Electronic Supporting Information

Zero-Dimensional Organic-Inorganic Hybrid Manganese Bromide with Coexistence of Dielectric−Thermal Double Switches and Efficient Fluorescence

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More characterizations

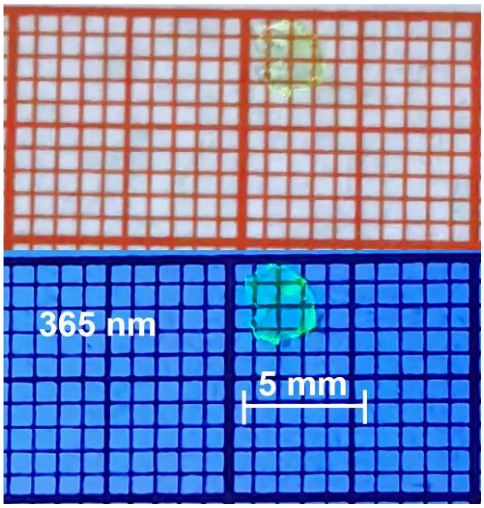

Fig. S1 The macroscopic shape of the single crystal of crystal **1**.

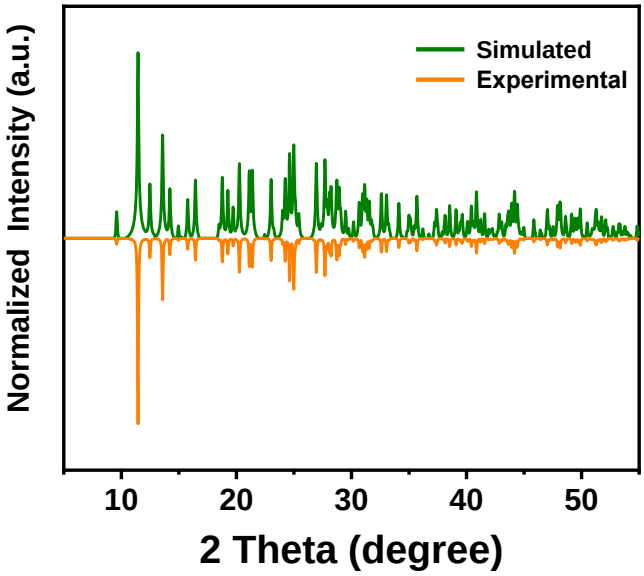

Fig. S2 The powder X-ray diffraction (PXRD) patterns for **1**.

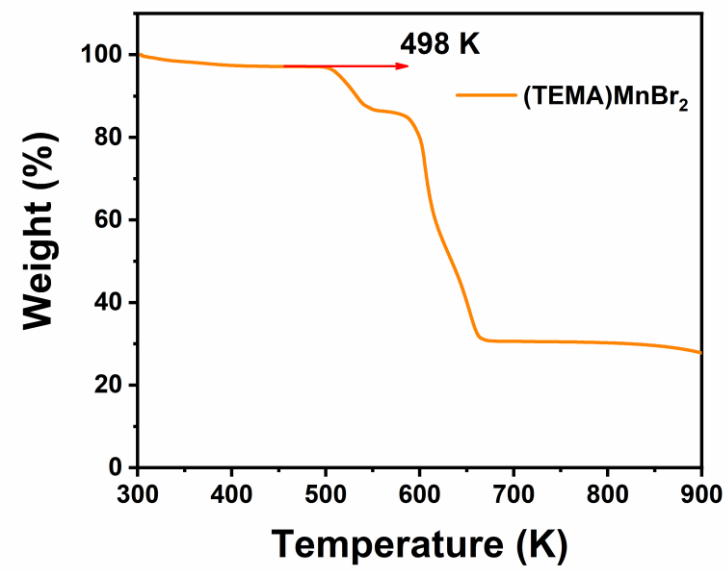

Fig. S3 TG curve of $(TEMA)_2MnBr_4$ in the temperature range of 300 – 900 K.

