Supporting Information

Luminescence Tuning in a zero-dimensional inorganic-inorganic hybrid metal halide Family of $(C_7H_{18}N_2)MBr_4$ (M = Cd, Zn, and Mn)

*Zhongliang Gong,[a‡] Xiaodong Yi,[b‡] Xi-Gui Gao,[c] Huwenyu Huang,[a] Yu-Xin Ma,[a] Zi-Xuan Liu,[a] Jingmei Zhao,[a] Lijuan Feng,[a] Cheng-Yang Yue[a]**

[a] Research institute of Optoelectronic Functional Materials, School of Chemistry, Chemical Engineering and Materials, Jining University, Qufu, Shandong, 273155, P. R. China

[b] CAS Key Laboratory of Design and Assembly of Functional Nanostructures, Fujian Key Laboratory of Nanomaterials, and State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

[c] Shandong Provincial Key Laboratory of Green and Low-Carbon Recycling and Application of Rare Earth Materials, Zhongxi Tianma New Material Technology Co., Ltd, Jining, Shandong, 272620, P. R. China

[‡] These authors contributed equally to this work.

* Corresponding author.

E-mail addresses: yuechengyang@126.com

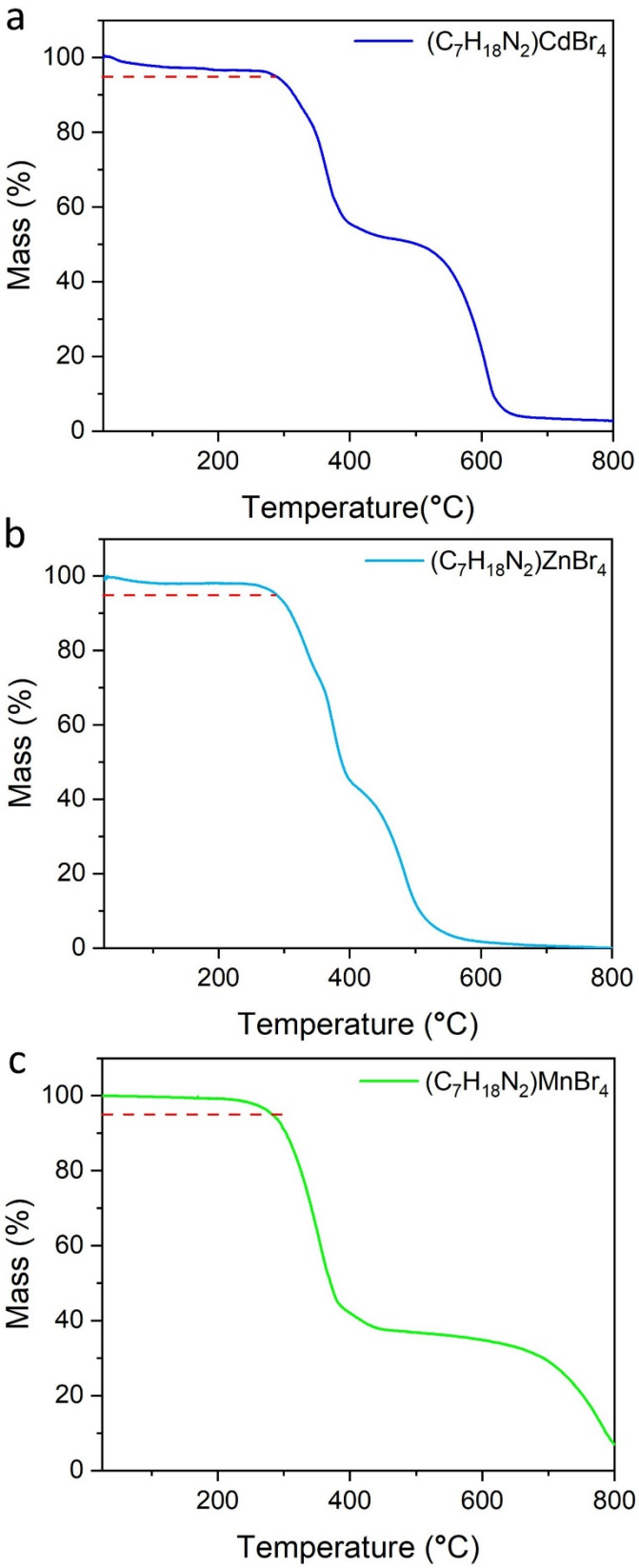

Fig. S1 Thermal gravimetric analysis curves of $(C_7H_{18}N_2)CdBr_4$ (a), $(C_7H_{18}N_2)ZnBr_4$ (b), and $(C_7H_{18}N_2)MnBr_4$ (c).

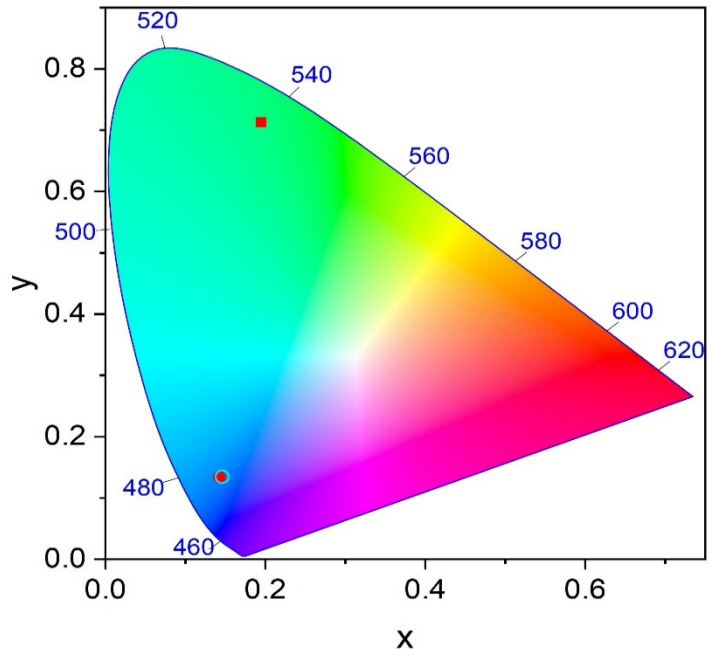

Fig. S2 CIE coordinate of $(C_7H_{18}N_2)CdBr_4$ (red point), $(C_7H_{18}N_2)ZnBr_4$ (cyan circle), and $(C_7H_{18}N_2)MnBr_4$ (red square).

