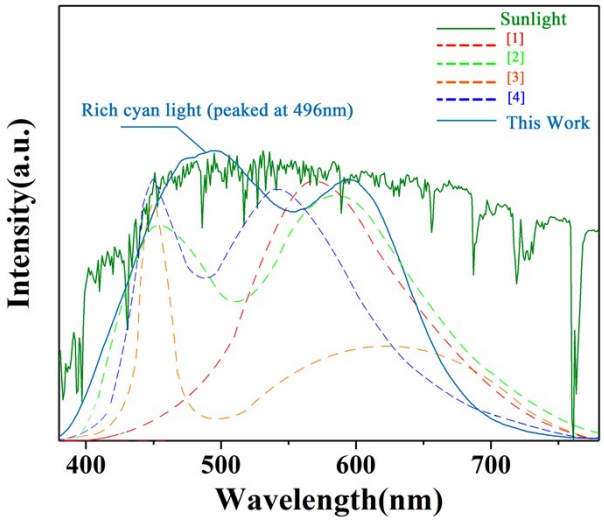

Fig S1 The emission spectrum of the sunlight, previous works and $CsCd_{0.6}$ $(Cl_{0.9}Br_{0.1})_3$: $0.4Mn^{2+}$

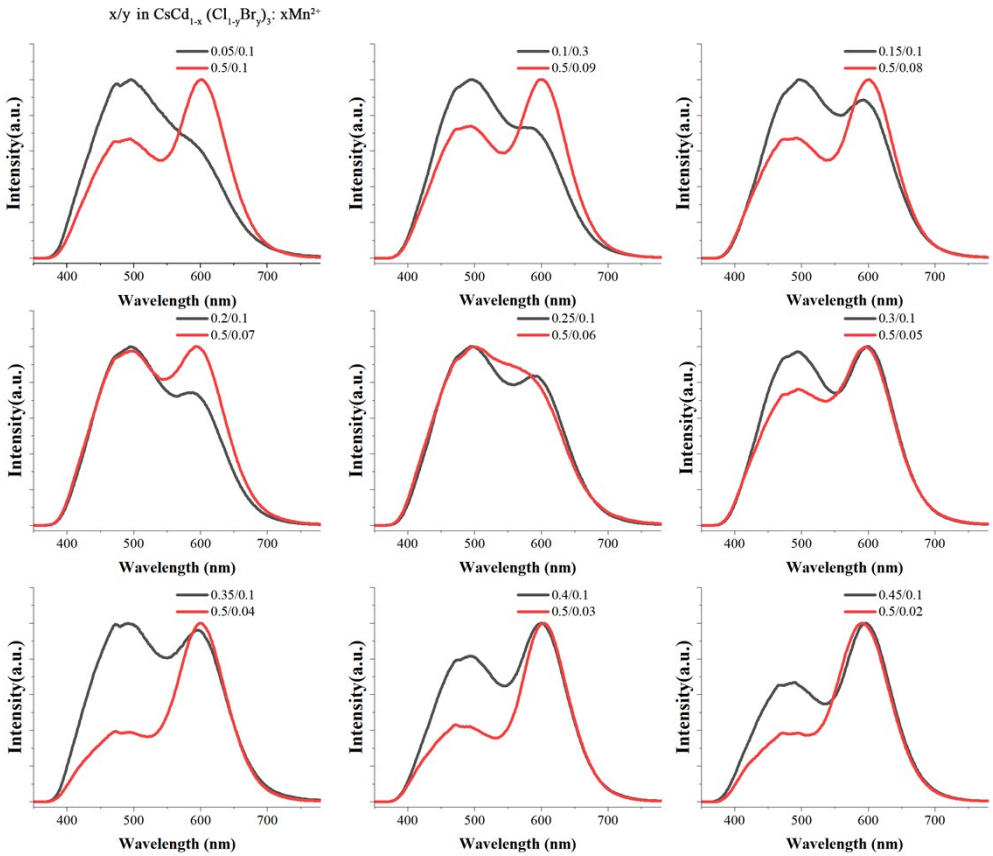

Fig S2 Normalized PL spectrum of $CsCd(Cl_{1-y}Br_y)_3:xMn^{2+}$ (excited at 254 nm) with different x/y ratios