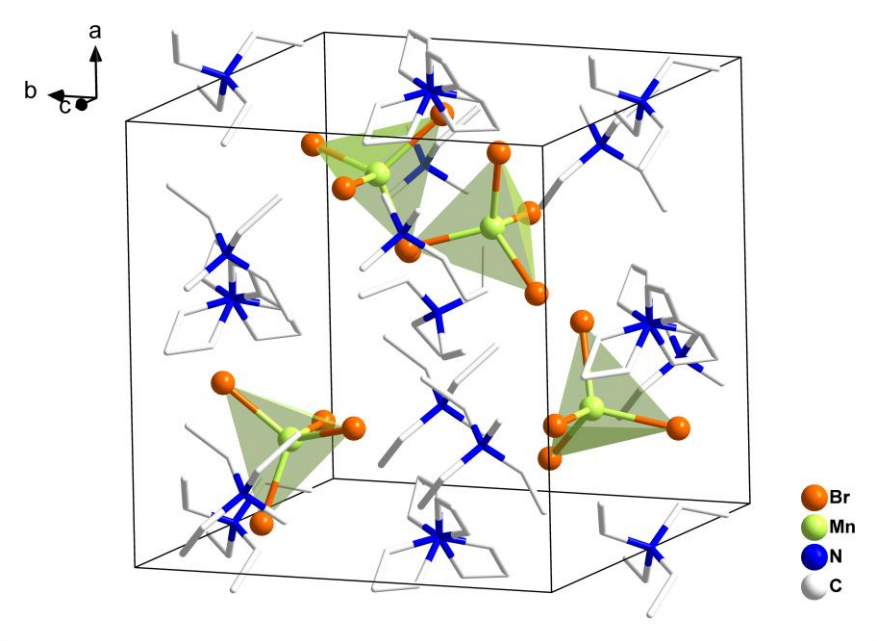

Fig. S4 Packing diagram of compound **1**. The H atoms are omitted for clarity.

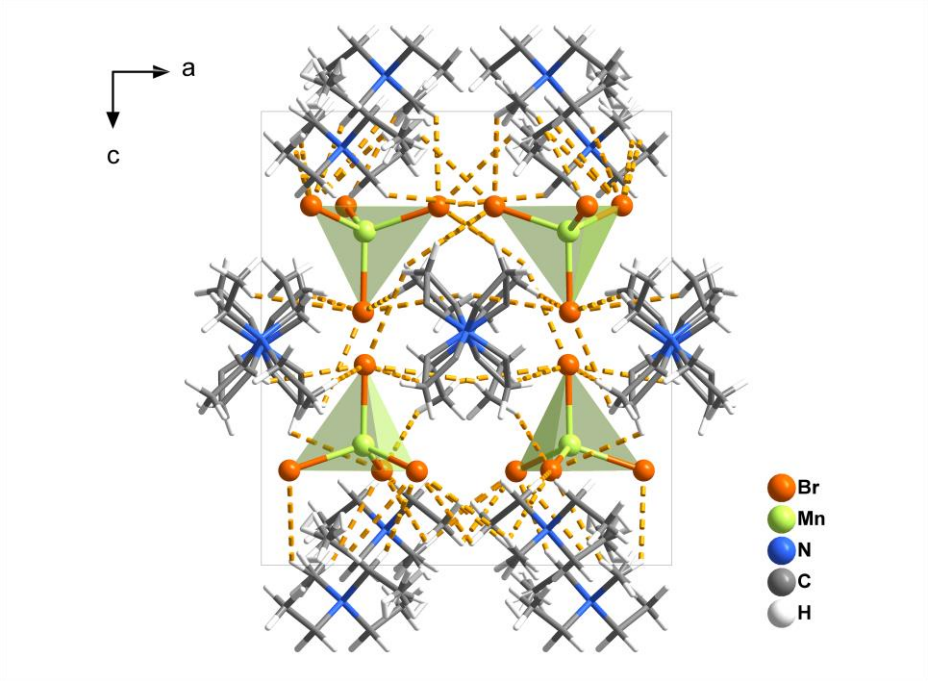

Fig. S5 Hydrogen bonding chain diagram of $(TEMA)_2MnBr_4$.