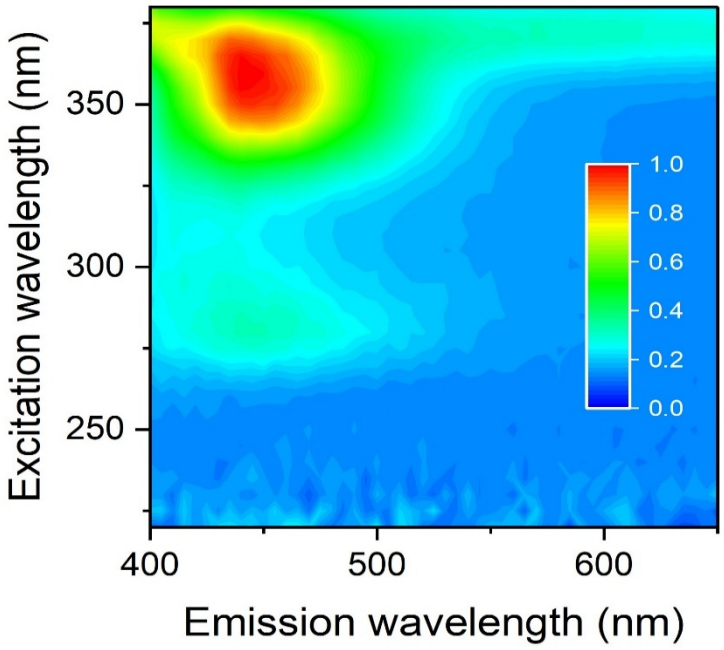

Fig. S3 3D consecutive PL excitation and emission map of $(C_7H_{18}N_2)CdBr_4$ at 300 K.

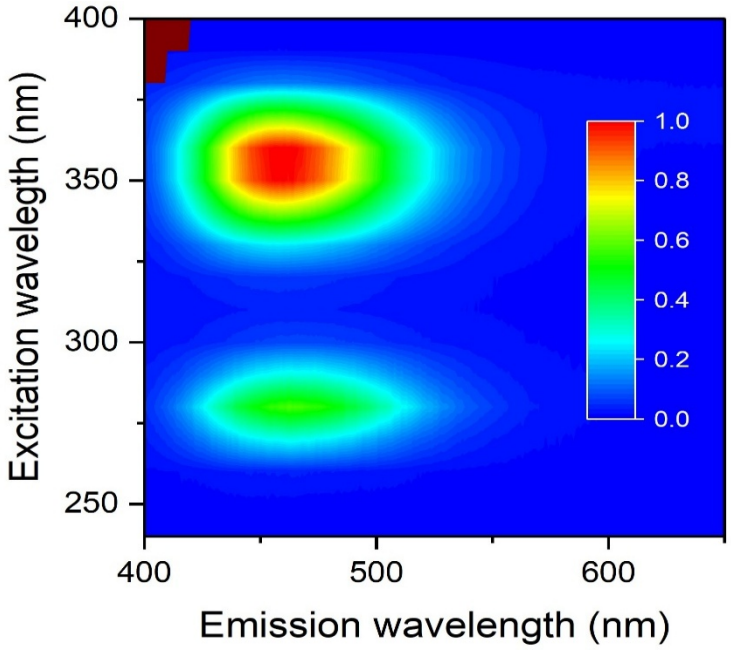

Fig. S4 3D consecutive PL excitation and emission map of $(C_7H_{18}N_2)ZnBr_4$ at 300 K.

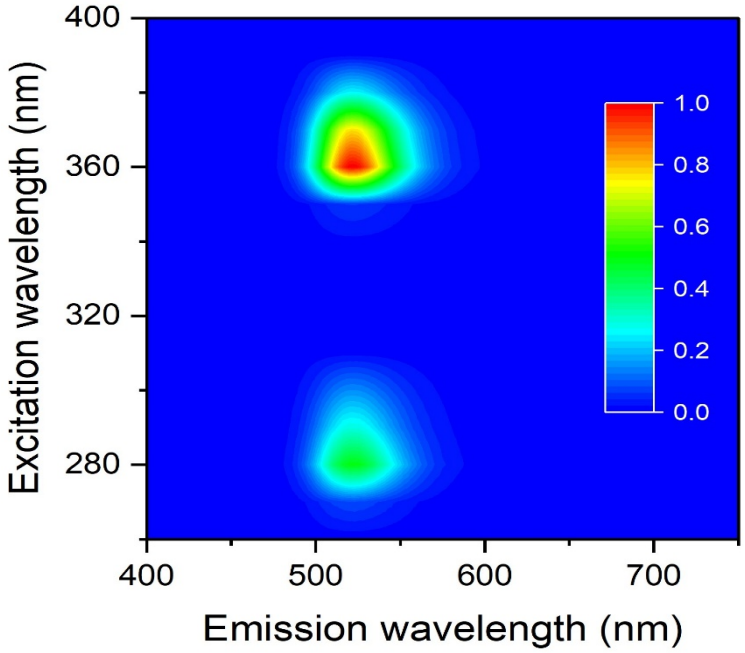

Fig. S5 3D consecutive PL excitation and emission map of $(C_7H_{18}N_2)MnBr_4$ at 300 K.