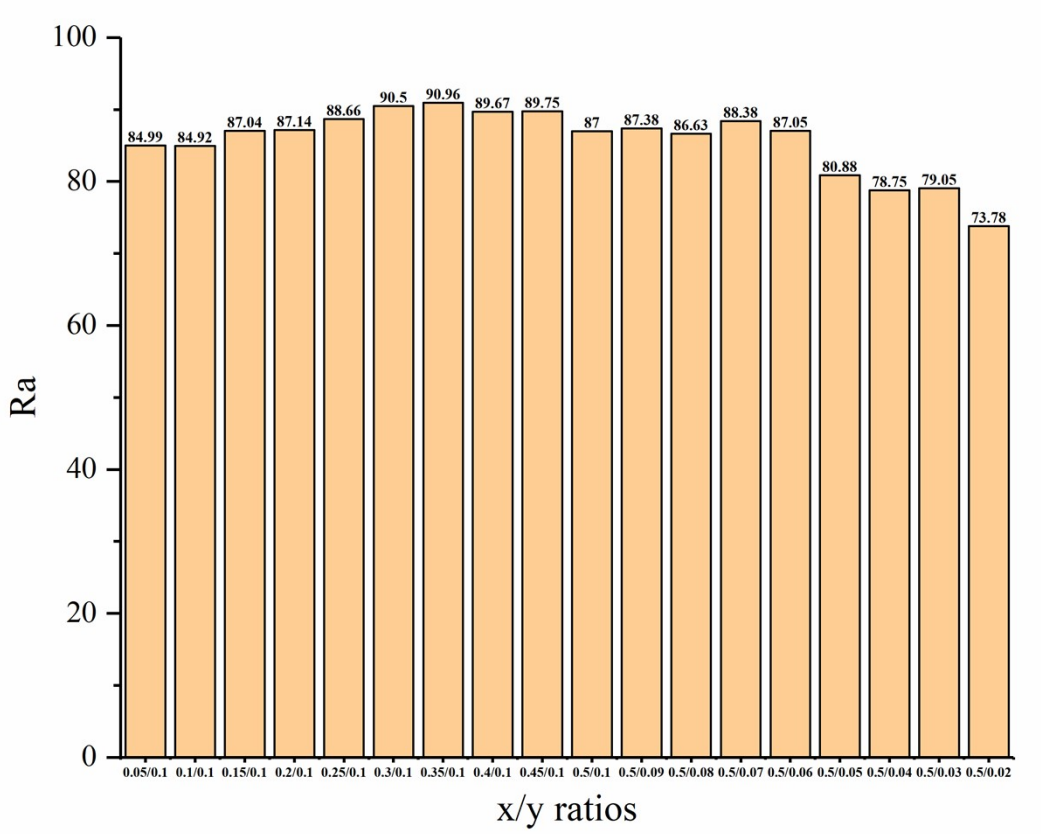

Fig S3 Colour rendering index (Ra) of $CsCd(Cl_{1-y}Br_y)_3$: xMn^{2+} with different x/y ratios

