Supporting Information

Thermally Induced Reversible Phase Transition and Photoluminescence Switching Behavior of $(NH_4)_2MnBr_4(H_2O)_2$ Crystals

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Bond precision:	Mn- O = 0.0150 A	Wavelength=0.71073	
Cell:	a=7.8991(11)	b=7.8991(11)	c=8.5307(19)
	alpha=90	beta=90	gamma=90
Temperature:	307 K		
	Calculated	Reported	
Volume	532.28(19)	532.28(19)	
Space group	I 4/m m m	I 4/m m m	
Hall group	-I 4 2	-I 4 2	
Moiety formula	Br4 H4 Mn O2, H8 N2	2(Br2 H2 Mn0.5 O),0.25(H32 N8)	
Sum formula	Br4 H12 Mn N2 O2	Br4 H12 Mn N2 O2	
Mr	446.66	446.70	
Dx,g cm-3	2.787	2.787	
Z	2	2	
Mu (mm-1)	16.206	16.206	
F000	414.0	414.0	
F000’	412.87		
h,k,lmax		11,9,11	
Nref		236	
Tmin, Tmax	0.119,0.143	0.002,1.000	
Tmin’	0.090		

Table S1. Coefficients of $(NH_4)_2MnBr_4(H_2O)_2$ Crystal Structure.

Sample	N/(Atomic %)	Mn/(Atomic%)	Br/(Atomic%)	O/(Atomic %)
30 ℃	**23**	**8.67**	**39.69**	**28.64**

Table S2. EDS analysis of $(NH_4)_2MnBr_4(H_2O)_2$ at 30 ℃.

Sample	50 mesh	100 mesh	200 mesh	300 mesh
Heating time	32 s	27s	23s	18s
Turn off time	53 min	40 min	29 min	21 min

Table S3. The reversible luminescence response time of samples with different particle sizes tested under an air humidity of 40%.

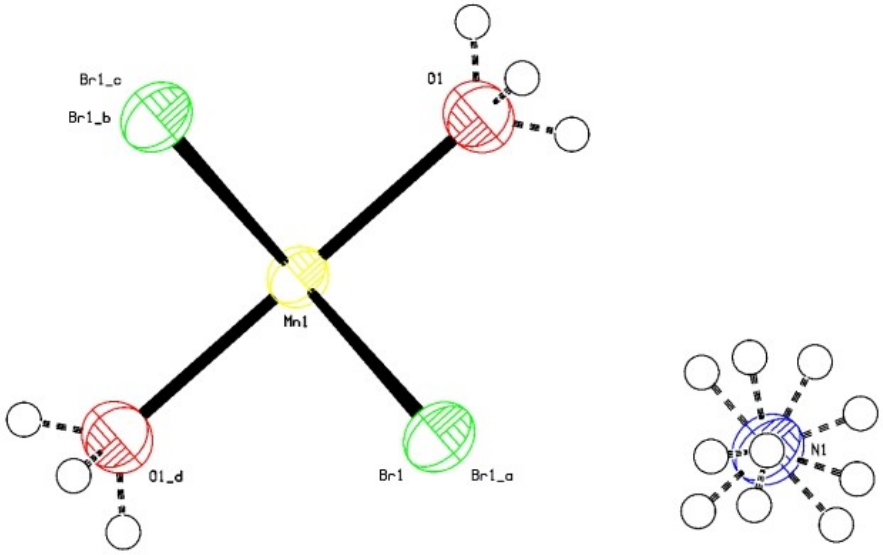

Figure S1. Schematic diagram of the disordered $(NH_4)_2MnBr_4(H_2O)_2$ crystal structure (H atoms have four sites but have no effect on the lattice parameters).