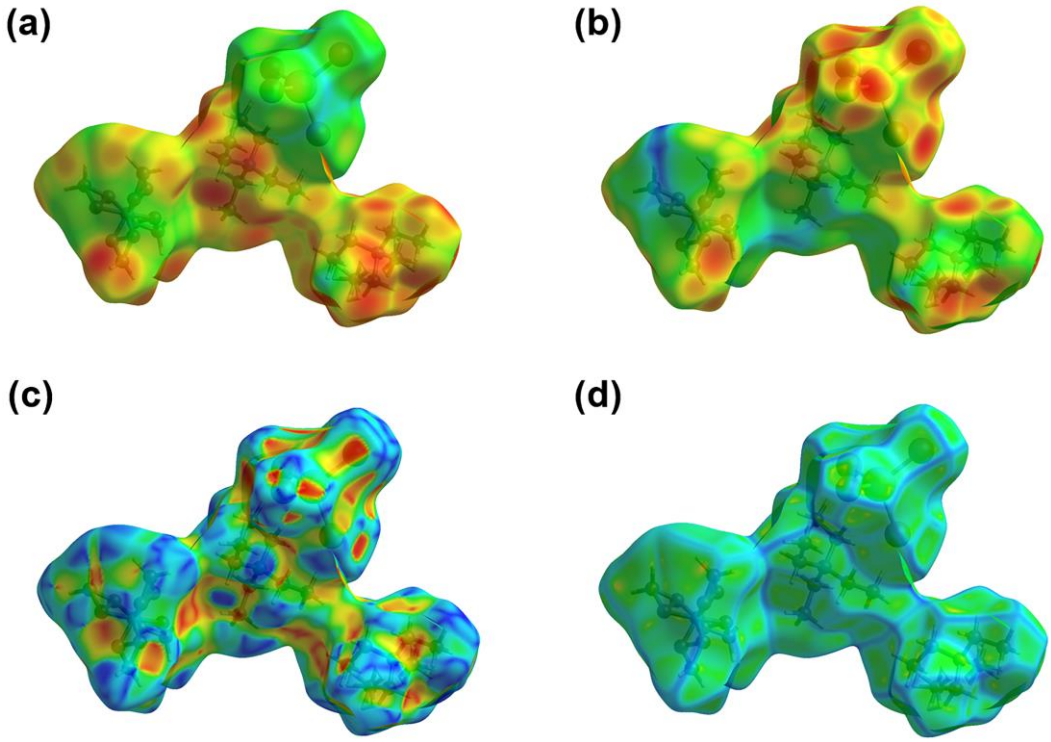

Fig. S6 The 3D color mapping Hirshfield surface analysis of $(TEMA)_2MnBr_4$ at 298 K showing (a) *di*, (b) *de*, (c) shape index, and (d) curvedness.

di is the distance from the Hirshfeld surface to the inner nearest nucleus, *de* is the distance from the Hirshfeld surface to the nearest nucleus off the surface. d_{norm} is defined as the sum of *de* and *di*, both normalized by the van der Waals radius (r^{vdw}).

