Electronic Supplementary Material (ESI) for Materials Advances.

Supporting information

Magnetic-dielectric bistabilities and magnetodielectric coupling effect in a new layered hybrid perovskite: $(C_6H_5(CH_2)_4NH_3)_2[MnCl_4]$

Bo Huang,[a,b] Ping Wang,[b] Wei-Xiong Zhang*[,a], Xiao-Ming Chen[a]

[a] MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou, 510275, P. R. China.

[b] Faculty of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming, 650500, P. R. China.

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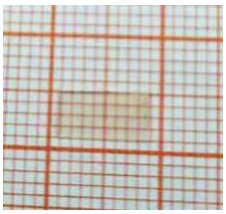

Fig. S1 Photo of a crystal of **1** viewed along the *c* axis.

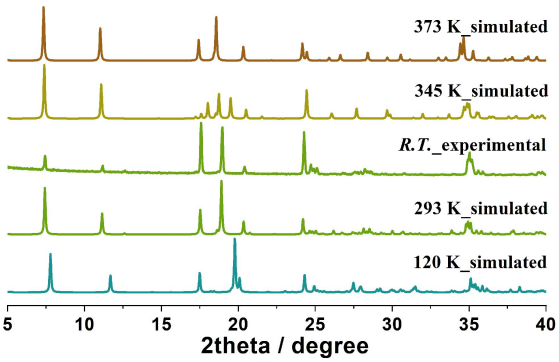

Fig. S2 Experimental powder X-ray diffraction patterns compared with the simulated one.

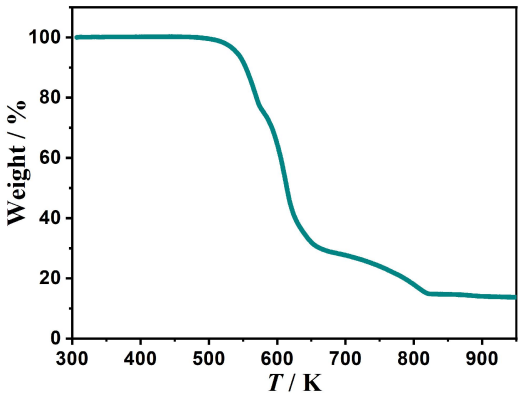

Fig. S3 Thermogravimetric curve of **1** under N_2 atmosphere at a heating rate of 5 K/min.

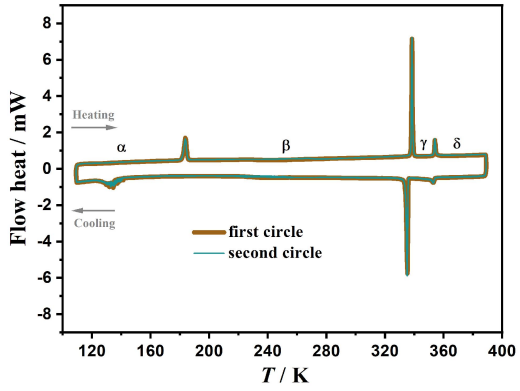

Fig. S4 Two heating-cooling circles of differential scanning calorimetry curves for **1**.

