

High phase transition temperature and photoluminescent properties in low-dimensional molecular perovskite ferroelastic crystals

Jia-Mei Zhang,^a Zhe-Kun Xu,^a Yan Qin,^a Peng-Fei Li^{*a} and Zhong-Xia Wang^{*ab}

^aOrdered Matter Science Research Center, Nanchang University, Nanchang 330031, People's Republic of China

^bCollege of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou 341000, People's Republic of China.

E-mail: lipf@ncu.edu.cn; zhongxiawang@ncu.edu.cn

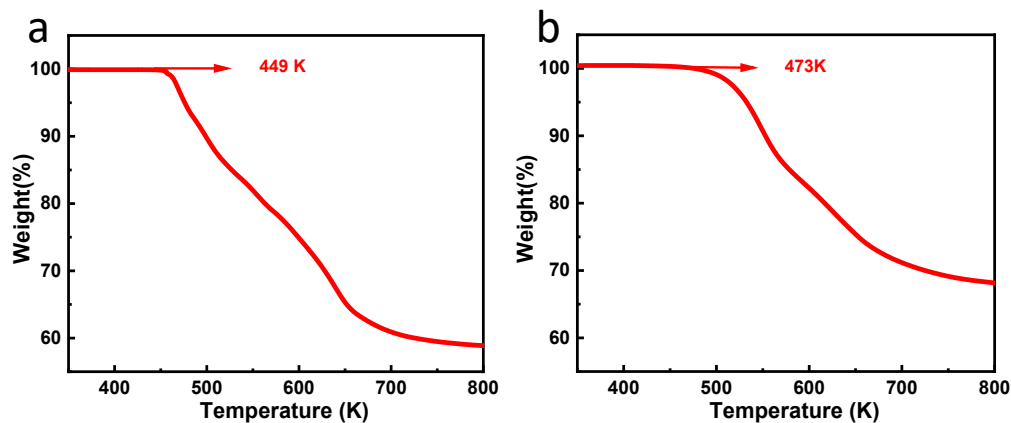


Figure S1. TGA curves of [DMPA]CdCl₃(a) and [DMPA]MnCl₃(b).

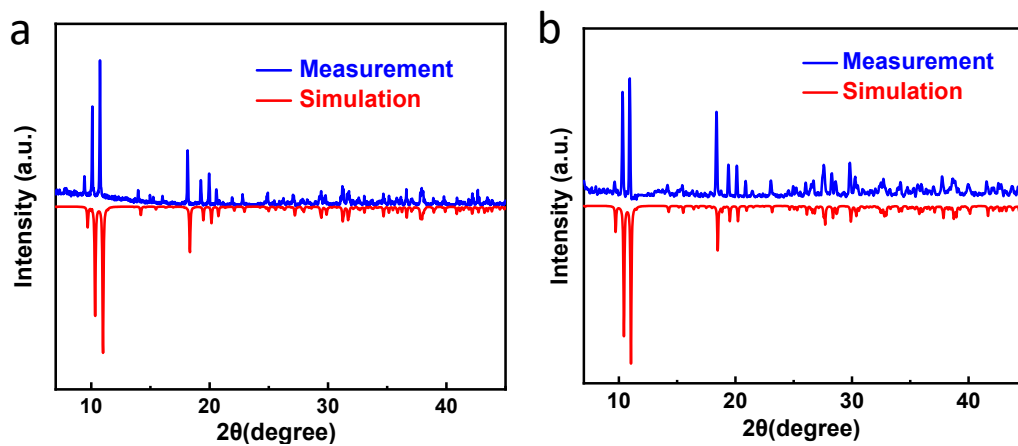


Figure S2. The experimental PXRD patterns of [DMPA]CdCl₃(a) and [DMPA]MnCl₃(b) at 300 K match well with their simulated ones.