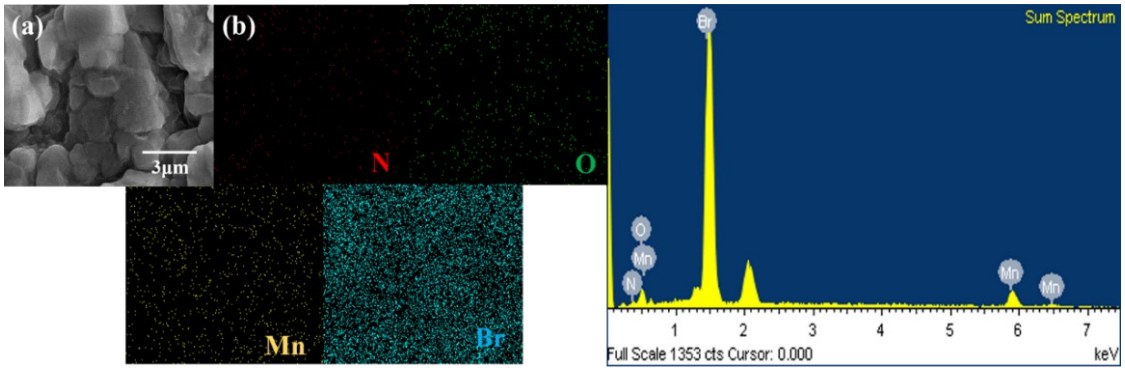

Figure S2. (a) SEM images and (b) EDS mapping of $(NH_4)_2MnBr_4(H_2O)_2$.

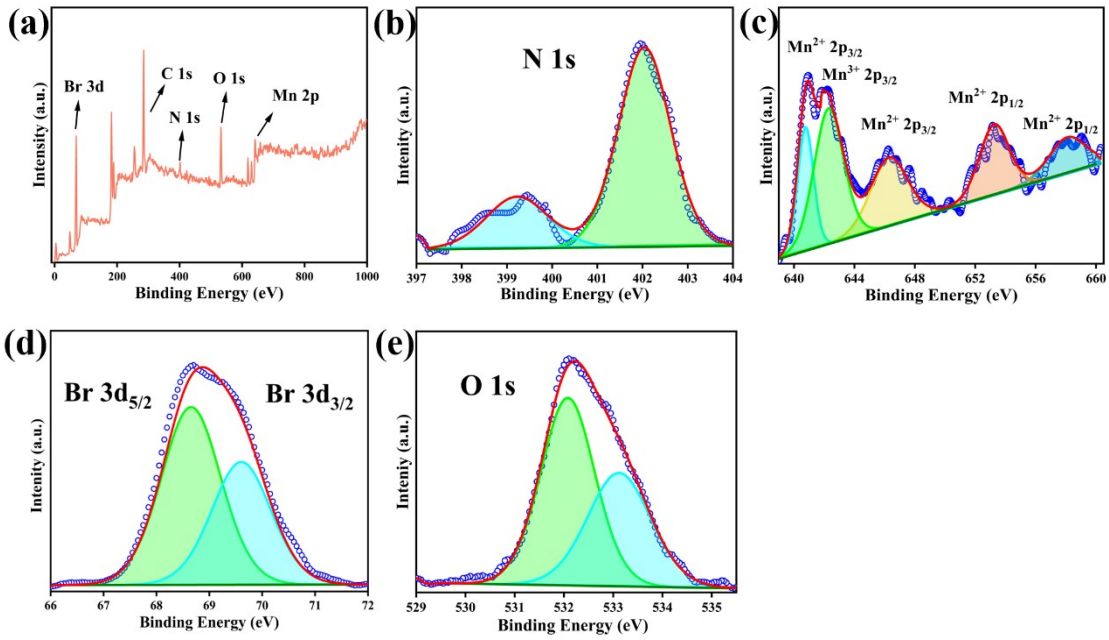

Figure S3. (a)XPS patterns of $(NH_4)_2MnBr_4(H_2O)_2$. High-resolution spectra of (b) N 1s, (c) Mn 2p, (d) Br 3d and (e) O 1s.