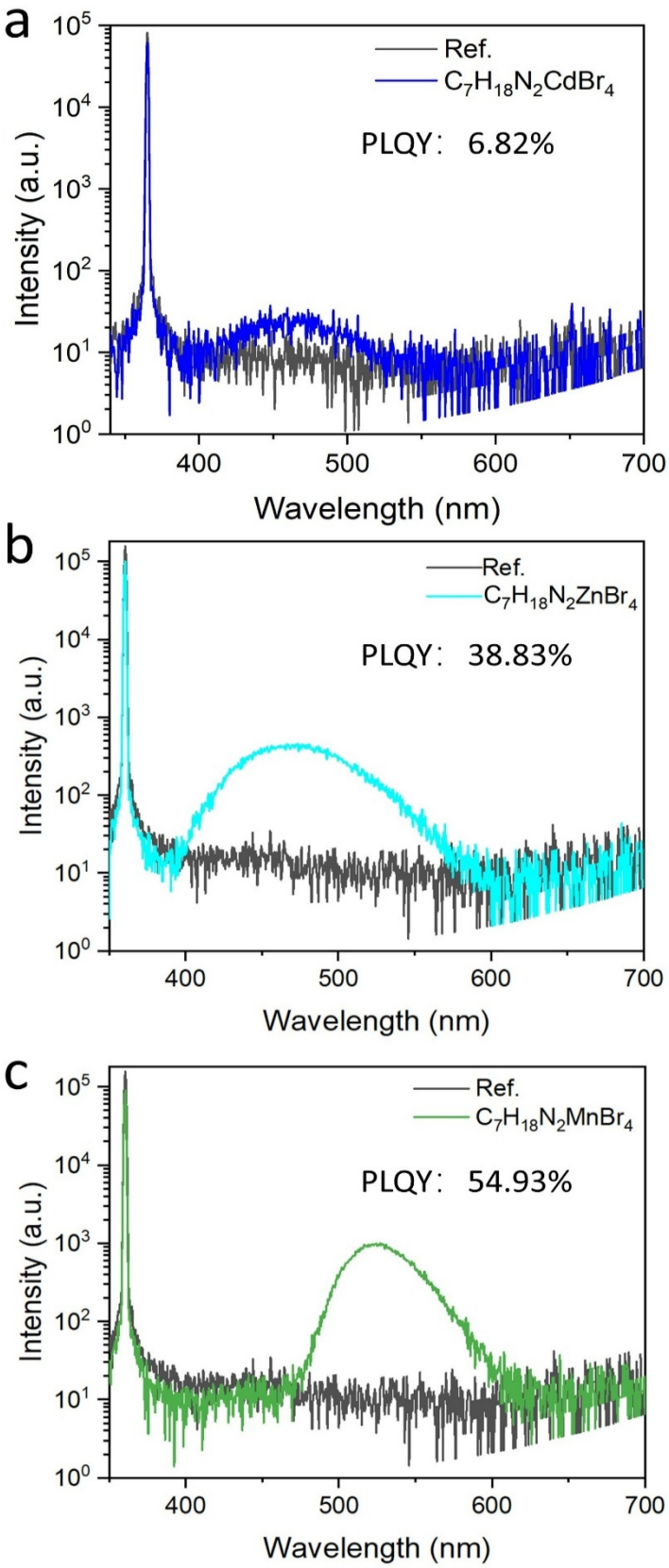

Fig. S6 The absolute PLQYs of $(C_7H_{18}N_2)CdBr_4$ (a), $(C_7H_{18}N_2)ZnBr_4$ (b), and $(C_7H_{18}N_2)MnBr_4$ (c) at 300 K.

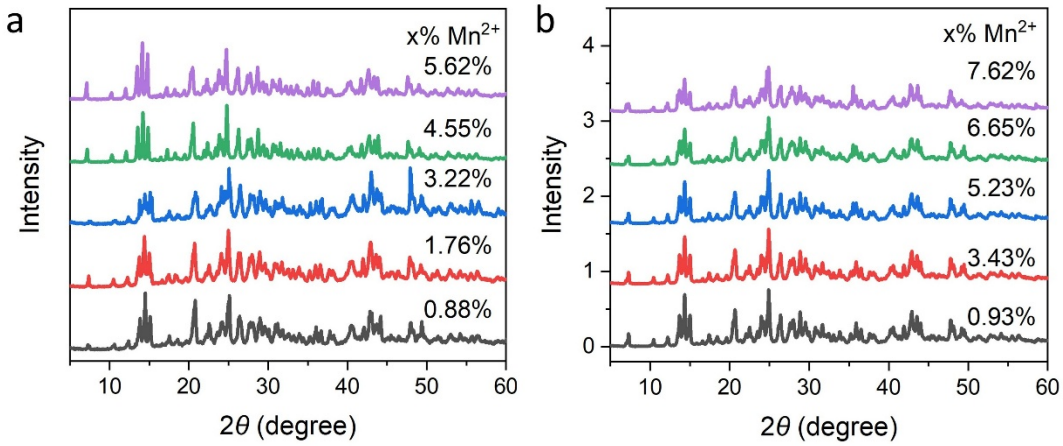

Fig. S7 PXRD patterns of Mn^{2+} doped $(C_7H_{18}N_2)CdBr_4$ (a) and $(C_7H_{18}N_2)ZnBr_4$ (b).

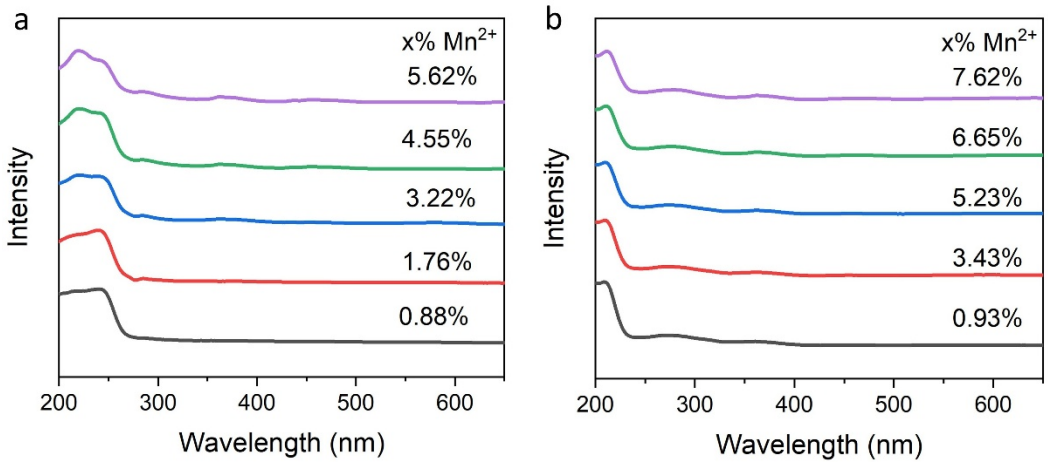

Fig. S8 UV-Vis absorption spectra of Mn^{2+} doped $(C_7H_{18}N_2)CdBr_4$ (a) and $(C_7H_{18}N_2)ZnBr_4$ (b).

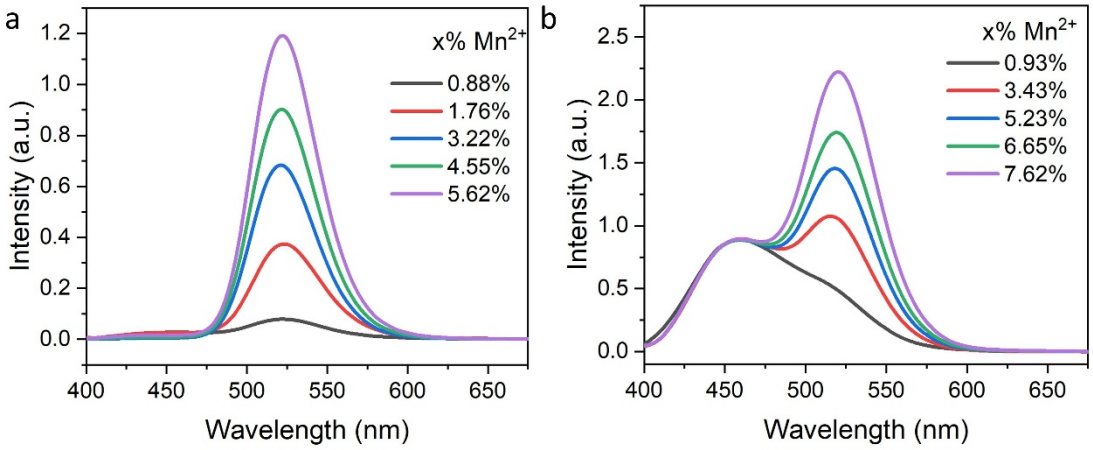

Fig. S9 PL spectra of Mn^{2+} doped $(C_7H_{18}N_2)CdBr_4$ (a) and $(C_7H_{18}N_2)ZnBr_4$ (b) (λ_{ex} = 360 nm).