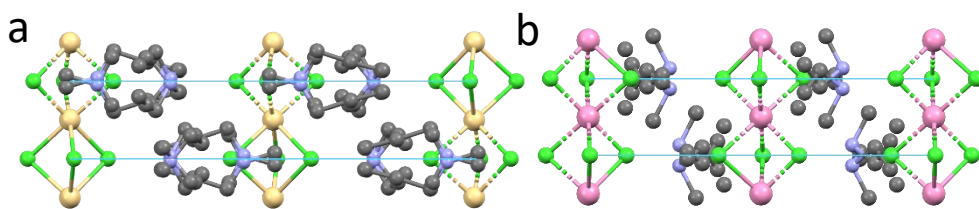


Figure S3. Crystal structure of [DMPA]CdCl₃ (a) and [DMPA]MnCl₃ (b) in HTP. The blue solid lines stand for the mirror plane.

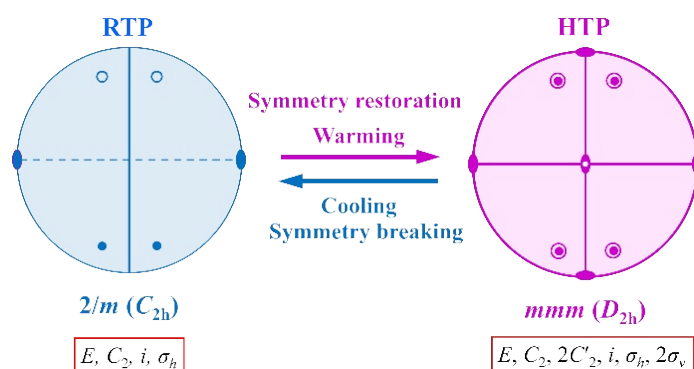


Figure S4. Spatial symmetry operations changes of [DMPA]CdCl₃ and [DMPA]MnCl₃.

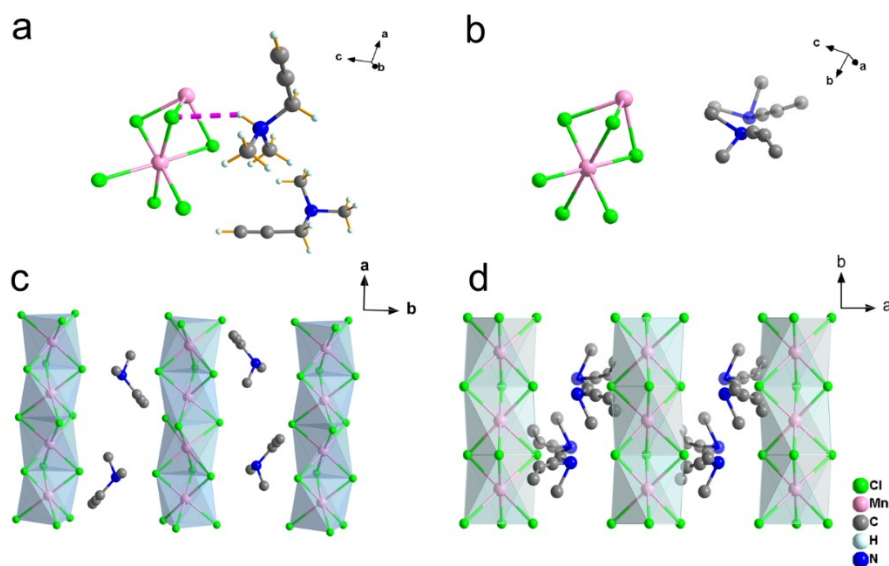


Figure S5. Crystal structure of $[\text{DMPA}]\text{MnCl}_3$ at 300 K (RTP) (a) and 428 K (HTP) (b); Packing views of the structure along the a -axis of $[\text{DMPA}]\text{MnCl}_3$ at 300 K (RTP) (c) and along the b -axis of $[\text{DMPA}]\text{MnCl}_3$ at 428 K (HTP) (d). The pink dotted line represents the hydrogen bond.