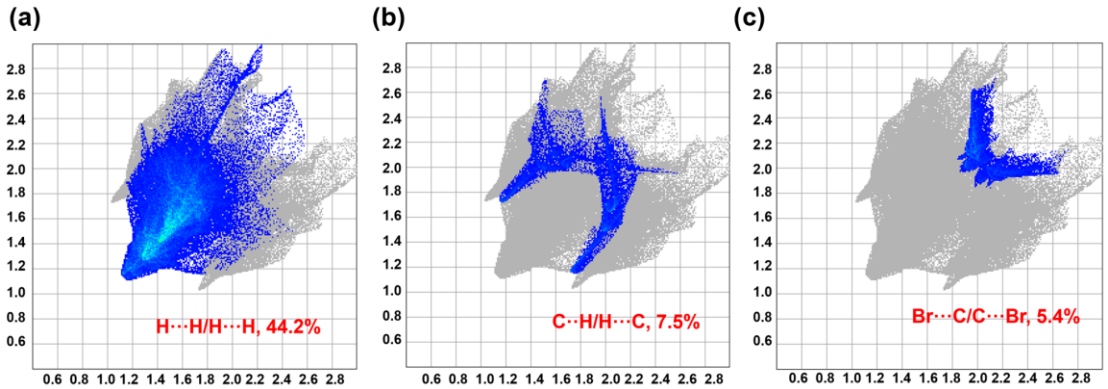

Fig. S7 2D Fingerprint plot (*di* vs *de*) of $(TEMA)_2MnBr_4$ at 150 K.

d_{norm} is defined as the sum of *de* and *di*, both normalized by the van der Waals radius (r^{vdw}). Blue indicates a small contribution to the surface, while red indicates the greatest contribution.

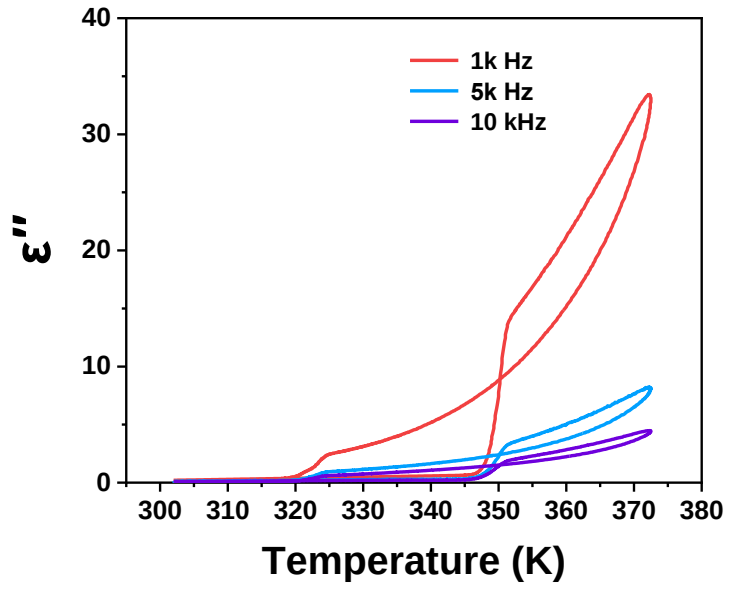

Fig. S8 The ε″ of $(TEMA)_2MnBr_4$ at different frequencies.

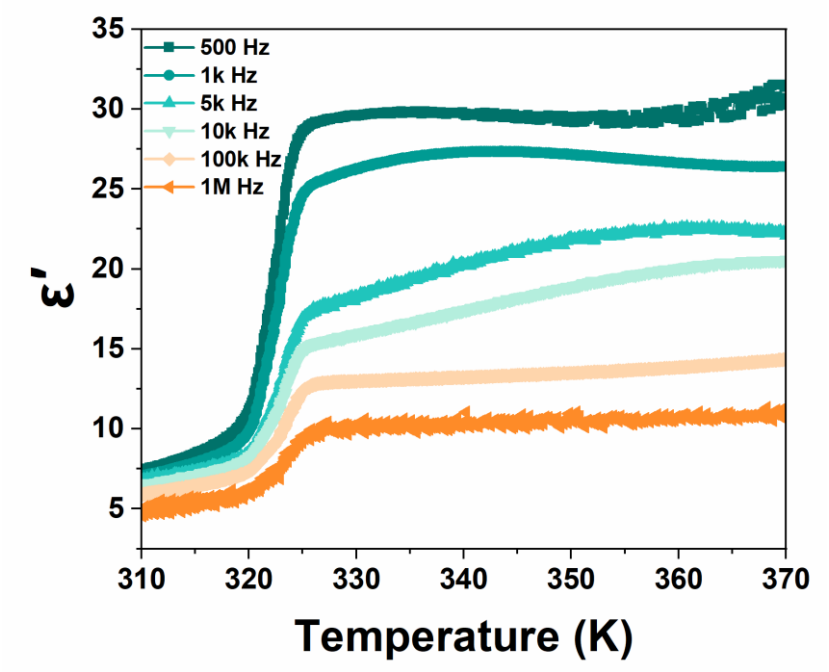

Fig. S9 The dielectric constant of $(TEMA)_2MnBr_4$ at different frequencies.