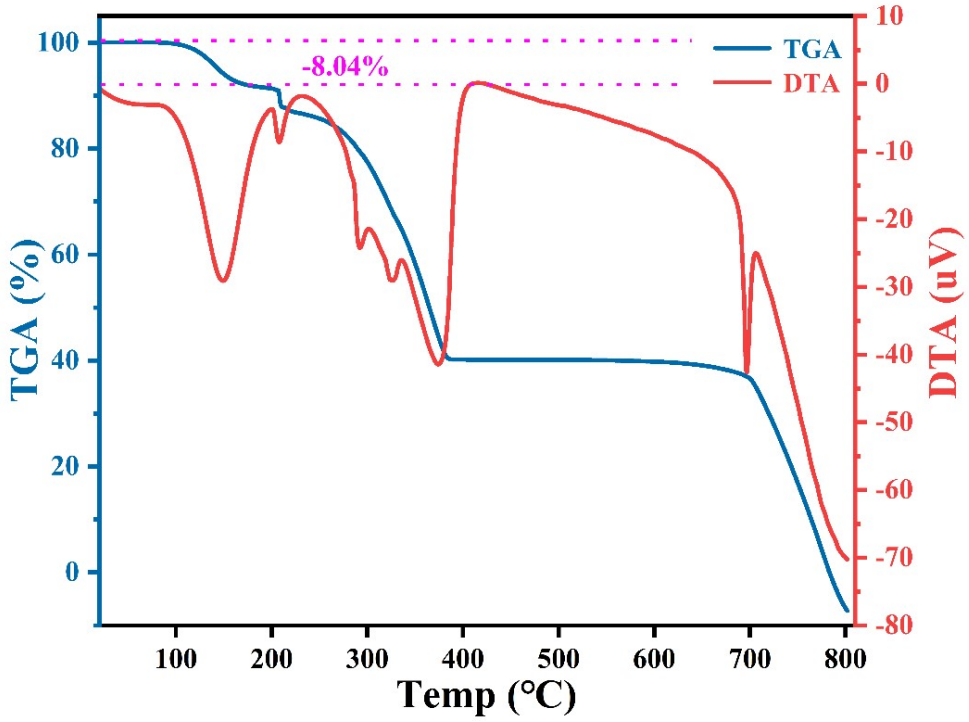

Figure S4. TGA and DTA of $(NH_4)_2MnBr_4(H_2O)_2$ powder.

