Supporting information

High temperature Synergetic Response of Magnetism, Dielectricity and Luminescence in a Mn(II) based molecular organic-inorganic hybrid

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Experimental section

The materials used are commercially available and without further purification.

Synthesis of $(TPA)_2MnBr_4$:

TPA (0.53 g, 2 mmol) and $MnBr_2 \cdot 4H_2O$ (0.28 g, 1mmol) were dissolved in 4 mL HBr solution and stirred for 5 min to obtain a clear solution. The mixture was slowly volatilized at room temperature. Flake green single crystals were obtained after several days. The single crystals were filtered and dry at 50 ℃ in oven. Polycrystalline samples are prepared by grinding dry crystals into powder. The purity was verified by powder X-ray diffraction (PXRD) spectra. The IR spectrum of compound **1** is shown in the Fig. S1. IR data (KBr, cm^{-1}): 3838(m), 3730(m), 3550(w), 3475(w), 3417(w), 3973(s), 3878(w), 1620(m), 1467(s), 1382(w), 1324(m), 1268(m), 1174(m), 1107(m), 1041(m), 976(s), 920(m), 850(m), 756(s), 621(m), 473(m).

Single-crystal diffraction.

Single crystal structure at low temperature and unit cell at high temperature were measured by using Mo-Kα radiation (λ = 0.71073 Å) on the XtLAB Synergy R, HyPix single crystal diffractometer. We collected the low temperature single crystal structure of compound **1**. The structure of the compound was solved by the direct method and then refined by SHELXLTL software through the full-matrix least-squares refinements based on F^2. Anisotropic refinement was performed on all non-hydrogen atoms by using all reflections of $I > 2\sigma(I)$. All hydrogen atoms were obtained geometrically.

Differential scanning calorimetry (DSC).

DSC measurements of compounds were carried out with NETZSCH DSC 214 Polyma DSC21400A-1032-L instrument. The heating/cooling processes of the compound were carried out in a nitrogen environment at a rate of 20 K/min.

Dielectric measurements.

Dielectric constant ($\varepsilon = \varepsilon' - i$) of compound **1** is tested by TH2828A variable temperature dielectric meter. The test frequency is 1 MHz and the applied voltage is 1.0 v.

Powder X-ray diffraction (PXRD).

The powder diffraction diagrams were measured by the Rigaku D/MAX diffractometer (Cu-Kα = 1.54056 Å).

TG measurements.

A Netzsch STA 449C device was used for thermogravimetry (TG) analysis, with a temperature range of 295–1050 K and a heating rate of 10 K min^{-1}.

Magnetic measurements.

The DC susceptibilities of compound **1** were measured using Quantum Design SQUID-based MPMSXL-3-type magnetometer. Magnetic data of compound **1** were recorded in the temperature range of 2.0-430 K with a magnetic field of 1000 Oe. At the same time, in order to study the effect of phase transition on magnetism, the magnetic data changes during cooling and heating were recorded. The magnetization of compound **1** was recorded in field range of 0-7 T and temperature of 2 K.

Photoluminescence spectroscopic measurements.

The emission, excitation spectra and absolute quantum yields (QYs) of compound **1** were measured at room temperature using a fluorimeter (Edinburgh, FLS980) with a xenon flash lamp and an integrating sphere.

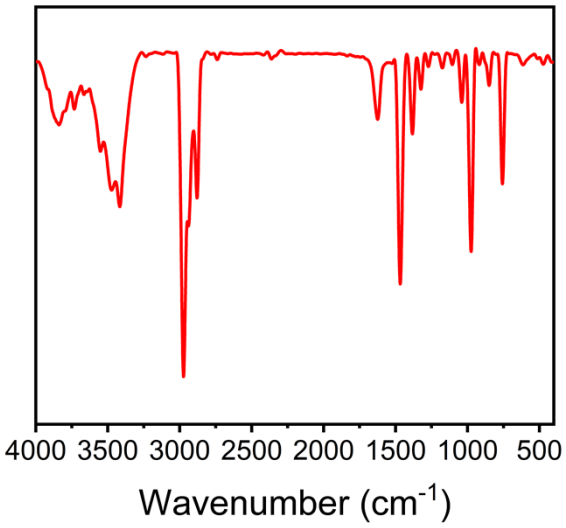

Fig. S1. IR spectra of compounds **1**.