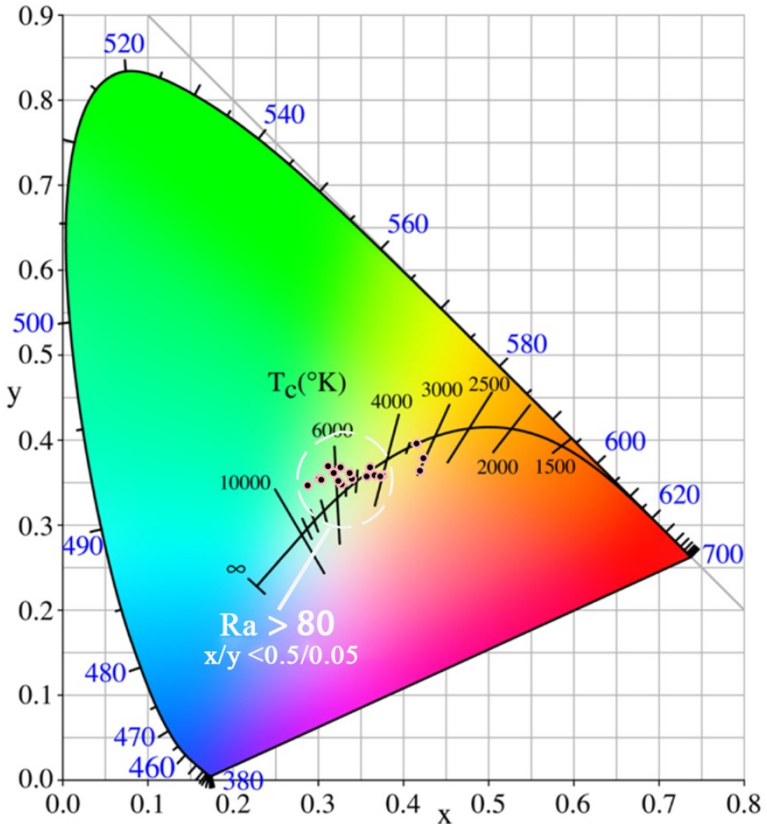

Fig S4 CIE 1931 diagram of $CsCd(Cl_{1-y}Br_y)_3$: xMn^{2+} with different x/y ratios

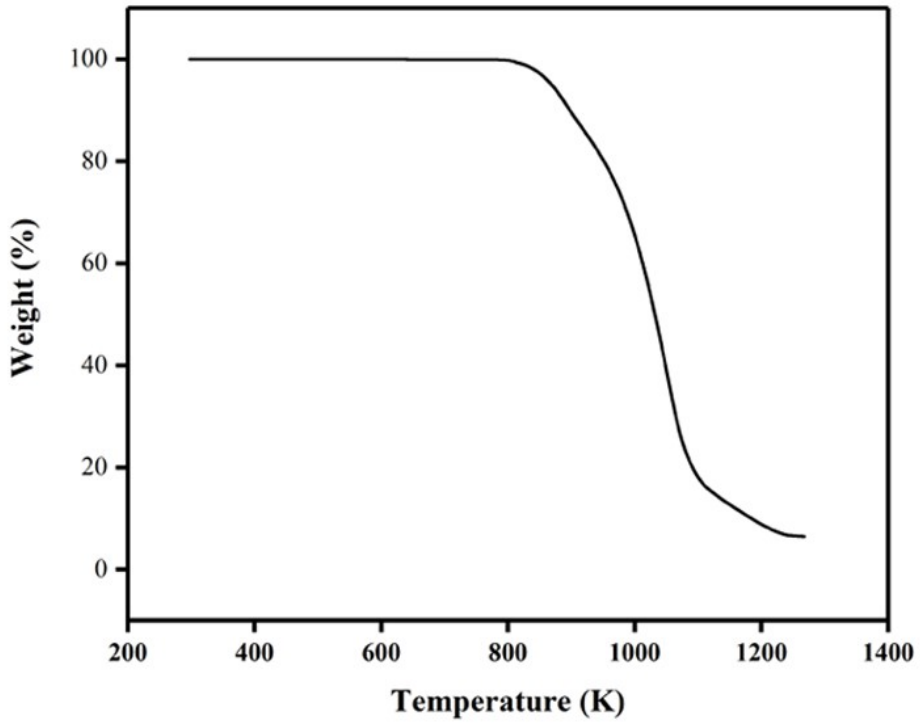

Fig S5 The thermogravimetric analysis of $CsCd_{0.6}$ $(Cl_{0.9}Br_{0.1})_3$: $0.4Mn^{2+}$