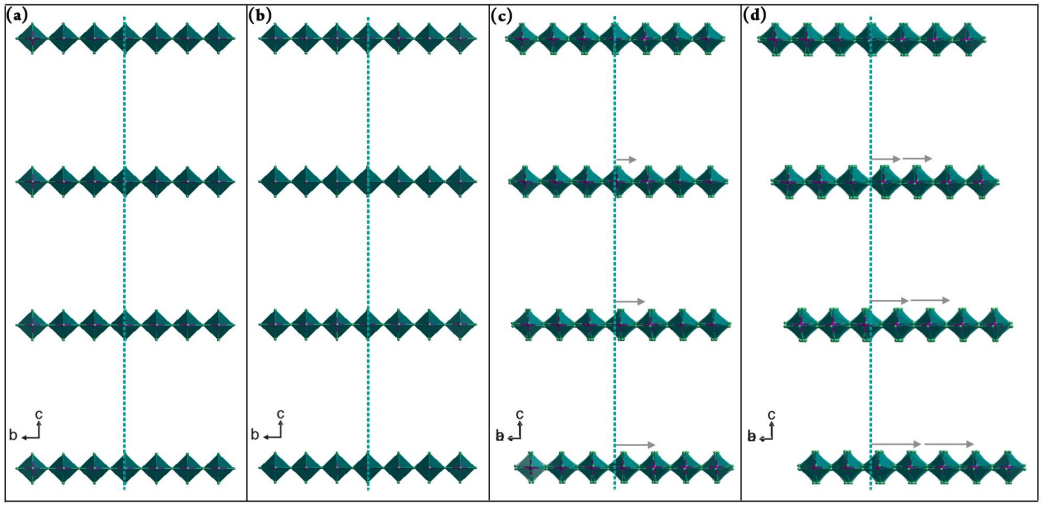

Fig. S5 Inorganic layers of **1** at 373 K (a), 345 K (b), 293 K (c), and 120 K (d). Mn and Cl atoms are shaded in violet and green. The teal dotted lines are guide to the relative displacement of the inorganic layers. The grey arrows represent the direction of the relative movement.

Table S1. Summary of crystal data and structural refinements of **1** at 120, 293, 345, and 373 K.

Empirical formula			$C_{20}H_{32}N_2MnCl_4$	
Formula weight			497.22	
***T* / K**	120(2)	293(2)	345(2)	373(2)
Phase type	**α**	**β**	**γ**	**δ**
Space group	$P2_1/a$	$P2_1/a$	*Bmmm*	*P4/mmm*
***a* / Å**	7.1398(5)	7.2244(4)	5.1706(4)	5.2046(4)
***b* / Å**	7.3173(6)	7.3495(4)	5.1534(4)	5.2046(4)
***c* / Å**	22.892(2)	23.812(1)	47.842(2)	24.06(2)
β / degree	82.472(2)	88.311(1)	90	90
***V* / Å³**	1185.7(2)	1263.8(1)	1274.8(2)	651.77(8)
Z	2	2	2	1
D_{calcd} **/ g cm⁻³**	1.393	1.307	1.295	1.267
***μ* / mm⁻¹**	1.016	0.953	0.945	0.924
GOF	1.034	1.016	0.959	1.016
R_1, wR_2 $[I > 2\sigma(I)]^a$	0.0418, 0.0997	0.0338, 0.0831	0.0655, 0.1536	0.0507, 0.1105
R_1, wR_2 **(all data)**	0.0513, 0.1058	0.0457, 0.0902	0.0900, 0.1726	0.0696, 0.1199

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

Table S2. Selected bond lengths (Å) for **1** at 120, 293, 345, and 373 K.

			120 K		
Mn1–Cl1	2.5122(5)	Mn1–Cl2	2.5745(5)	Mn1–Cl2^{A}	2.5874(5)
			293 K		
Mn1–Cl1	2.4889(6)	Mn1–Cl2	2.5878(5)	Mn1–Cl2^{A}	2.5968(5)
			345 K		
Mn1–Cl1	2.4544(19)	Mn1–Cl2	2.5767(2)	Mn1–Cl3	2.5853(2)
			373 K		
Mn1–Cl1	2.457(4)	Mn1–Cl2	2.6023(2)		

Symmetry codes: $^{A)}$-1/2-*x*, -1/2+*y*, 1-*z*

Table S3. Selected angles (°) for **1** at 120, 293, 345, and 373 K.

			120 K		
Cl1–Mn1–Cl1^{A}	180.000(4)	Cl1–Mn1–Cl2	91.085(17)	Cl1–Mn1–Cl2^{A}	88.915(17)
Cl1–Mn1–Cl2^{B}	88.916(17)	Cl1^{A}–Mn1–Cl2^{A}	91.085(17)	Cl1^{A}–Mn1–Cl2^{B}	91.084(17)
Cl2–Mn1–Cl2^{A}	180.00(2)	Cl2–Mn1–Cl2^{B}	87.978(7)	Cl2–Mn1–Cl2^{C}	92.022(7)
Cl2^{B}–Mn1–Cl2^{C}	180.000(1)	Mn1–Cl2–Mn1^{C}	164.02(2)		
			293 K		
Cl1–Mn1–Cl1^{A}	180	Cl1–Mn1–Cl2	90.548(19)	Cl1–Mn1–Cl2^{A}	89.452(19)
Cl1–Mn1–Cl2^{B}	88.582(19)	Cl1–Mn1–Cl2^{C}	91.418(19)	Cl2–Mn1–Cl2^{A}	180.000
Cl2–Mn1–Cl2^{B}	88.502(5)	Cl2–Mn1–Cl2^{C}	91.498(5)	Cl2^{A}–Mn1–Cl2^{C}	88.502(5)
Mn1–Cl2–Mn1^{D}	167.31(3)				
			345 K		
Cl1–Mn1–Cl1^{A}	180	Cl1–Mn1–Cl2	90	Cl1–Mn1–Cl3	180
Cl2–Mn1–Cl2^{B}	180	Cl2–Mn1–Cl3	90	Cl3–Mn1–Cl3^{C}	180
Mn1–Cl2–Mn1^{D}	180	Mn1–Cl3–Mn1^{E}	180		
			373 K		
Cl1–Mn1–Cl1^{A}	180	Cl1–Mn1–Cl2	90	Cl2–Mn1–Cl2^{B}	90
Cl2–Mn1–Cl2^{C}	180	Mn1–Cl2–Mn1	180		