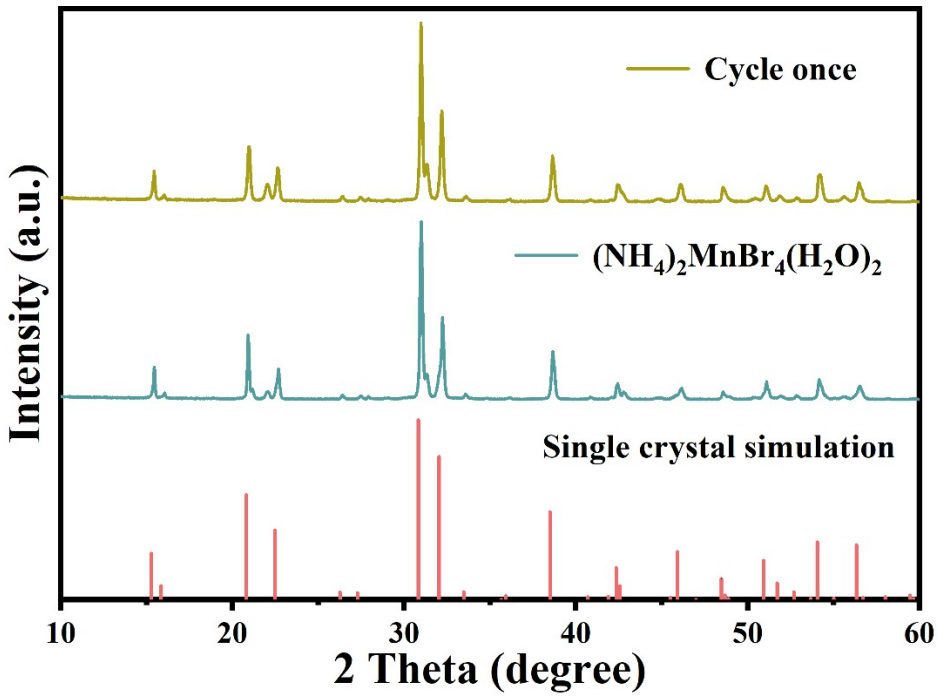

Figure S5. XRD patterns of pristine $(NH_4)_2MnBr_4(H_2O)_2$ and after one heating and cooling cycle.

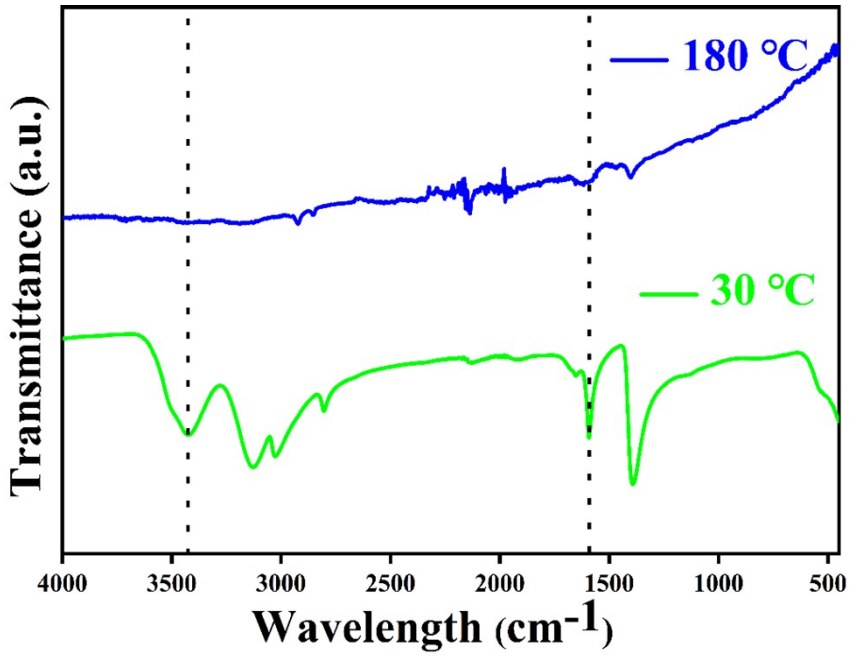

Figure S6. FT-IR spectra of $(NH_4)_2MnBr_4(H_2O)_2$ crystals with different temperature.