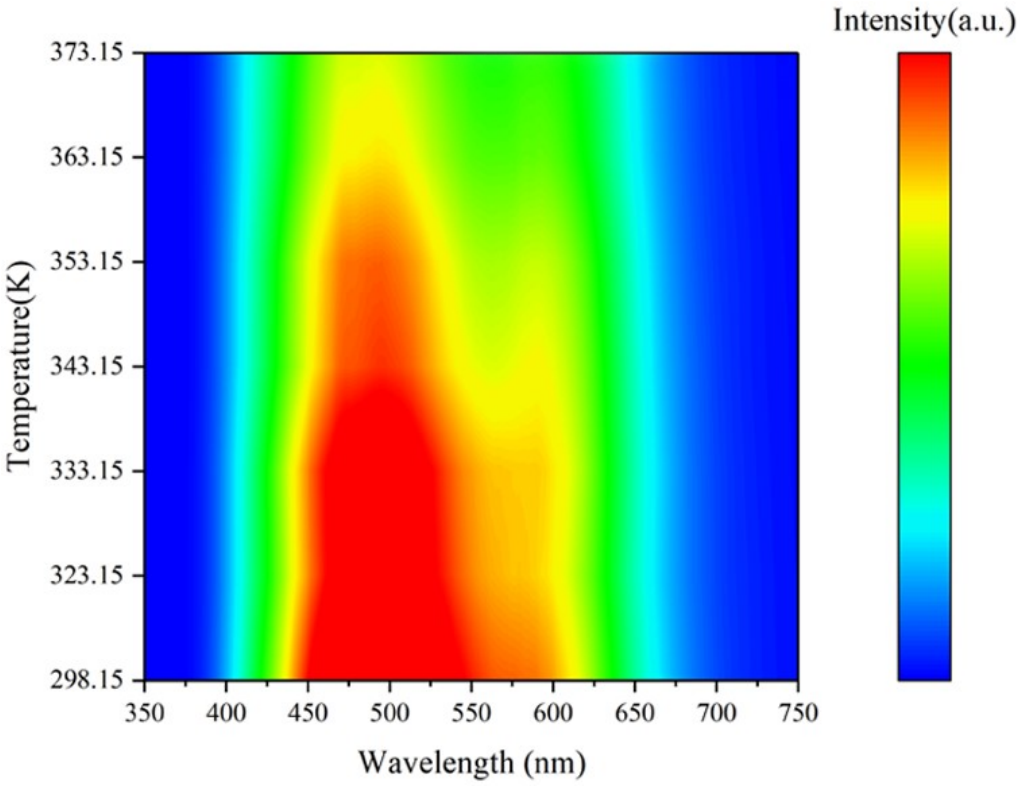

Fig S6 The temperature corresponding PL intensity spectrum of $CsCd_{0.6}$ $(Cl_{0.9}Br_{0.1})_3$: $0.4Mn^{2+}$

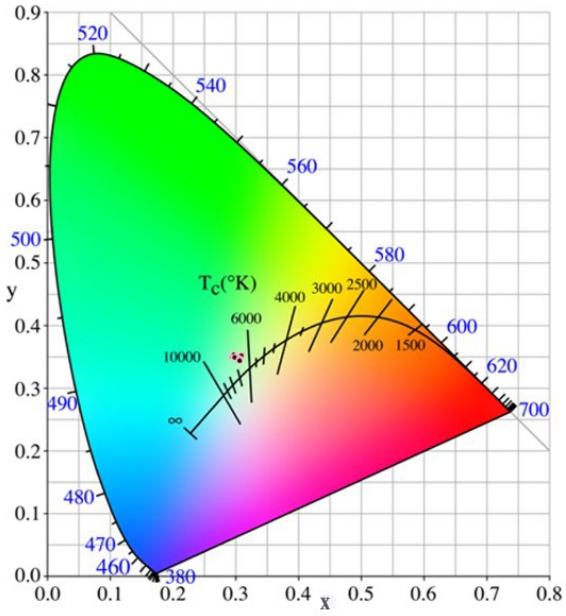

Fig S7 The temperature corresponding CIE 1931 scheme of $CsCd_{0.6}$ $(Cl_{0.9}Br_{0.1})_3$: $0.4Mn^{2+}$