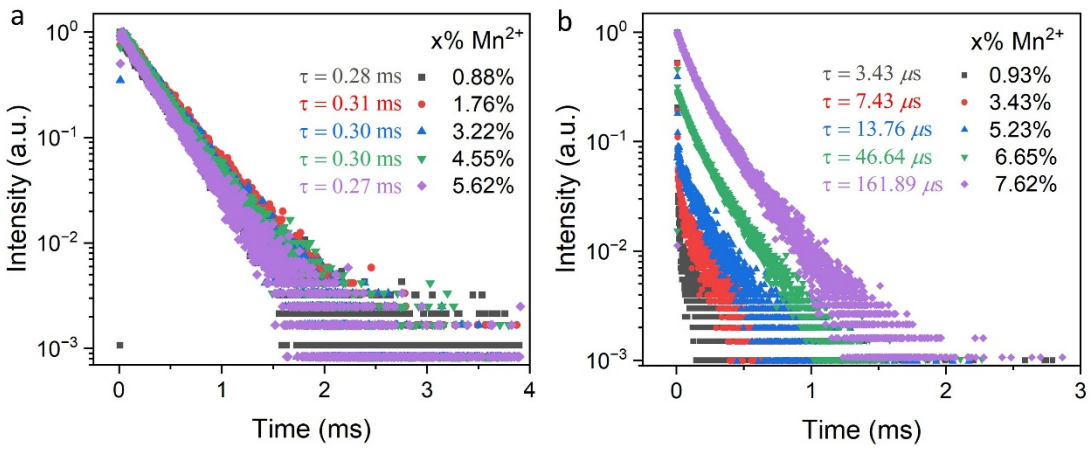

Fig. S10 PL decay curves of Mn^{2+} doped $(C_7H_{18}N_2)CdBr_4$ (a) and $(C_7H_{18}N_2)ZnBr_4$ (b) (λ_{ex} = 360 nm, λ_{em} = 520 nm).

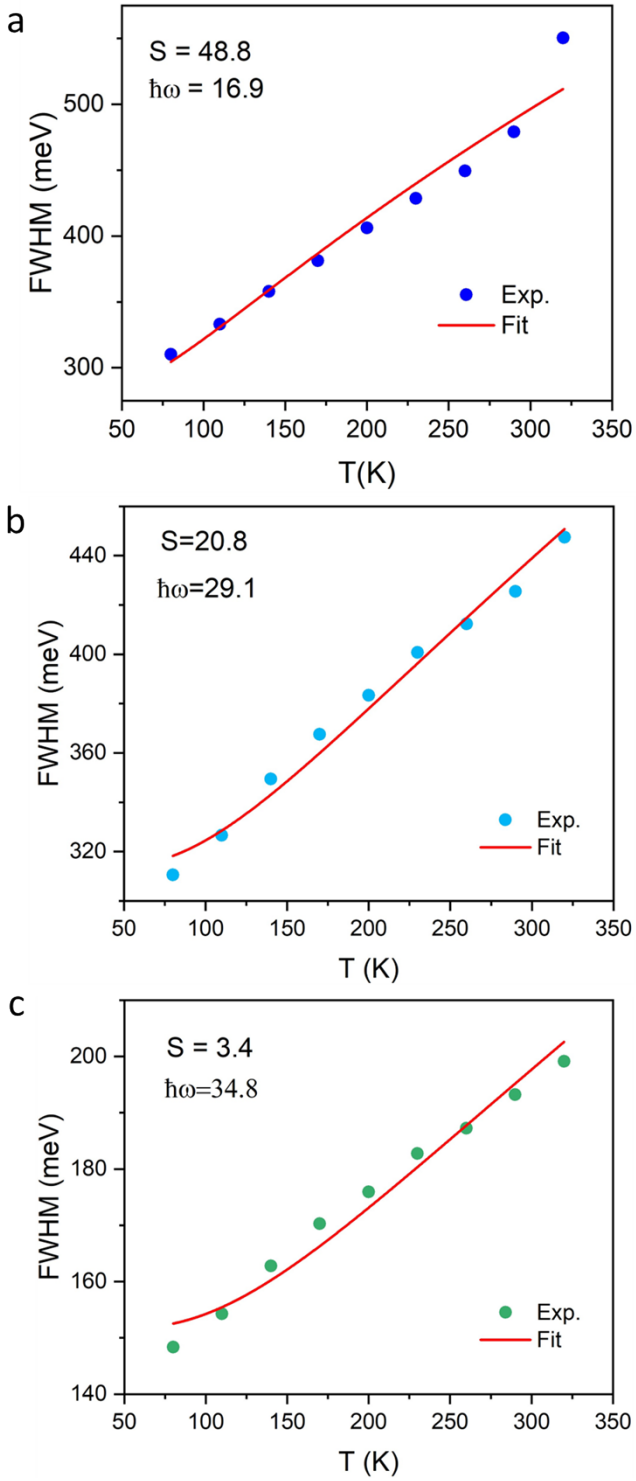

Fig. S11 FWHM of the PL emission as a function of temperature and the fitting to extract the phonon energy ($\hbar\omega$) and the Huang-Rhys factor (S) for$(C_7H_{18}N_2)CdBr_4$ (a), $(C_7H_{18}N_2)ZnBr_4$ (b), and $(C_7H_{18}N_2)MnBr_4$ (c).

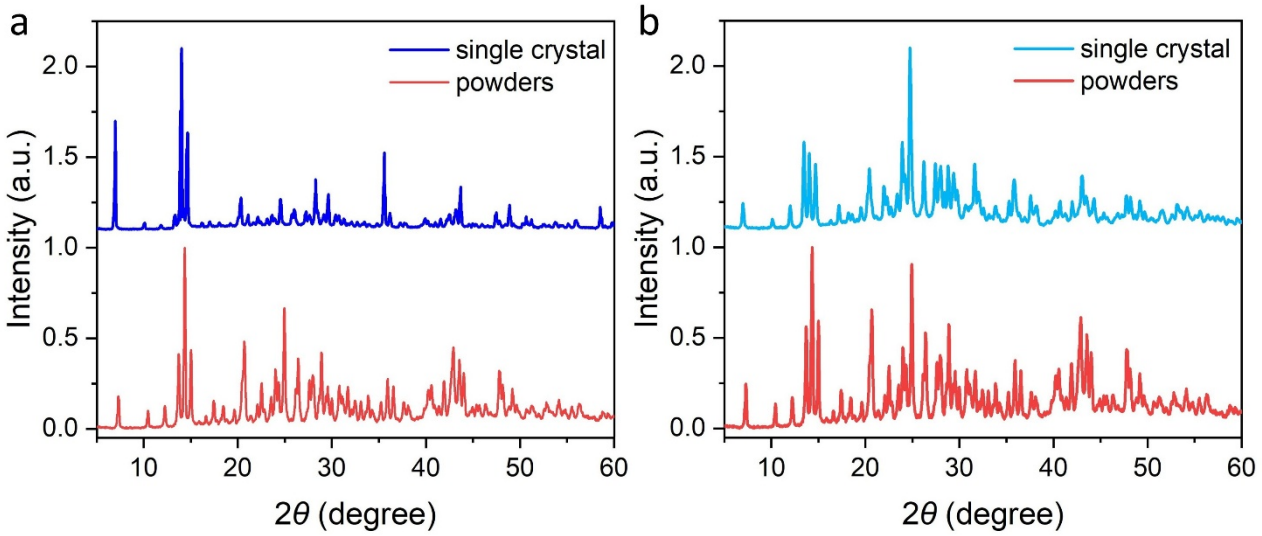

Fig. S12 Comparison of XRD patterns between powders and single crystals for $(C_7H_{18}N_2)CdBr_4$ (a) and $(C_7H_{18}N_2)ZnBr_4$ (b).