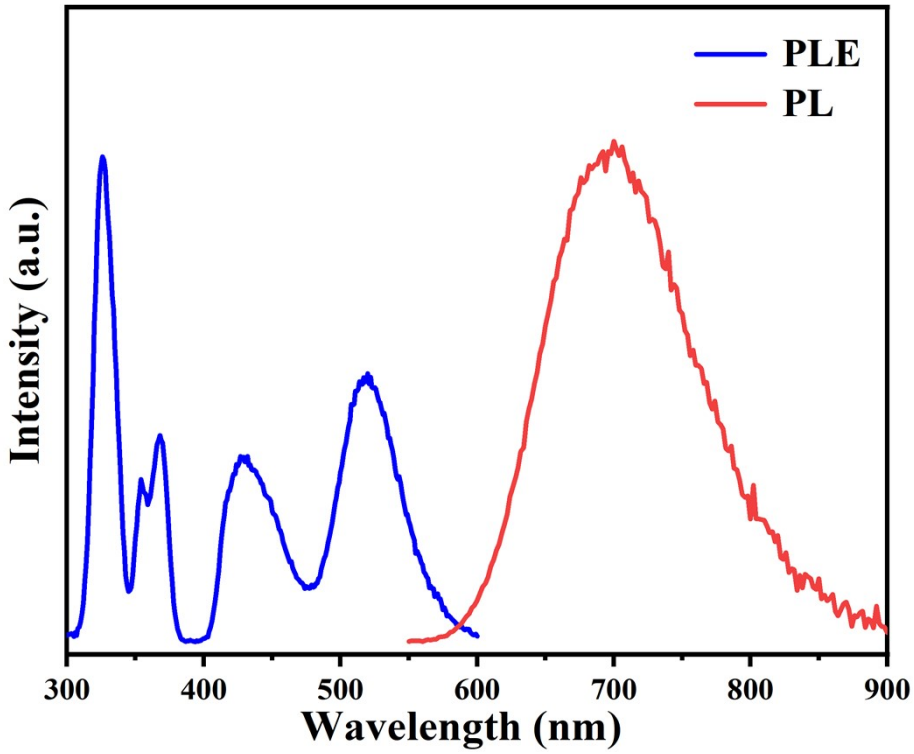

Figure S7. Excitation emission spectrum of $(NH_4)_2MnBr_4(H_2O)_2$ at room temperature.

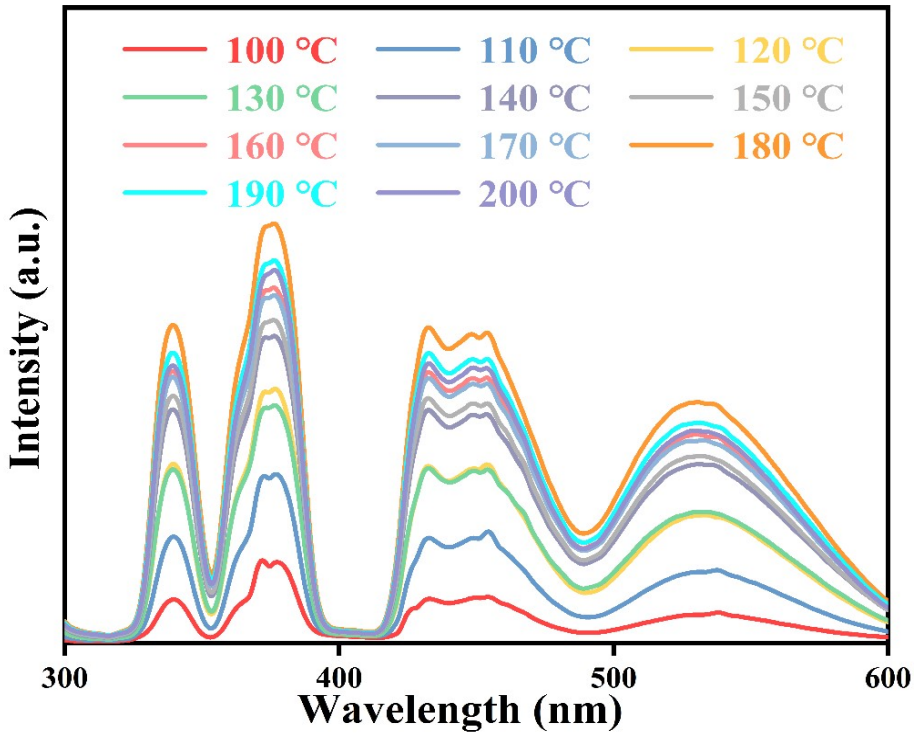

Figure S8. Temperature-dependent excitation spectrum of $(NH_4)_2MnBr_4(H_2O)_2$.