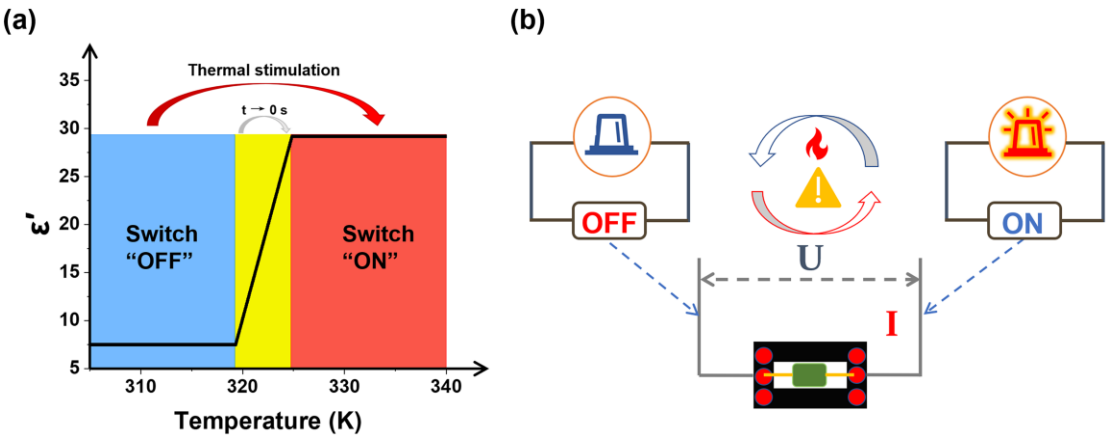

Fig. S10 (a) Schematic diagram of fast switching of thermally sensitive dielectric switching materials based on compound **1**, "t" represents the response time. (b) Schematic diagram of the integrated switch applied to the thermal sensor.

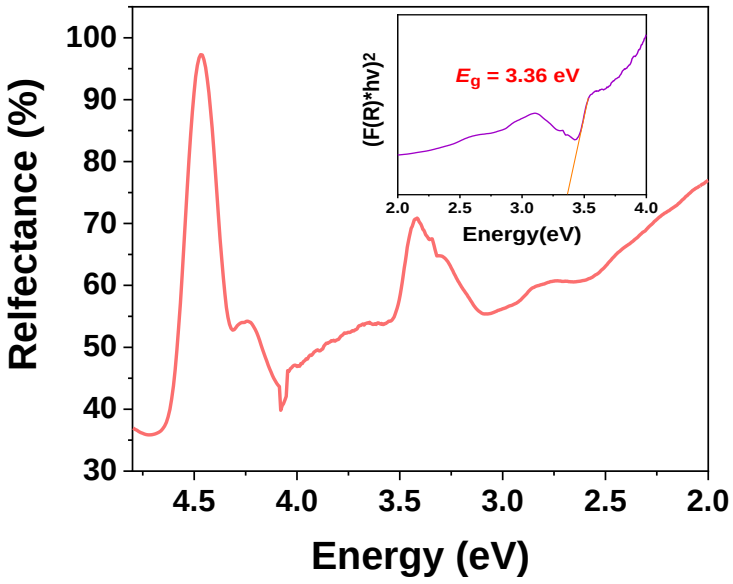

Fig. S11 UV absorption spectrum of $(TEMA)_2MnBr_4$.