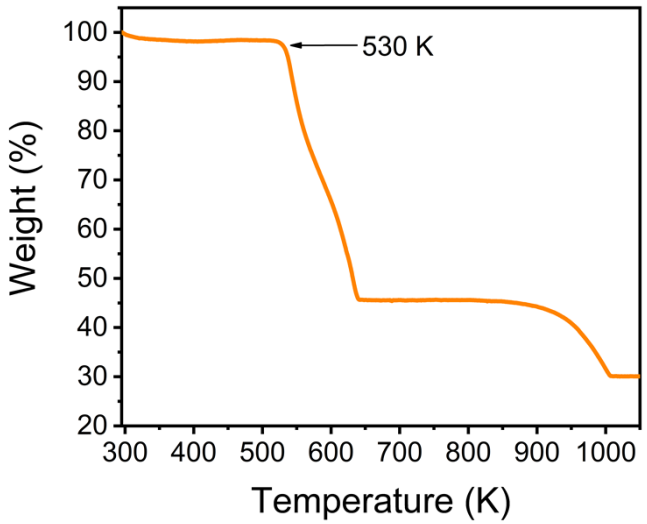

Fig. S2. TG analysis diagram of compound **1**.

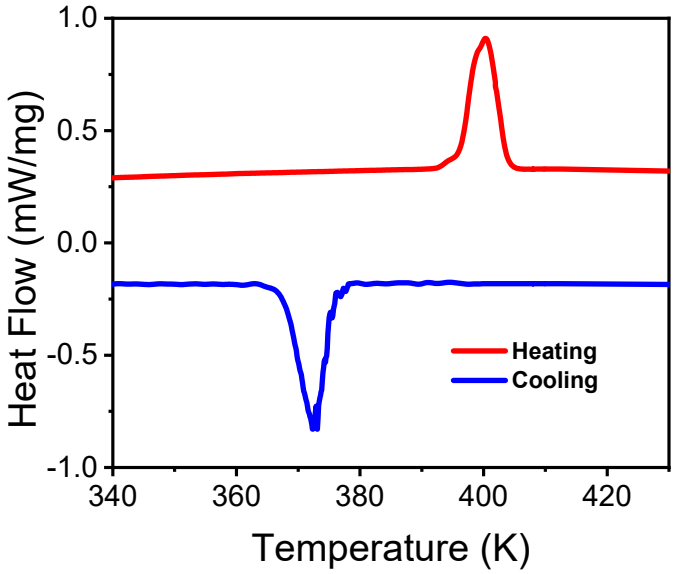

Fig. S3. DSC curves of compound **1** (The rate of change temperature is 5 K/min).