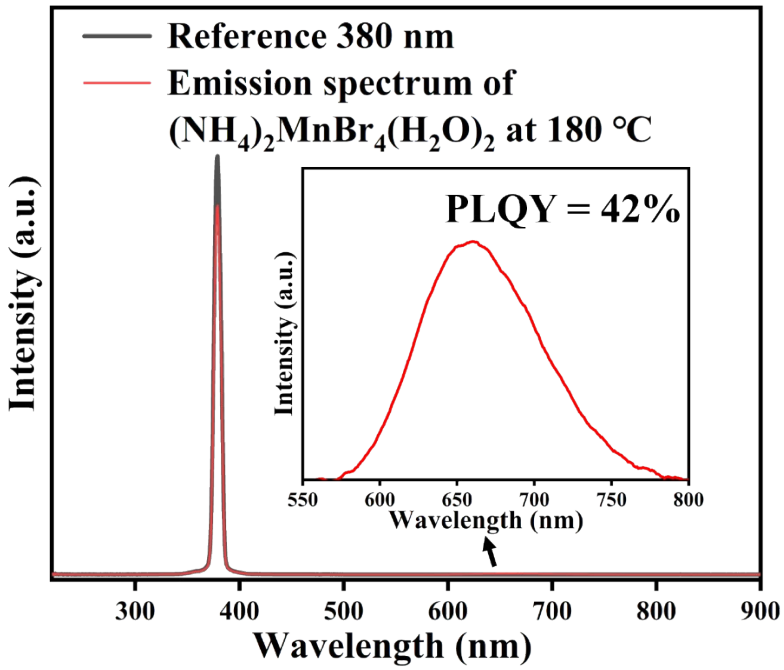

Figure S9. PLQY of $(NH_4)_2MnBr_4(H_2O)_2$ after heat treatment at 180 ℃.