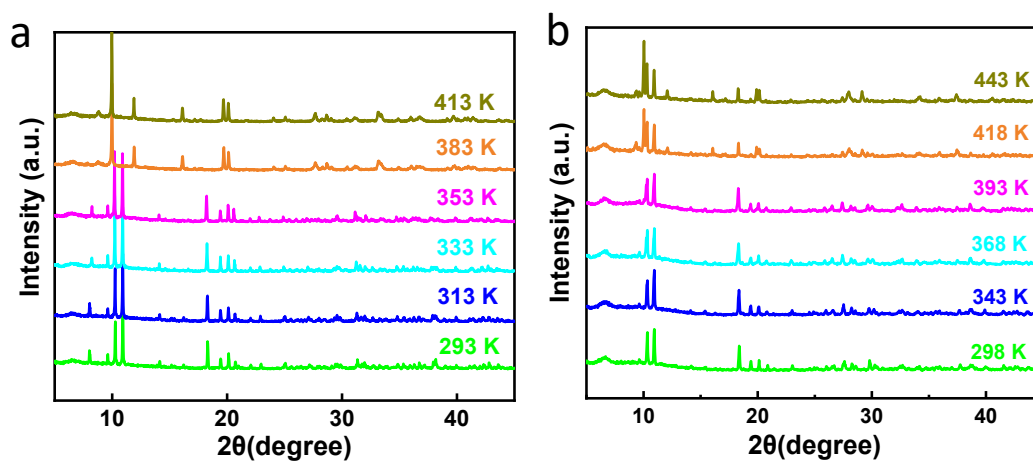


Figure S6. The experimental PXRD patterns of $[\text{DMPA}]\text{CdCl}_3$ (a) and $[\text{DMPA}]\text{MnCl}_3$ (b) at different temperatures.

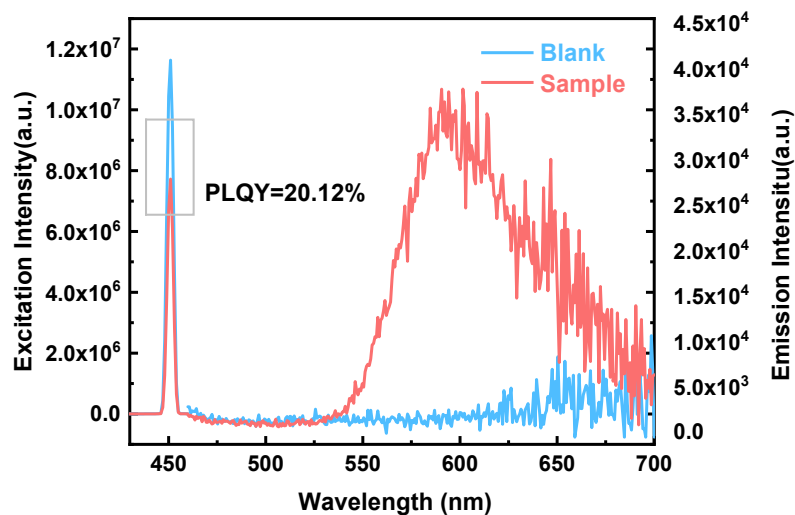


Figure S7. The PL quantum yield of [DMPA]MnCl₃ at room temperature.