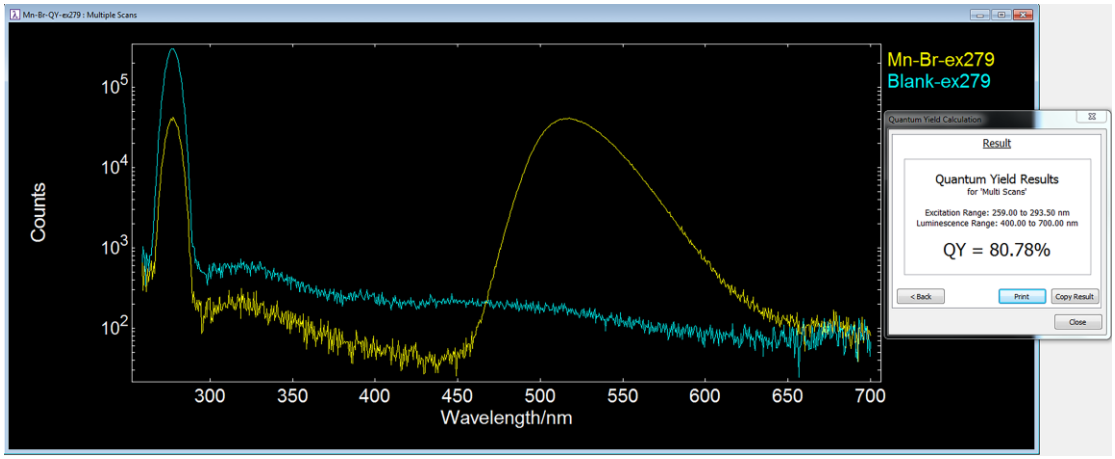

Fig. S12 (a) Excitation line of reference (279 nm) and emission spectrum of $(TEMA)_2MnBr_4$ collected by an integrating sphere.

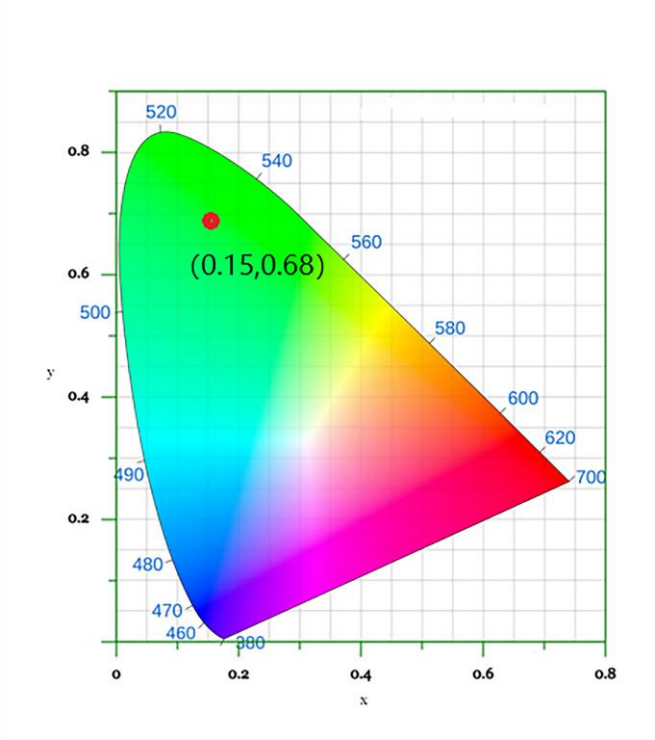

Fig. S13 The CIE diagram of $(TEMA)_2MnBr_4$ under the excitation of 365 nm.

Table S1 Crystal structure and refinement detail of **$(TEMA)_2MnBr_4$**.