Symmetry codes:

120 K: $^{A)}$ -1-*x*, 2-*y*, 1-*z*; $^{B)}$-1/2+*x*, 5/2-*y*, *z*; $^{C)}$-1/2-*x*, -1/2+*y*, 1-*z*;

293 K: $^{A)}$ -1-*x*, 2-*y*, 1-*z*; $^{B)}$-1/2+*x*, 3/2-*y*, *z*; $^{C)}$ -1/2-*x*, 1/2+*y*, 1-*z*; $^{D)}$-1/2-*x*, -1/2+*y*, 1-*z*;

353 K: $^{A)}$-*x*, -*y*, -*z* ; $^{B)}$ *x*, -1+*y*, *z*; $^{C)}$1+*x*, *y*, *z*; $^{D)}$*x*, 1+*y*, *z*; $^{E)}$-1+*x*, *y*, *z;*

373 K: $^{A)}$ -*x*, -*y*, -*z*; $^{B)}$ -*y*, *x*, *z*; $^{C)}$1+*x*, *y*, *z*

Table S4. The geometry (Å, °) of hydrogen bonds for **1** at 120, 293, 345, and 373 K.

	D–H···A	D–H	H···A	D···A	∠D–H···A
120 K	N1–H1A···Cl2	0.943	2.357	3.253	158.51
	N1–H1B···Cl1	0.943	2.297	3.224	167.75
	N1–H1C···Cl1	0.952	2.342	3.274	166.12
293 K	N1–H1A···Cl1	0.890	2.391	3.274	171.73
	N1–H1B···Cl2^{A}	0.890	2.439	3.317	168.75
	N1–H1C···Cl1^{B}	0.890	2.602	3.402	149.88
	N1–H1C···Cl2^{C}	0.890	2.770	3.384	127.27
345 K	N1–H1A···Cl2^{A}	0.890	2.784	3.578	149.27
	N1–H1A···Cl3^{B}	0.890	2.733	3.309	123.61
	N1–H1B···Cl1^{C}	0.890	2.564	3.407	158.39
	N1–H1B···Cl2	0.890	2.817	3.325	117.68
	N1–H1C···Cl1	0.890	2.973	3.671	136.69
	N1–H1C···Cl3^{A}	0.890	2.855	3.581	139.70
373 K	N1–H1A···Cl1^{A}	0.890	2.673	3.463	148.53
	N1–H1A···Cl2^{B}	0.890	2.708	3.296	124.69
	N1–H1B···Cl2^{A}	0.890	2.888	3.382	116.69
	N1–H1B···Cl1^{C}	0.890	2.905	3.770	164.32
	N1–H1C···Cl2^{D}	0.890	2.648	3.537	175.84

Symmetry codes:

120 K: $^{A)}$ *x*, -*y*+3/2, *z*-1/2, *z*; $^{B)}$ *x*, *y*, *z*-1;

293 K: $^{A)}$ *x*-1/2, -*y*+5/2, *z*; $^{B)}$*x*+1/2, -*y*+5/2, *z*; $^{C)}$*x*, *y*+1, *z*;

345 K: $^{A)}$ *x*+1, *y*, *z*; $^{B)}$ *x*+1, *y*+1, *z*; $^{C)}$*x*, *y*+1, *z*;

373 K: $^{A)}$ *x*+1, *y*+1, *z*; $^{B)}$ -*y*+1, *x*+1, *z*; $^{C)}$ *x*, *y*+1, *z*; $^{D)}$ *x*+1, *y*, *z*