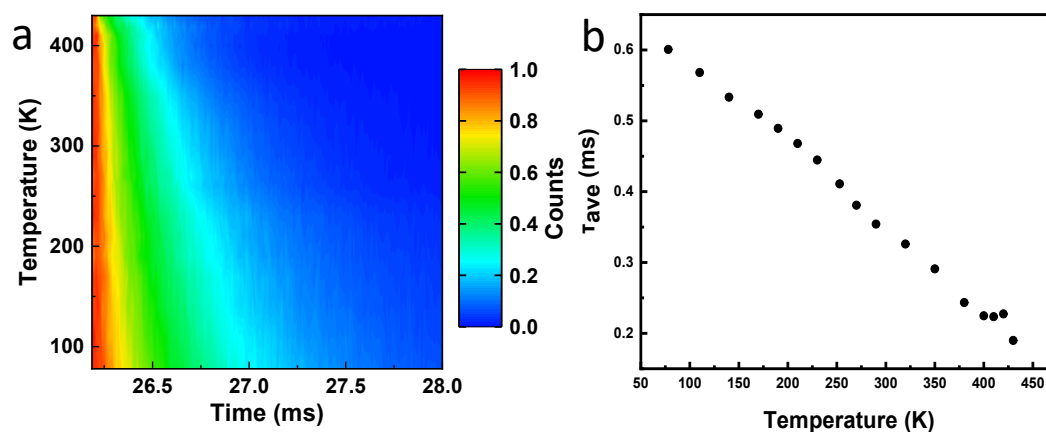


Figure S8. Fluorescence lifetime versus temperature plot for [DMPA]MnCl₃.

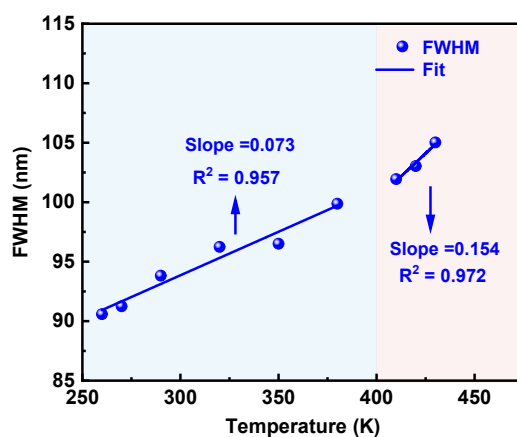


Figure S9. The variation of the full width at half maximum with temperature in VT-PL spectra of [DMPA]MnCl₃.

Table S1. The crystal data for [DMPA]CdCl₃ at different temperatures.

Compound	[DMPA]CdCl ₃	
Temperature (K)	300	403
System	Monoclinic	Orthorhombic
Space group	<i>P2₁/n</i>	<i>Pnma</i>
<i>a</i> (Å)	6.6640(9)	17.6713(11)
<i>b</i> (Å)	17.112(2)	6.7314(3)
<i>c</i> (Å)	18.366(3)	18.1716(10)
α (°)	90	90
β (°)	97.266(11)	90
γ (°)	90	90
<i>V</i> (Å ³)	2077.6(5)	2161.6(2)
<i>Z</i>	4	2
<i>R</i> ₁	0.0552	0.0836
<i>wR</i> ₂	0.0999	0.3203
GOF	1.011	1.066

Table S2. Hydrogen Bonds for [DMPA]CdCl₃ at 300 K.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/
N2	H2	C12 ¹	0.98	2.41	3.236(4)	141.5
N1	H1	C11	0.98	2.51	3.344(4)	143.4