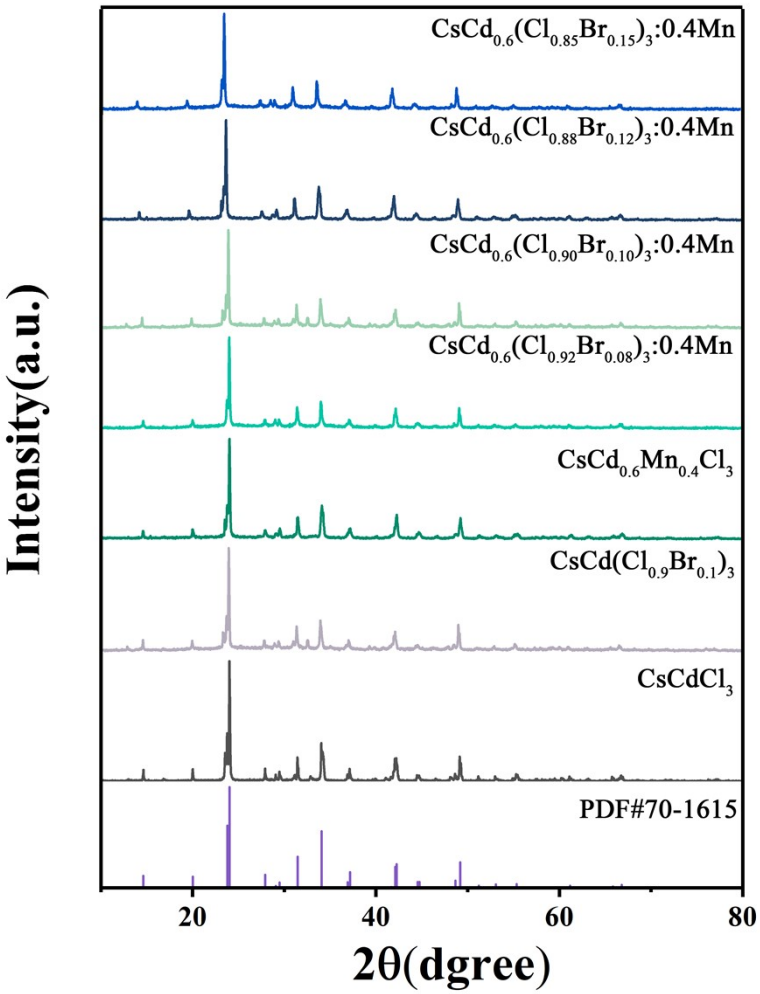

Fig S8 The XRD spectrum of $CsCd_{1-x}(Cl_{1-y}Br_y)_3$:$xMn^{2+}$

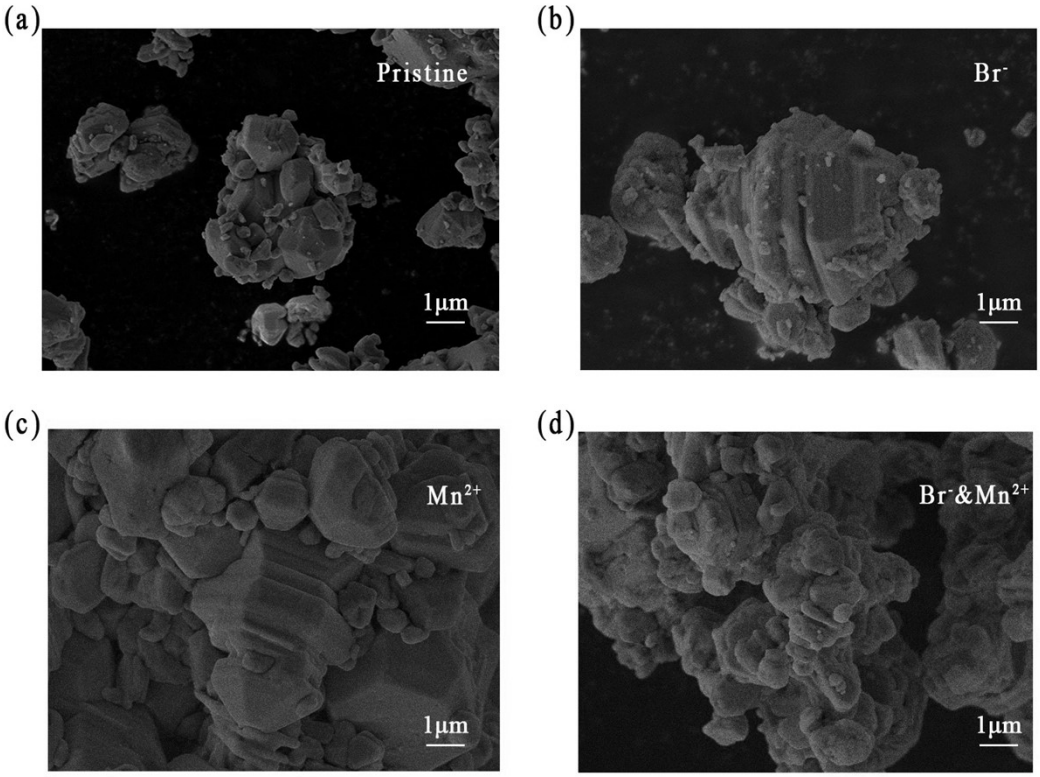

Fig S9(a-d) The Scanning electron microscopy of $CsCdCl_3$, $CsCd(Cl_{0.9}Br_{0.1})_3$, $CsCd_{0.6}Mn_{0.4}Cl_3$, and $CsCd_{0.6}(Cl_{0.9}Br_{0.1})_3$:$0.4Mn^{2+}$