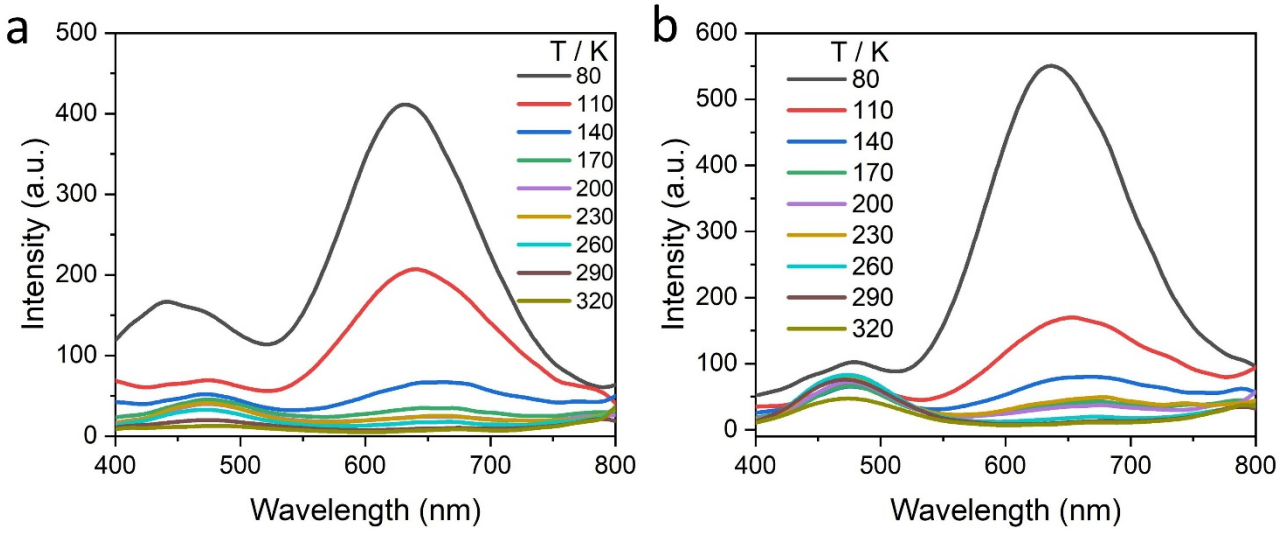

Fig. S13 Temperature-dependent PL spectra of $(C_7H_{18}N_2)CdBr_4$ (a) and $(C_7H_{18}N_2)ZnBr_4$ (b) by monitoring the excitation wavelength at 290 nm.

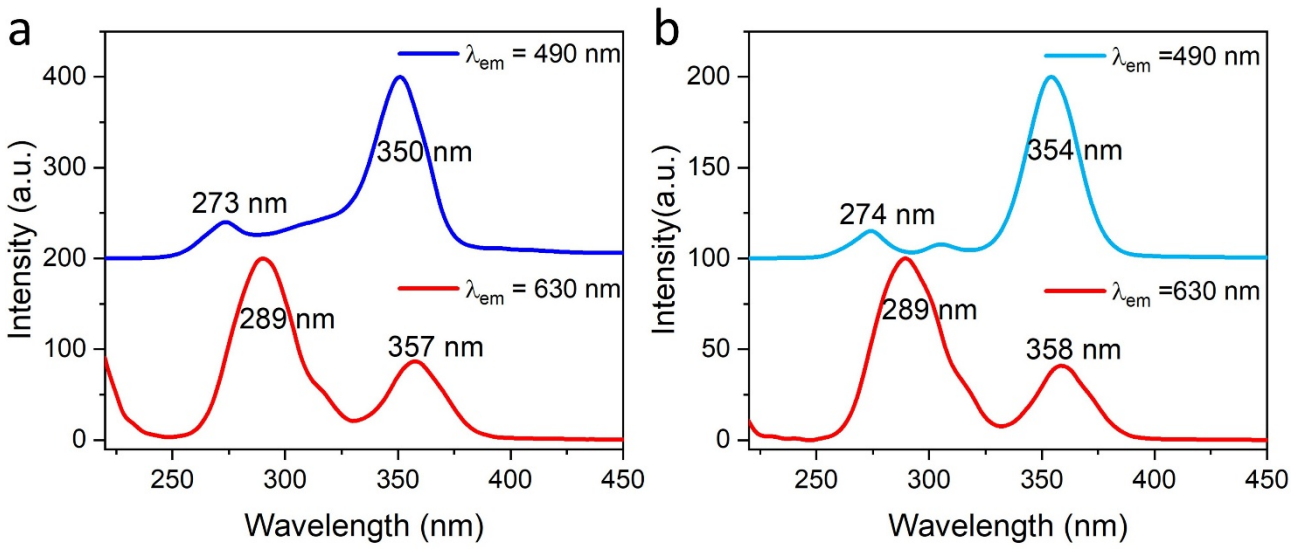

Fig. S14 The excitation spectra of $(C_7H_{18}N_2)CdBr_4$ (a) and $(C_7H_{18}N_2)ZnBr_4$ (b) at 80 K were monitored at 490 nm and 630 nm.