¹-1/2+X,1/2-Y,-1/2+Z

Table S3. Bond length (Å) and bond angle (°) of [DMPA]CdCl₃ at 300 K.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Cd1-Cd2 ¹	3.3501(6)	Cd2-Cl2 ²	2.6618(10)
Cd1-Cd2	3.3152(6)	Cd2-Cl5	2.6200(11)
Cd1-Cl1	2.6501(11)	Cd1-Cl6	2.6555(11)
Cd1-Cl4	2.6713(11)	Cd2-Cl1 ²	2.6962(11)
Cd1-Cl3	2.6396(10)	Cd2-Cl4	2.6465(11)
Cd1-Cl5	2.6144(11)	Cd2-Cl3 ²	2.6365(11)
Cd1-Cl2	2.6781(11)	Cd2-Cl6	2.7136(11)
Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
Cl1-Cd1-Cl4	90.04(3)	Cl4-Cd2-Cl6	84.97(3)
Cl1-Cd1-Cl2	84.75(3)	Cl3 ² -Cd2-Cl1 ²	84.95(3)
Cl4-Cd1-Cl2	97.01(3)	Cl3 ² -Cd2-Cl2 ²	84.03(3)
Cl3-Cd1-Cl1	85.82(3)	Cl3 ² -Cd2-Cl6	97.86(3)
Cl3-Cd1-Cl2	83.66(3)	Cl5-Cd2-Cl4	84.91(3)
Cl3-Cd1-Cl6	98.59(3)	Cl5-Cd2-Cl3 ²	91.24(3)
Cl5-Cd1-Cl1	99.81(3)	Cl5-Cd2-Cl1 ²	98.93(3)
Cl5-Cd1-Cl4	84.52(3)	Cl5-Cd2-Cl6	84.64(3)
Cl5-Cd1-Cl3	95.16(3)	Cl2 ² -Cd2-Cl1 ²	84.17(3)
Cl5-Cd1-Cl6	85.92(3)	Cl2 ² -Cd2-Cl6	92.53(3)

¹-1+X,+Y,+Z; ²1+X,+Y,+Z

Table S4. Bond length (Å) and bond angle (°) of [DMPA]CdCl₃ at 403 K.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Cd1-Cd1 ¹	3.3472(14)	Cd1-Cl4	2.670(3)
Cd1-Cd1 ²	3.3842(14)	Cd1-Cl5	2.624(3)
Cd1-Cl1	2.658(3)	Cd1-Cl2	2.643(3)
Cd1-Cl3	2.649(3)	Cd1-Cl6	2.606(4)
Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
Cl6-Cd1-Cl1	97.08(12)	Cl6-Cd1-Cl4	85.11(11)
Cl6-Cd1-Cl3	95.14(11)	Cl2-Cd1-Cl4	96.08(12)
Cl6-Cd1-Cl5	83.97(12)	Cd1 ² -Cl1-Cd1	79.06(11)
Cl3-Cd1-Cl1	82.76(11)	Cd1-Cl3-Cd1 ²	79.39(11)
Cl1-Cd1-Cl2	84.34(12)	Cl5-Cd1-Cl2	94.65(11)
Cl5-Cd1-Cl4	82.62(12)	Cl2-Cd1-Cl3	83.69(11)
Cl5-Cd1-Cl3	98.45(11)	Cl1-Cd1-Cl4	96.17(11)
Cd1-Cl4-Cd1 ²	77.62(11)	Cd1-Cl5-Cd1 ²	79.24(12)
Cd1-Cl2-Cd1 ²	79.62(12)	Cd1-Cl6-Cd1 ²	79.92(13)

¹+X,3/2-Y,+Z; ²+X,1/2-Y,+Z

Table S5. The crystal data for compounds [DMPA]MnCl₃ at different temperatures.

Compound	[DMPA]MnCl ₃	
Temperature (K)	300	428
System	Monoclinic	Orthorhombic
Space group	<i>P2₁/n</i>	<i>Pnma</i>
<i>a</i> (Å)	6.3709(3)	14.6427(16)
<i>b</i> (Å)	16.9377(9)	6.4940(8)
<i>c</i> (Å)	18.3300(10)	10.999(2)
α (°)	90	90
β (°)	97.538(5)	90
γ (°)	90	90
<i>V</i> (Å ³)	1960.87(18)	1045.9(3)
<i>Z</i>	4	4
<i>R</i> ₁	0.0573	0.2541
<i>wR</i> ₂	0.1744	0.4352
GOF	1.095	1.028

Table S6. Hydrogen Bonds for [DMPA]MnCl₃ at 300 K

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N2	H2	Cl3 ¹	0.98	2.55	3.371(6)	141.2
N2	H2	Cl5 ²	0.98	2.79	3.495(5)	129.3
N1	H1	Cl1	0.98	2.41	3.227(6)	140.0

¹-1/2+X,3/2-Y,-1/2+Z; ²-3/2+X,3/2-Y,-1/2+Z

Table S7. Bond length (Å) and bond angle (°) of [DMPA]MnCl₃ at 300 K.