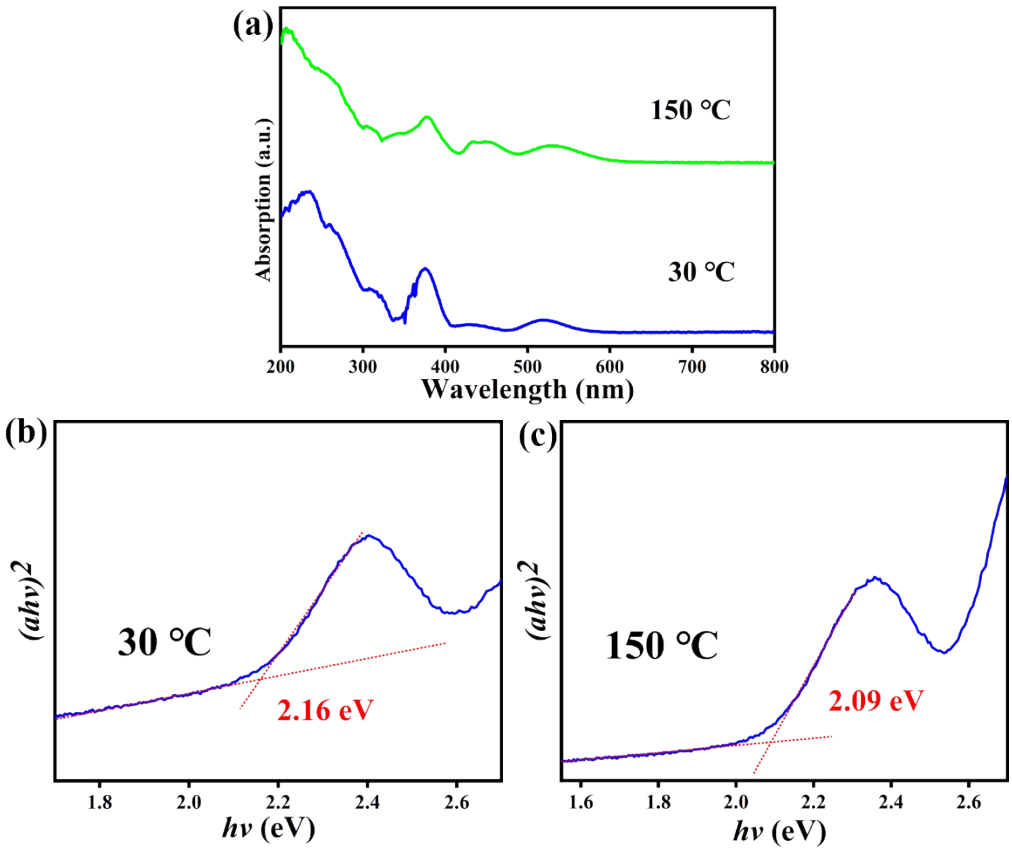

Figure S10. (a) Absorption spectra of $(NH_4)_2MnBr_4(H_2O)_2$ after heat treatment at 30 ℃ and 150 ℃, the fitted band gap of $(NH_4)_2MnBr_4(H_2O)_2$ after heat treatment at (b) 30 ℃ and (c) 150 ℃.