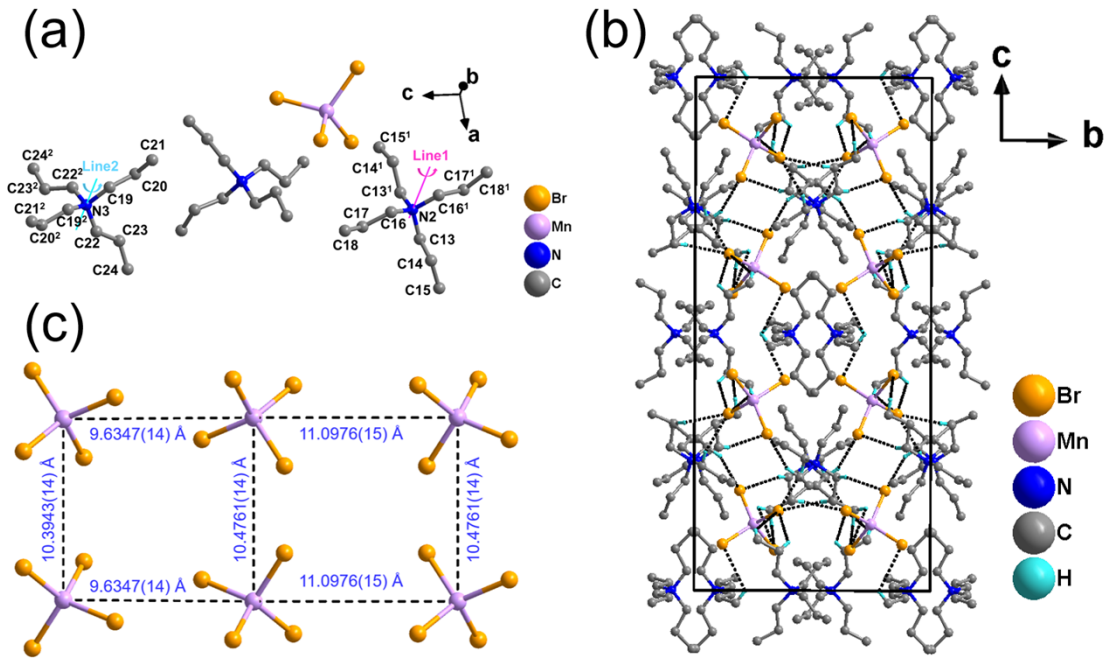

Fig. S4. (a) Molecular structure of compound **1.** (b) Packing picture of compound **1**. Black lines indicate hydrogen bonds. (c) The Mn-Mn distance of compound **1**.

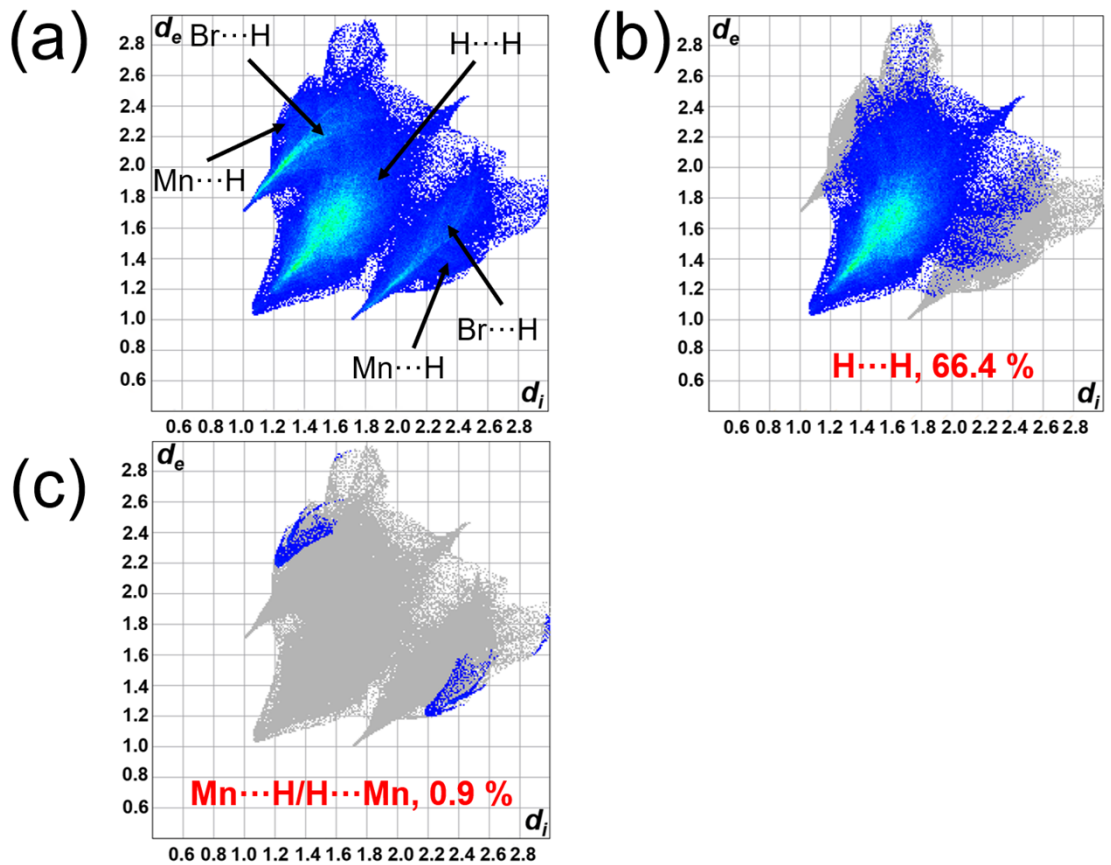

Fig. S5. (a) (b) (c) are plots of 2D-Fingerprint (d_e vs d_i) of **1**.