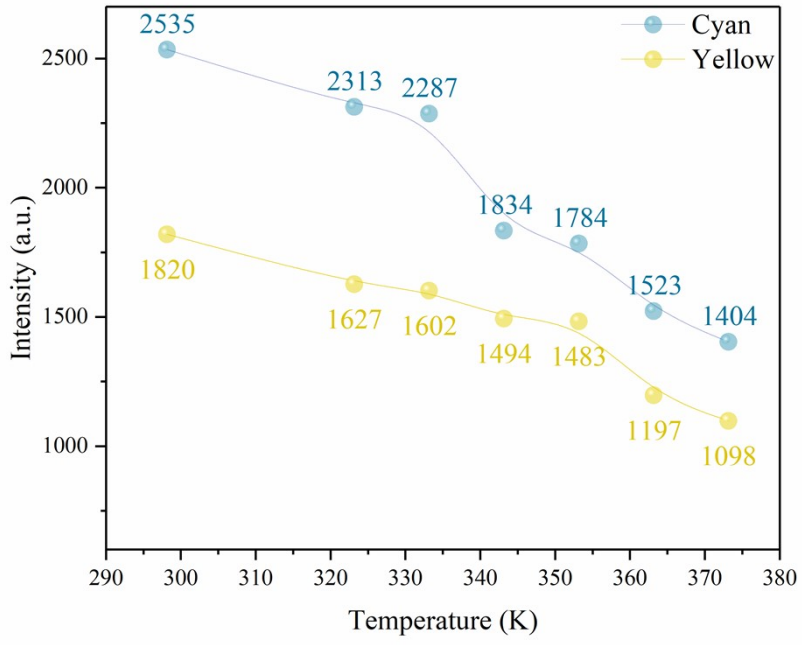

Fig S10 Temperature-dependent PL intensities of $CsCd_{0.6}(Cl_{0.9}Br_{0.1})_3$:$0.4Mn^{2+}$

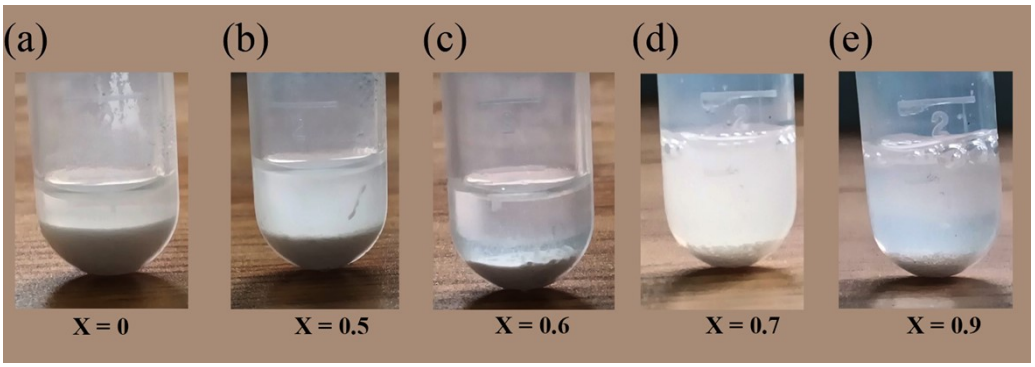

Fig S11 The solubility of $CsCd_{1-x}Mn_xCl_3$ in water increases with increasing x value