Atom- Atom	Length/Å	Atom- Atom	Length/Å
Cl2- Mn1	2.5317(17)	Mn2- Cl1	2.5631(17)
Cl2- Mn2	2.5374(17)	Mn2- Cl4 ²	2.5121(17)
Cl3-Mn1	2.5720(17)	Cl5-Mn2 ¹	2.5646(17)
Cl3-Mn2	2.5439(17)	Cl6-Mn1	2.5935(18)
Cl6-Mn2 ¹	2.5565(17)	Mn1-Cl1	2.5594(17)
Cl5-Mn1	2.5587(17)	Mn1-Cl4	2.5112(17)
Atom- Atom- Atom	Angle/°	Atom- Atom-Atom	Angle/°
Cl2- Mn2-Cl3	85.39(6)	Cl2-Mn1-Cl1	84.17(5)
Cl2- Mn2-Cl6	97.38(6)	Cl3-Mn1-Cl5 ²	90.35(6)
Cl2- Mn2-Cl1	84.36(5)	Cl3-Mn1-Cl1	85.12(5)
Cl5- Mn2-Cl3	92.41(6)	Cl6 ² -Mn1-Cl1	90.03(6)
Cl5- Mn2-Cl6	85.05(5)	Cl1-Mn1-Cl5 ²	96.56(6)
Cl5- Mn2-Cl1	99.02(6)	Cl4 ² -Mn1-Cl2	94.61(6)
Cl1- Mn2-Cl3	84.62(6)	Cl4 ² -Mn1-Cl3	99.12(6)
Cl1- Mn2-Cl6	92.01(6)	Cl4 ² -Mn1-Cl6 ²	85.87(6)
Cl4- Mn2-Cl2	91.67(6)	Cl4 ² -Mn1-Cl5 ²	84.96(6)
Cl4- Mn2-Cl6	85.10(6)	Cl2-Mn1-Cl3	85.86(6)
Cl4- Mn2-Cl5	85.10(6)	Cl2-Mn1-Cl6 ²	98.18(6)
Cl4- Mn2-Cl3	98.50(6)	Cl6 ² -Mn1-Cl5 ²	85.69(6)

¹1+X,+Y,+Z; ²-1+X,+Y,+Z**Table S8.** Bond length (Å) and bond angle (°) of [DMPA]MnCl₃ at 428 K.

Atom-Atom	Length/Å	Atom-Atom	Length/Å
Cl1-Mn1 ¹	2.422(8)	Mn1-Cl3 ²	2.567(11)
Cl1-Mn1	2.422(8)	Mn1-Cl4	2.639(6)
Mn1-Cl3	2.567(11)	Mn1-Cl4 ²	2.639(6)
Atom-Atom-Atom	Angle/°	Atom-Atom-Atom	Angle/°
Mn1 ¹ -Cl1-Mn1	84.2(4)	Cl3-Mn1-Cl4 ²	86.4(3)
Cl1 ² -Mn1-Cl4 ²	95.1(3)	Cl3 ² -Mn1-Cl4 ²	93.6(3)
Cl1-Mn1-Cl3 ²	100.9(4)	Cl3-Mn1-Cl4	93.6(3)
Cl1 ² -Mn1-Cl3	100.9(4)	Cl3 ² -Mn1-Cl4	86.4(3)
Cl1 ² -Mn1-Cl3 ²	79.1(4)	Cl1-Mn1-Cl4 ²	84.9(3)
Cl1-Mn1-Cl3	79.1(4)	Cl1 ² -Mn1-Cl4	85.9(3)
Cl1-Mn1-Cl4	95.1(3)		

¹1-X,1/2+Y,1-Z; ²1-X,-Y,1-Z; ³1-X,-1/2+Y,1-Z