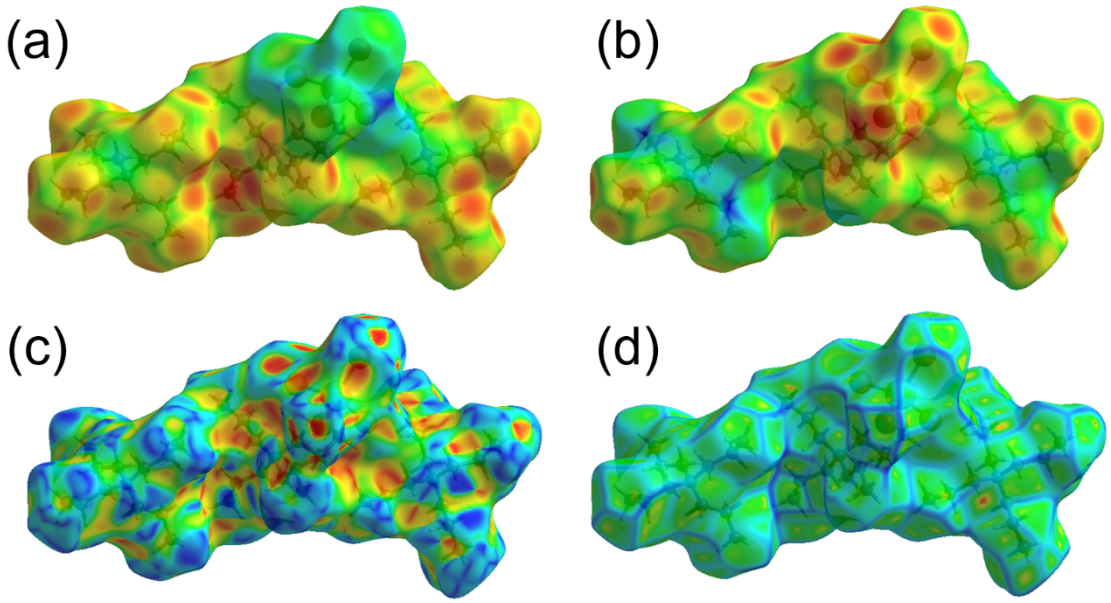

Fig. S6 The 3D color mapping Hirshfield surface analysis of **1** showing (a) d_i, (b) d_e, (c) shape index and (d) curvedness.

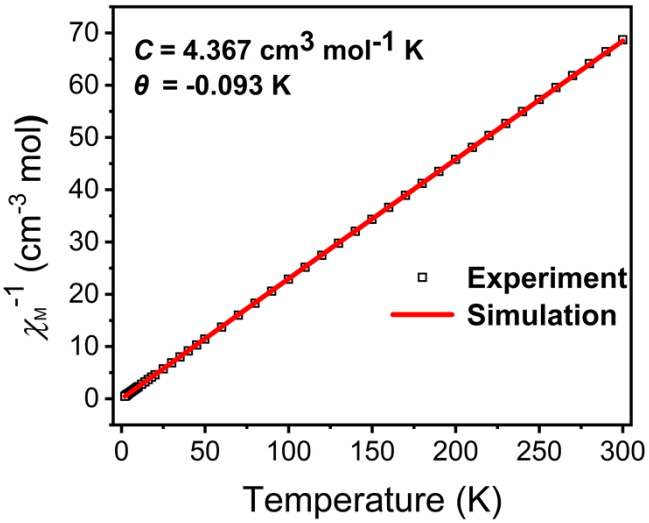

Fig. S7 The temperature dependence curve of χ_M^{-1} for compound **1**. The solid line represents the fitting by Curie-Weiss law.

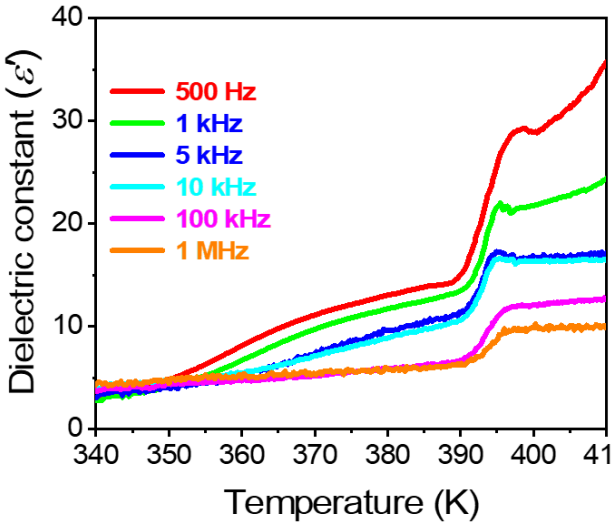

Fig. S8 Plots of dielectric frequency dependence for **1**.