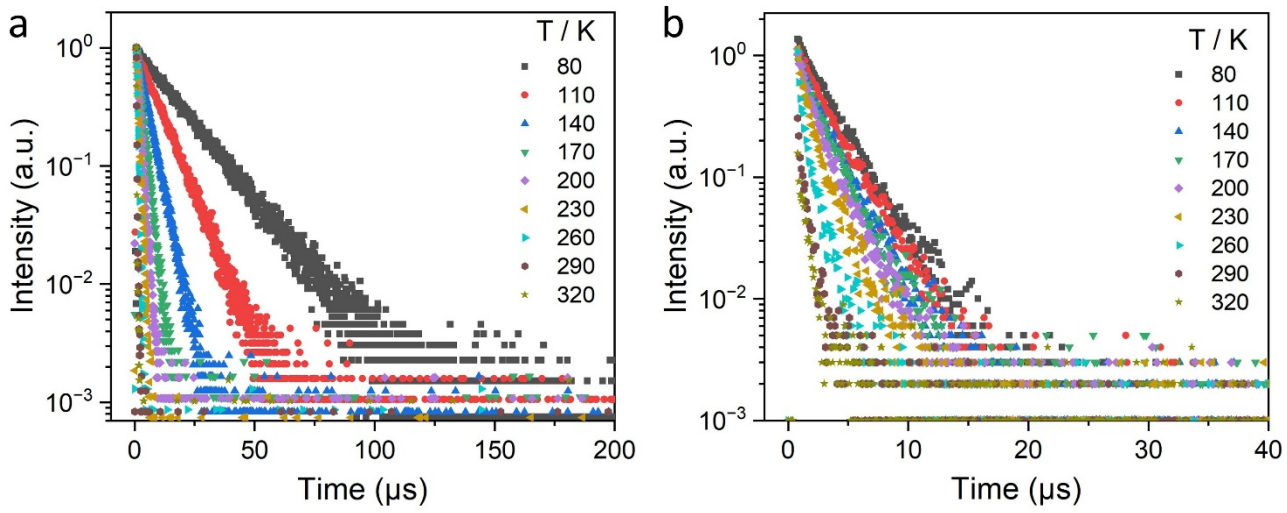

Fig. S15 The PL decay curves of $(C_7H_{18}N_2)CdBr_4$ monitoring at 460 nm (a) and 630 nm (b).

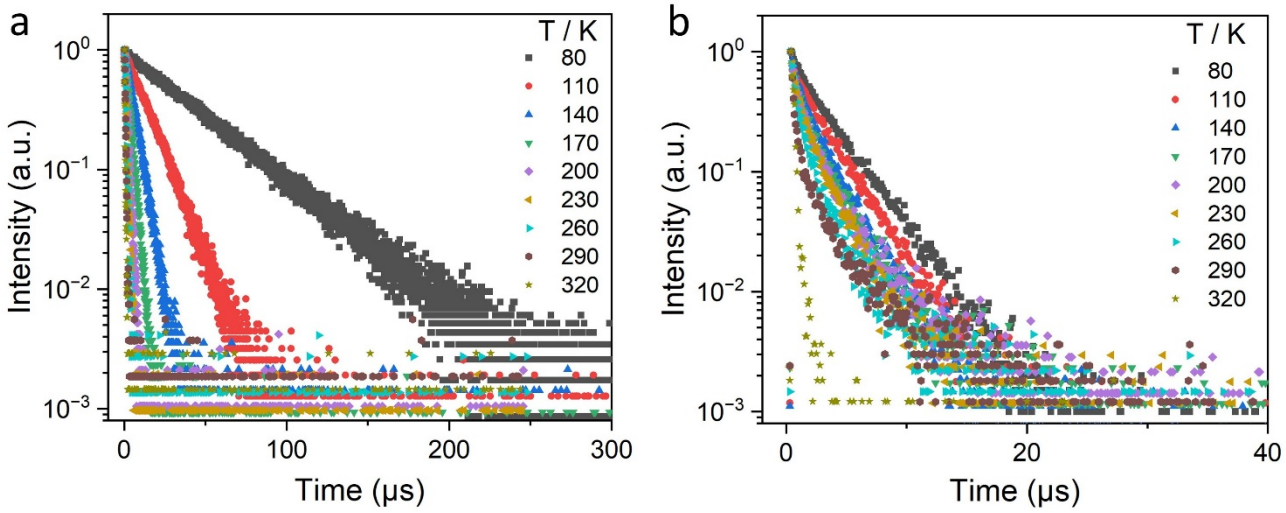

Fig. S16 The PL decay curves of $(C_7H_{18}N_2)ZnBr_4$ monitoring at 460 nm (a) and 630 nm (b).

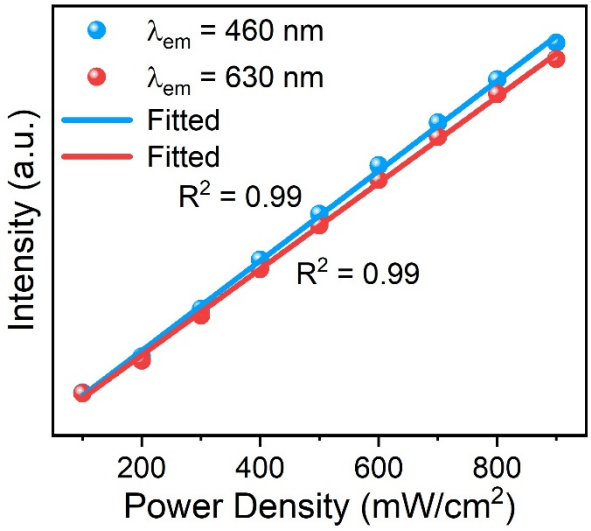

Fig. S17 The relationship between the integrated PL intensity and the excitation power of the $(C_7H_{18}N_2)CdBr_4$ after grinding at 80 K (λ_{ex} = 375 nm).

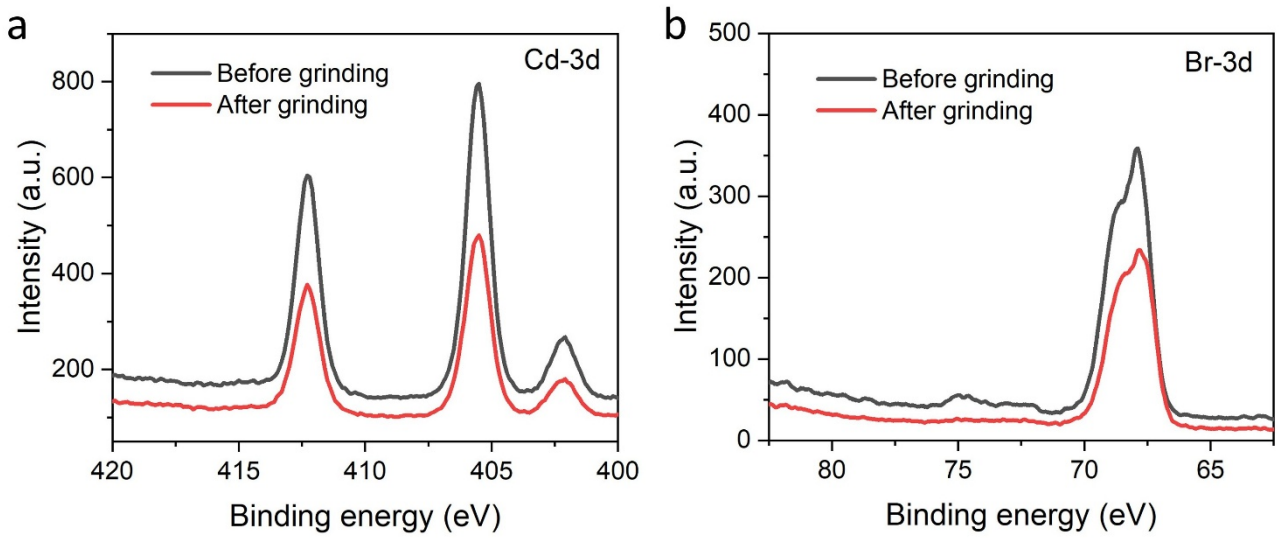

Fig. S18 XPS spectra of Cd-3d (a) and Br-3d (b) in $(C_7H_{18}N_2)CdBr_4$ before and after grinding.