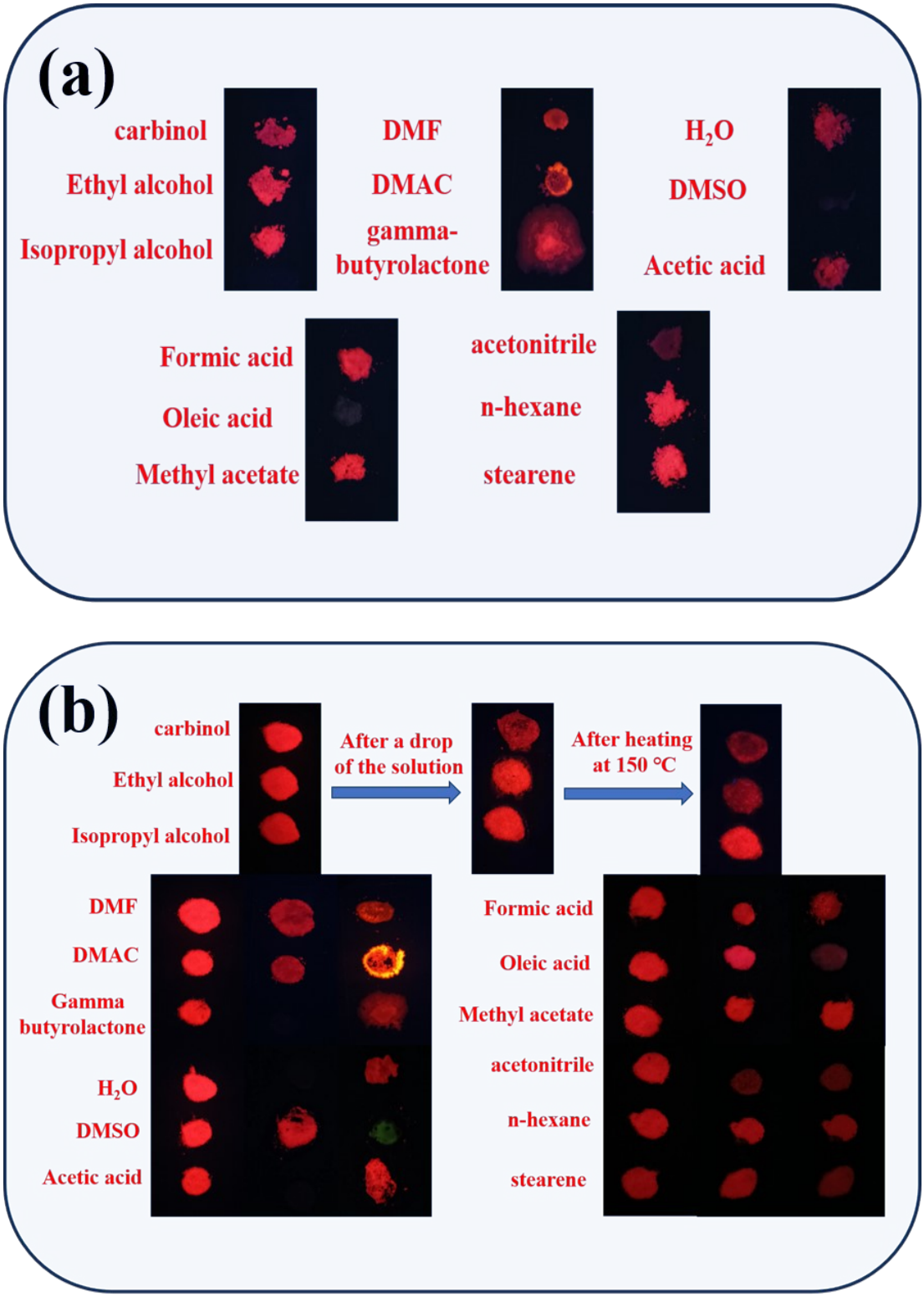

Figure S11. (a)First add the solvent dropwise, and then heat the $(NH_4)_2MnBr_4(H_2O)_2$ material. (b) After glowing, add solvent dropwise and heat again.

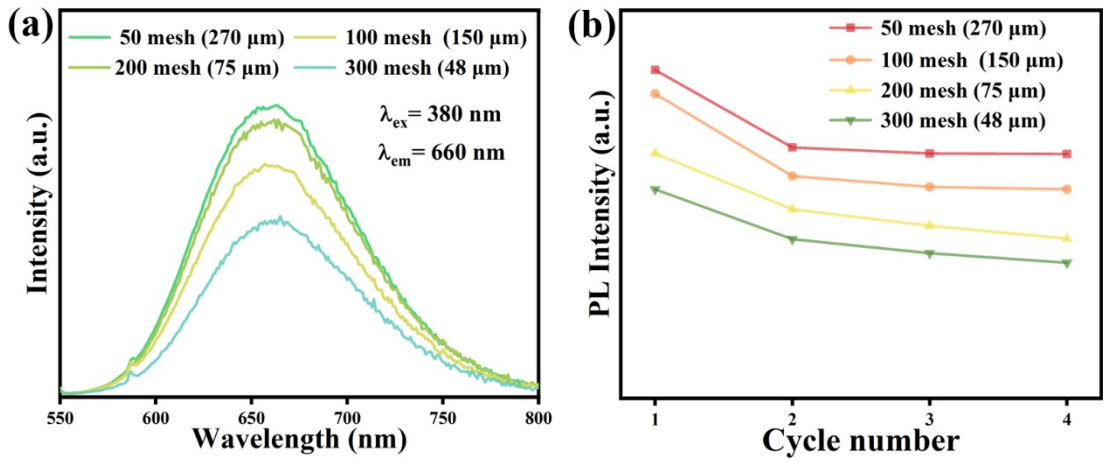

Figure S12. The samples were distinguished using meshes of different sizes. (a) PL intensity of samples with different particle sizes, (b) PL stability of different samples after four cycles.

The Calculations of Tanabe-Sugano (T-S) Matrices. The crystal field Dq, Racah B parameters and tree correction α were obtained using the modified energy terms derived by Tanabe and Sugano as follows:

$$\triangle = 10Dq \quad (1)$$

$$6S \rightarrow {}^4A_1; {}^4E({}^4G) = 10B + 5C + 20\alpha \quad (2)$$

$$6S \rightarrow {}^4E({}^4D) = 17B + 5C + 6\alpha \quad (3)$$

$$6S \rightarrow {}^4T_2({}^4D) = 13B + 5C + 8\alpha \quad (4)$$

$$6S \rightarrow {}^4T_2({}^4G) = -10Dq + 18B + 6C - (26B^2 /10Dq) + 22\alpha \quad (5)$$