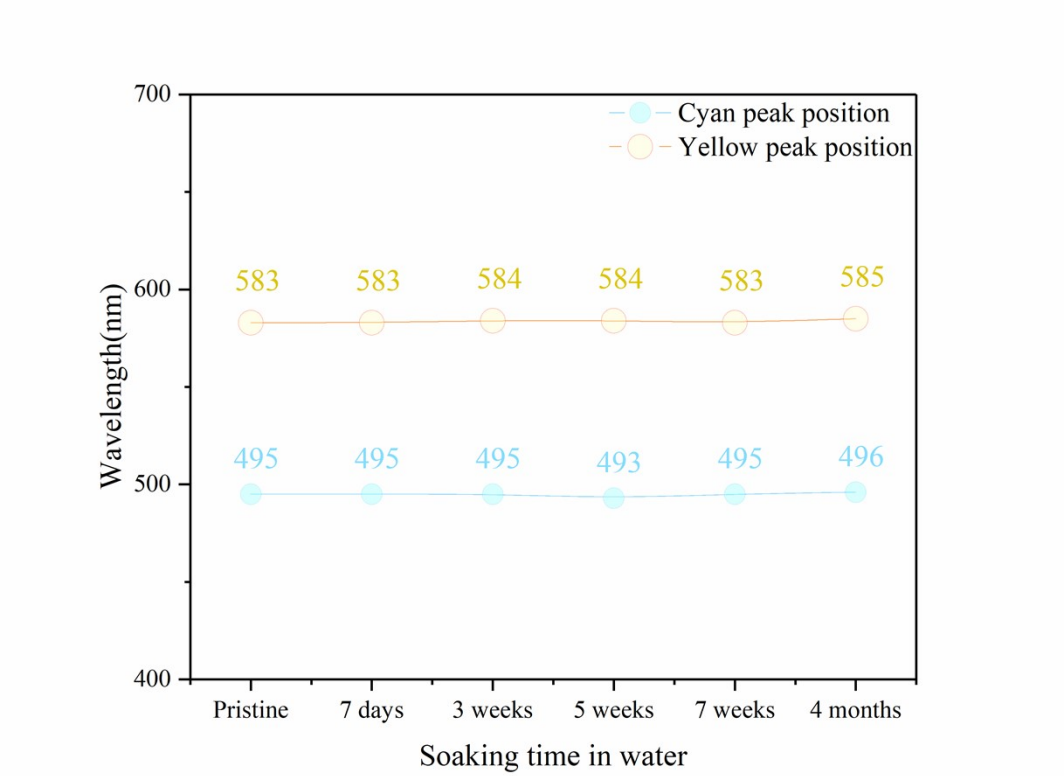

Fig S12 Variation of peak position of $CsCd(Cl_{1-y}Br_y)_3$: xMn^{2+} at different soaking time in the water.

Table S1 give the lattice parameters of each sample (Calculated by Jade6.5), the three groups of edge lengths of the crystal cell are a, b, c, and the included angle between the three groups of edges are α, β, γ.

Table S1 The lattice parameters of each sample

Samples	a	b	c	α	β	γ
$CsCdCl_3$	7.41114	7.41114	18.42848	90	90	120
$CsCd(Cl_{0.9}Br_{0.1})_3$	7.41971	7.41971	18.44307	90	90	120
$CsCd_{0.6}Mn_{0.4}Cl_3$	7.41036	7.41036	18.43312	90	90	120
$CsCd(Cl_{0.98}Br_{0.08})_3$:$0.4Mn^{2+}$	7.41153	7.41153	18.43375	90	90	120
$CsCd_{0.6}(Cl_{0.9}Br_{0.1})_3$:$0.4Mn^{2+}$	7.41168	7.41168	18.432	90	90	120
$CsCd(Cl_{0.88}Br_{0.12})_3$:$0.4Mn^{2+}$	7.42278	7.42278	18.45203	90	90	120
$CsCd(Cl_{0.85}Br_{0.15})_3$:$0.4Mn^{2+}$	7.42658	7.42658	18.4578	90	90	120

Table S2 UV-pumped WLED parameters with different x/y of $CsCd_{1-x}(Cl_{1-y}Br_y)_3:xMn^{2+}$

x/y	CCT(K)	Ra	Luminous flux(lm)	luminous efficiencies (lm W^{-1})
0.1/0.1	8042	83	16.945	33.89
0.3/0.1	5198	90.5	19.68	39.36
0.3/0.02	3039	73.2	11.77	23.84

Reference

1. J. Luo, X. Wang, S. Li, J. Liu, Y. Guo, G. Niu, L. Yao, Y. Fu, L. Gao, Q. Dong, C. Zhao, M. Leng, F. Ma, W. Liang, L. Wang, S. Jin, J. Han, L. Zhang, J. Etheridge, J. Wang, Y. Yan, E. H. Sargent and J. Tang, *Nature*, 2018, **563**, 541-545.
2. B. Zhou, Z. Liu, S. Fang, H. Zhong, B. Tian, Y. Wang, H. Li, H. Hu and Y. Shi, *ACS Energy Letters*, 2021, **6**, 3343-3351.
3. F. Li, Z. Xia, C. Pan, Y. Gong, L. Gu, Q. Liu and J. Z. Zhang, *ACS Appl Mater Interfaces*, 2018, **10**, 11739-11746.
4. P.-P. Dai, C. Li, X.-T. Zhang, J. Xu, X. Chen, X.-L. Wang, Y. Jia, X. Wang and Y.-C. Liu, *Light: Science & Applications*, 2016, **5**, e16024-e16024.