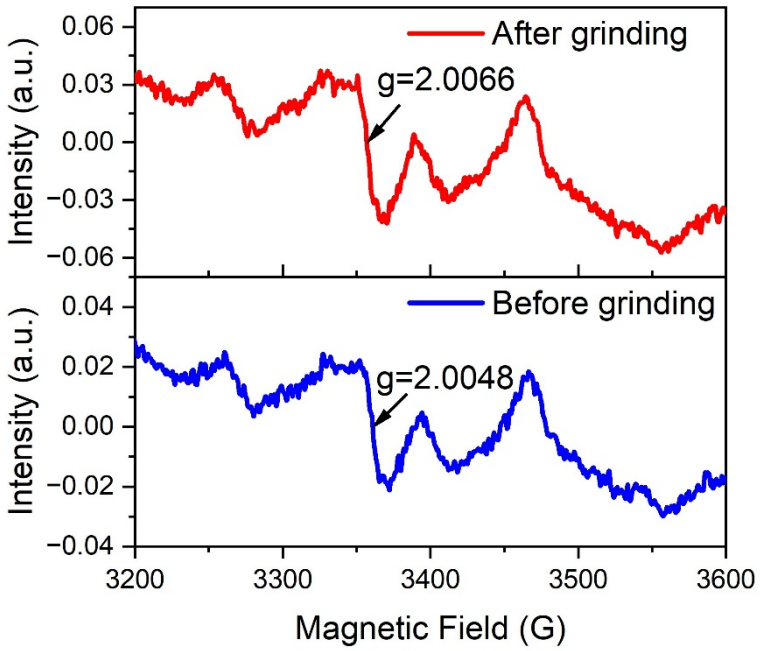

Fig. S19 EPR spectra of $(C_7H_{18}N_2)CdBr_4$ before and after grinding.

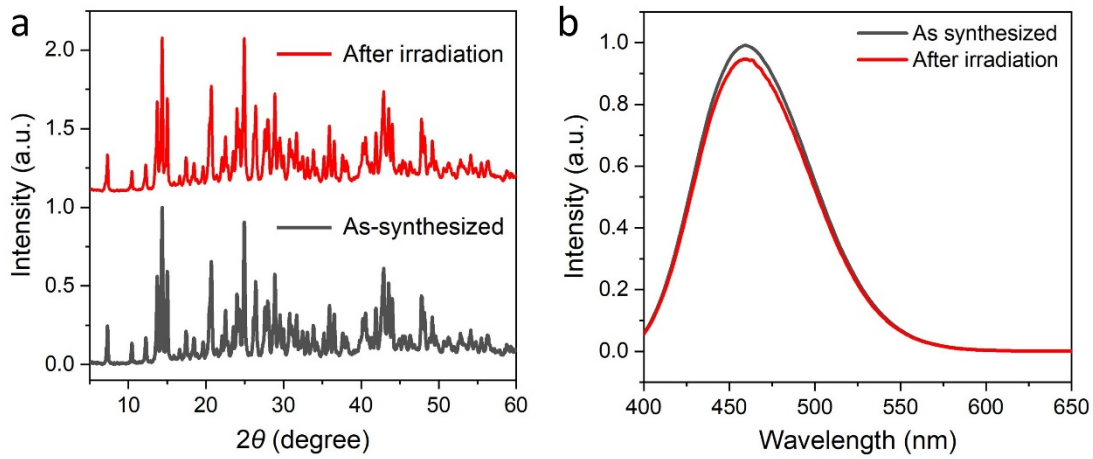

Fig. S20 The comparative PXRD patterns (a) and PL emission spectra (b) of as-synthesized $(C_7H_{18}N_2)ZnBr_4$ and the sample after UV light irradiation for one day.

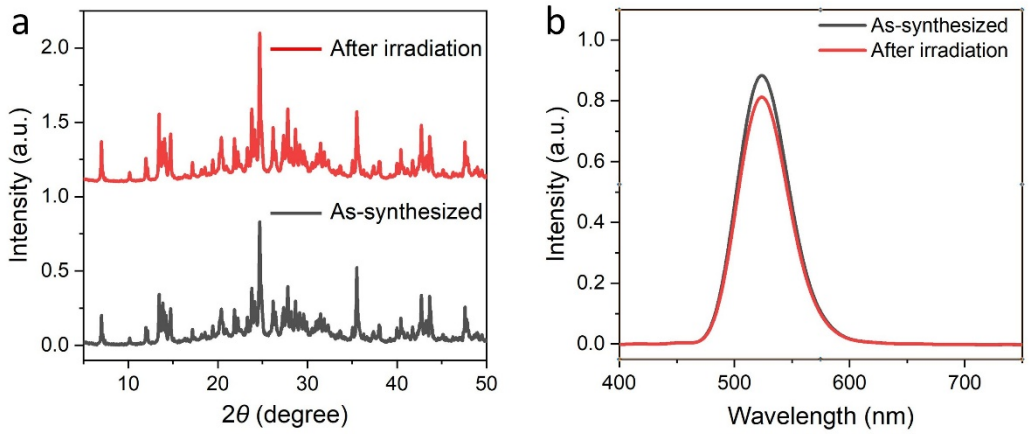

Fig. S21 The comparative PXRD patterns (a) and PL emission spectra (b) of as-synthesized $(C_7H_{18}N_2)MnBr_4$ and the sample after UV light irradiation for one day.

Table S1. Crystal data and structural refinements for $(C_7H_{18}N_2)ZnBr_4$, $(C_7H_{18}N_2)MnBr_4$, and $(C_7H_{18}N_2)CdBr_4$.

Compound	$(C_7H_{18}N_2)ZnBr_4$	$(C_7H_{18}N_2)MnBr_4$	$(C_7H_{18}N_2)CdBr_4$
chemical formula	$C_7H_{18}N_2ZnBr_4$	$C_7H_{18}N_2MnBr_4$	$C_7H_{18}N_2CdBr_4$
fw	515.24	504.18	562.27
Space group	*Pbca* (No. 61)	*Pbca* (No. 61)	*Pbca* (No. 61)
Crystal system	orthorhombic	orthorhombic	orthorhombic
a/Å	11.9707(4)	12.0129(9)	12.0323(3)
b/Å	9.9680(4)	10.0635(7)	10.1195(3)
c/Å	25.0354(8)	25.1751(18)	25.1920(8)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V(Å^3)	2987.32(18)	3043.5(4)	3067.40(15)
Z	8	8	8
D_{calcd} (g·cm^{-3})	2.291	2.203	2.435
Temp (K)	273.15	273.15	273.15
μ (mm^{-1})	12.316	11.343	11.817
F (000)	1952.0	1912.0	2096.0
Reflections collected	29409	36406	46280
Unique reflections	3700	2676	3821
GOF on F^2	0.984	1.021	1.035
[a]R_1, wR_2 ($I > 2\sigma(I)$)	0.0400/0.0794	0.0333/0.0540	0.0283/0.0480
[b]R_1, wR_2 (all data)	0.0831/0.0935	0.0668/0.0628	0.0485/0.0527

[a]$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, [b]$wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond lengths (Å) and bond angles (°) for halide $(C_7H_{18}N_2)ZnBr_4$.