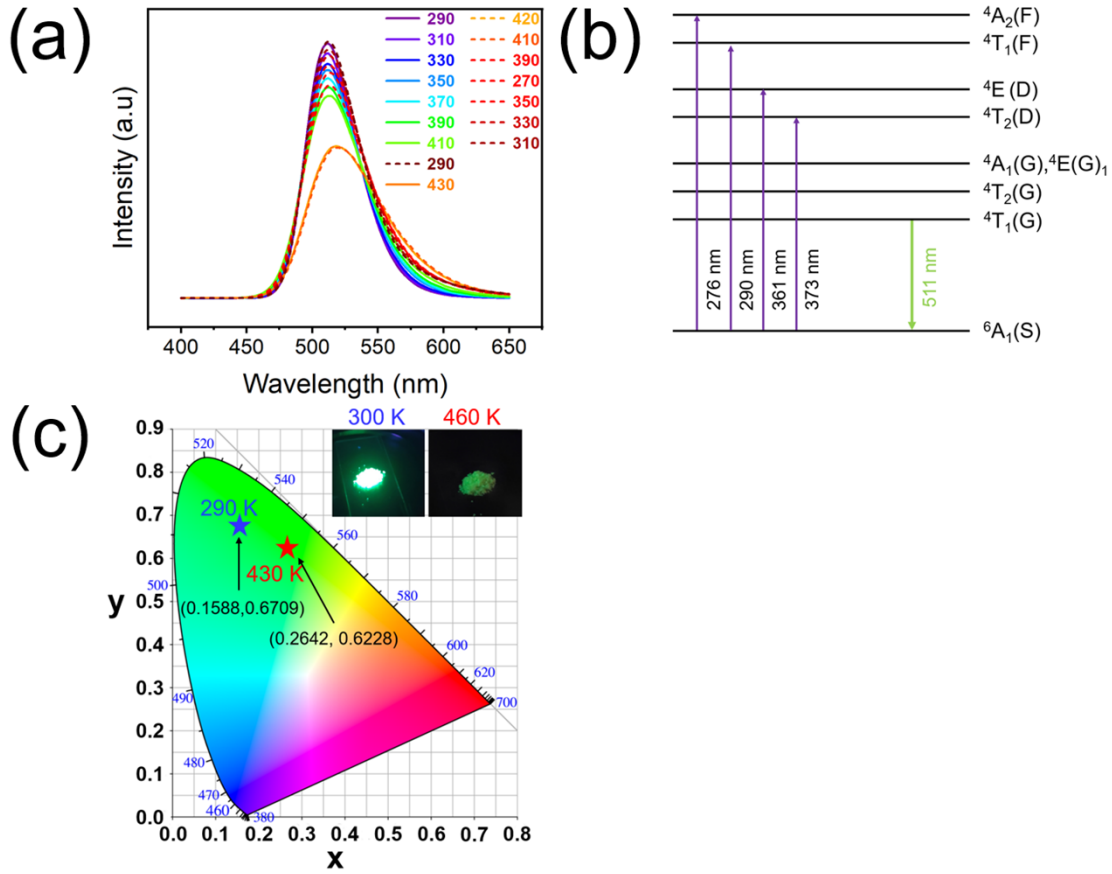

Fig. S9 (a) Emission spectra at different temperatures; (b) Energy state splitting and optical transitions; (c) CIE chromaticity coordinate diagram at 290 K and 430 K for **1**.