$(TEMA)_2MnBr_4$	
T / K	150.00(10)
Formula weight	602.99
Crystal system	Tetragonal
Space group	$P\bar{4}2_1m$
a / Å	12.8275(5)
b / Å	12.8275(5)
c / Å	14.1940(7)
V / Å^3	2335.5(2)
Z	4
λ	0.71073 Å
D_{calc} / g·cm^{-3}	1.715
μ / mm^{-1}	7.406
F(000)	1180
2θ *range* / °	5.33 − 57.462
Reflns collected	10791
Independent reflns (R_{int})	2718 (0.0407)
No. of parameters	129
R_1[a], wR_2[b] [I>2σ(I)]	0.0296, 0.0612
R_1, wR_2 [all data]	0.0416, 0.0642
GOF	1.062
$\Delta\rho$[c] / e·Å^{-3}	0.60, -0.62
CCDC	2268961

[a] $R_1 = \Sigma||F_o|-|F_c||/|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$; [c] maximum and minimum residual electron density.

Table S2 Selected hydrogen bonds data for the title compounds.

Compound **1**

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
C(8)-H(8A)···Br(3)[1]	0.99	2.84	3.60(2)	134.3
C(8)-H(8B)···Br(1)[2]	0.99	3.17	3.896(19)	131.7
C(8)-H(8B)···Br(1)[3]	0.99	3.17	3.896(19)	131.7
C(3)-H(3A)···Br(1)[4]	0.98	3.13	3.838(9)	130.4
C(4)-H(4A)···Br(1)[5]	0.99	2.99	3.835(6)	144.2
C(7)-H(7A)···Br(3)	0.99	2.88	3.784(6)	151.9
C(7)-H(7B)···Br(2)[3]	0.99	3.08	3.889(6)	140.2

[1]1-*x*, 1-*y*, +*z*; [2]-*y*, +*x*, -*z*; [3]+*y*,1-*x*, 1-*z*; [4]+*x*, +*y*, -1+*z*; [5]1-*y*, +*x*, 1-*z*.

Table S3 Hirshfeld surface analysis of **1** at 150 K.

Surface Property	Range (Minimum/Maximum)	Globularity and Asphericity	Surface volume (Å^3) and Area (Å^2)
di	1.0348/3.2508		
de	1.0375/3.0284		
d_{norm}	-0.1097/1.8713	0.622-0.143	776.10 and 656.53
Shape index	--1.0000/-1.0000		
Curvedness	-4.0000/0.4000		

Table S4 The separation distances (Å) of Mn···Mn for adjacent $[MnBr_4]^{2-}$ tetrahedrons.

Compounds	Shortest Mn−Mn distance (Å)	PLQY (%)	Refs
$(DMA)_2MnBr_4$	6.22, 6.85	7.8	1
$(PRD)_2MnBr_4$	6.09, 6.30	16	2
$(Bu_4N)_2MnBr_4$	8.95, 9.08	47	3
$(PRD2)_2MnBr_4$	8.03, 8.19	51	4
$(EPY)_2MnBr_4$	6.87, 9.76	63.92	5
$(DIPA)_2MnBr_4$	8.85, 9.06	62	6
$(EMMIM)_2MnBr_4$	8.58, 9.80	68.49	5
$(BMPR)_2MnBr_4$	9.25, 10.24	75.5	5
$(TEMA)_2MnBr_4$	9.07, 9.26	80.78	This Wrok
$(TMPEA)_2MnBr_4$	8.64, 9.06	98	1

Calculation of ΔS and N for compound **1**.

$$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{27.26\, J \cdot g^{-1} \times\ 602.99\, g \cdot mol^{-1}}{344.37\, K} = \frac{16437.50\, J \cdot mol^{-1}}{344.37\, K}$$

$$\approx 47.73\, J \cdot mol^{-1} \cdot K^{-1}$$

$$\Delta S = R \ln N$$

$$N = \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{47.73\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}}\right) = 5.74$$

References

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5. Y.-Y. Ma, Y.-R. Song, W.-J. Xu, Q.-Q. Zhong, H.-Q. Fu, X.-L. Liu, C.-Y. Yue and X.-W. Lei, *J. Mater. Chem. C*, 2021, **9**, 9952-9961.
6. C. Jiang, N. Zhong, C. Luo, H. Lin, Y. Zhang, H. Peng and C.-G. Duan, *Chem. Comm.*, 2017, **53**, 5954-5957.