Zn1-Br1	2.4446(8)	Zn1-Br2	2.3875(8)
Zn1-Br3	2.4255(8)	Zn1-Br4	2.3939(8)
Br1-Zn1-Br2	105.47(3)	Br1-Zn1-Br3	106.53(3)
Br1-Zn1-Br4	108.79(3)	Br2-Zn1-Br3	111.72(3)
Br2-Zn1-Br4	116.27(3)	Br3-Zn1-Br4	107.62(3)

Table S3. Selected bond lengths (Å) and bond angles (°) for halide $(C_7H_{18}N_2)MnBr_4$.

Mn1-Br1	2.4894(10)	Mn1-Br2	2.5171(10)
Mn1-Br3	2.5325(10)	Mn1-Br4	2.4802(10)
Br1-Mn1-Br2	107.04(4)	Br1-Mn1-Br3	107.98(4)
Br1-Mn1-Br4	118.24(4)	Br2-Mn1-Br3	106.68(3)
Br2-Mn1-Br4	112.11(4)	Br3-Mn1-Br4	104.15(4)

Table S4. Selected bond lengths (Å) and bond angles (°) for halide $(C_7H_{18}N_2)CdBr_4$.

Cd1-Br1	2.6001(5)	Cd1-Br2	2.5527(5)
Cd1-Br3	2.5631(5)	Cd1-Br4	2.6242(5)
Br1-Cd1-Br2	111.911(18)	Br1-Cd1-Br3	107.288(16)
Br1-Cd1-Br4	105.521(16)	Br2-Cd1-Br3	120.379(17)
Br2-Cd1-Br4	103.050(16)	Br3-Cd1-Br4	107.598(16)

Table S5. Hydrogen bonds data for halide $(C_7H_{18}N_2)ZnBr_4$.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(1)-H(1A)···Br(1)	0.89	2.64	3.373(4)	141
N(1)-H(1A)···Br(4)	0.89	2.91	3.492(4)	124
N(1)-H(1B)···Br(3)	0.89	2.56	3.410(4)	159
N(2)-H(2)···Br(1)	0.98	2.64	3.522(4)	149
C(2)-H(2A)···Br(1)	0.97	2.85	3.665(5)	142
C(3)-H(3A)···Br(3)	0.97	2.91	3.696(5)	139

Table S6. Hydrogen bonds data for halide $(C_7H_{18}N_2)MnBr_4$.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(1)-H(1C)···Br(3)	0.89	2.64	3.375(4)	140
N(1)-H(1D)···Br(2)	0.89	2.57	3.414(4)	158
N(2)-H(2)···Br(3)	0.98	2.63	3.514(4)	150
C(1)-H(1B)···Br(3)	0.97	2.84	3.656(5)	142
C(2)-H(2B)···Br(2)	0.97	2.91	3.692(5)	138

Table S7. Hydrogen bonds data for halide $(C_7H_{18}N_2)CdBr_4$.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N(1)-H(1A)···Br(1)	0.89	2.55	3.397(3)	158
N(1)-H(1B)···Br(4)	0.89	2.65	3.370(3)	139
N(2)-H(2)···Br(4)	0.98	2.60	3.481(3)	150
C(3)-H(3A)···Br(4)	0.97	2.85	3.652(4)	141
C(4)-H(4A)···Br(1)	0.97	2.90	3.685(4)	138

Table S8. Nominal and actual Mn^{2+} doping concentrations in $(C_7H_{18}N_2)CdBr_4$ and $(C_7H_{18}N_2)ZnBr_4$.

$(C_7H_{18}N_2)CdBr_4$		$(C_7H_{18}N_2)ZnBr_4$	
Nominal / mol%	Actual / mol%	Nominal / mol%	Actual / mol%
2	0.88	2	0.93
5	1.76	5	3.43
10	3.22	10	5.23
15	4.55	15	6.65
20	5.62	20	7.62

Table S9. Parameters of time-resolved PL spectra for $(C_7H_{18}N_2)CdBr_4$ and the fitted lifetimes.

Temperature / K	light source	Monitoring wavelength / nm	τ / μs
80	375 nm OPO laser	469	18.53
110	375 nm OPO laser	469	10.28
140	375 nm OPO laser	468	5.96
170	375 nm OPO laser	467	2.93
200	375 nm OPO laser	466	1.02
230	375 nm laser	465	0.73
260	375 nm laser	461	0.35
290	375 nm laser	460	0.06
320	375 nm laser	459	0.05

Table S10. Parameters of time-resolved PL spectra for $(C_7H_{18}N_2)ZnBr_4$ and the fitted lifetimes.

Temperature / K	light source	Monitoring wavelength / nm	$\tau / \mu s$
80	375 nm OPO laser	472	32.66
110	375 nm OPO laser	468	17.76
140	375 nm OPO laser	466	9.92
170	375 nm OPO laser	465	6.08
200	375 nm OPO laser	464	4.22
230	375 nm laser	463	2.21
260	375 nm laser	462	0.81
290	375 nm laser	460	0.28
320	375 nm laser	458	0.19

Table S11. Parameters of time-resolved PL spectra for $(C_7H_{18}N_2)MnBr_4$ and the fitted lifetimes.

Temperature / K	light source	Monitoring wavelength / nm	τ / ms
80		527	0.55
110		527	0.48
140		526	0.47
170	360 nm	525	0.43
200	microflash	524	0.40
230	lamp	524	0.37
260		522	0.36
290		522	0.32
320		521	0.26

Table S12. The comparison of LED parameters based on $(C_7H_{18}N_2)MBr_4$ and $Cs_3Cu_2X_5$ reported in the literature.

LED	CRI	CCT (K)	CIE coordinates	Stability	LER (lm/W)	Reference
F1	97.1	3864	(0.387,0.382)	fidelity index (R_f) exceeding 90	288	Adv. Mater. 2025, 37, 2500083
F2	97.8	4364	(0.366,0.366)		283	
F3	97.5	4876	(0.349,0.356)		276	
F4	96.6	5379	(0.335,0.343)		272	
F5	96.2	5931	(0.324,0.331)		262	
F6	94.3	6636	(0.312,0.320)		256	
F7	91.7	7230	(0.304,0.313)		244	
F8	90.6	9677	(0.282,0.292)		232	
This work	88.2	6816	(0.31, 0.32)	continuous operation exceeding 4 hours	10.2	