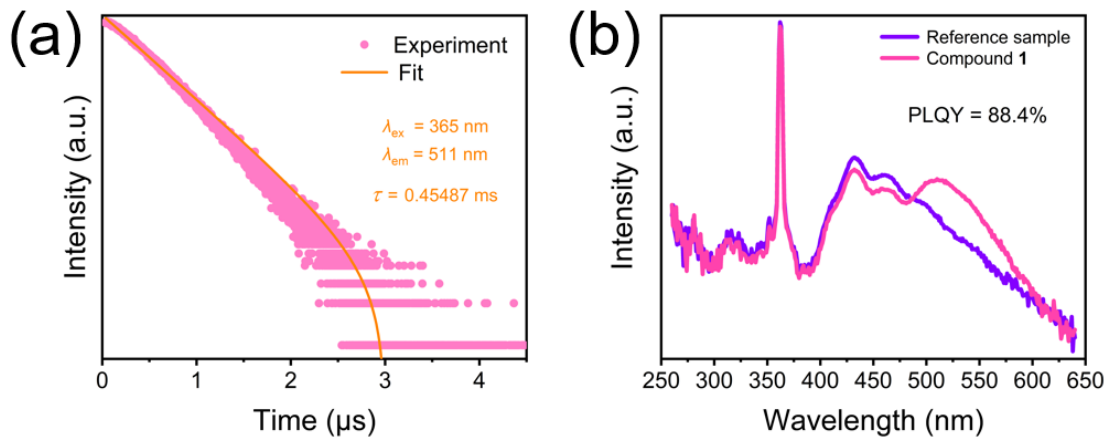

Fig. S10. (a) The fluorescence lifetime for 1 at room temperature. The solid line stands for linear fit to the equation: $I(t) = A_1 e^{\left(-\frac{t}{\tau_1}\right)} + I_0$. (b) Quantum yield of compound **1** (λ_{ex} = 365 nm).

Table S1. Crystallographic data and structural refinement parameters for **1**

Complex	**1**
Temperature (K)	298.57(10)
Chemica formula	$C_{24}H_{56}Br_4MnN_2$
Formula weight	747.278
Crystal system	monoclinic
Space group	*I*2/*a*
a (Å)	15.1145(8)
b (Å)	14.3917(8)
c (Å)	31.3543(18)
α (°)	90
β (°)	95.841(5)
γ (°)	90
Volume (Å^3)	6784.9(7)
Z	8
Density (g/cm^3)	1.463
μ / mm^{-1}	5.113
F (000)	3029.6
2θ range (°)	3.92 to 62.06
Reflections collected	23313
R_{int}	0.0459
Goodness-of-fit on F^2	0.978
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0696, wR_2 = 0.1882
Final *R* indexes [all data]	R_1 = 0.1613, wR_2 = 0.2292

Table S2. Bond lengths [Å] and angles [°] for **1**

	1		
Br1-Mn1	2.5281(12)	C10-C11	1.514(10)

Br2-Mn1	2.4972(13)	C4-C5	1.479(12)
Br3-Mn1	2.5060(12)	C8-C9	1.503(11)
Br4-Mn1	2.5257(14)	C16-C17	1.534(10)
N2-C13[1]	1.516(8)	C17-C18	1.507(10)
N2-C13	1.516(8)	C14-C15	1.512(11)
N2-C16	1.511(8)	C6-C5	1.509(12)
N2-C16[1]	1.511(8)	C11-C12	1.519(13)
N1-C1	1.515(8)	N3-C22[2]	1.383(10)
N1-C7	1.539(8)	N3-C22	1.383(10)
N1-C10	1.507(8)	N3-C19	1.497(12)
N1-C4	1.511(9)	N3-C19[2]	1.497(12)
C1-C2	1.491(10)	C24-C23	1.393(14)
C13-C14	1.519(10)	C21-C20	1.477(15)
C7-C8	1.517(11)	C22-C23	1.444(8)
C2-C3	1.499(11)	C20-C19	1.445(9)
Br2-Mn1-Br1	109.31(5)	C8-C7-N1	116.8(6)
Br3-Mn1-Br1	109.62(4)	C3-C2-C1	111.4(7)
Br3-Mn1-Br2	108.06(5)	C11-C10-N1	115.6(6)
Br4-Mn1-Br1	112.79(5)	C5-C4-N1	118.2(7)
Br4-Mn1-Br2	106.95(5)	C9-C8-C7	109.7(7)
Br4-Mn1-Br3	109.97(5)	C17-C16-N2	116.1(6)
C13-N2-C13[1]	106.0(7)	C18-C17-C16	109.9(7)
C16-N2-C13[1]	111.3(4)	C15-C14-C13	110.1(7)
C16-N2-C13	111.0(4)	C12 C11 C10	109.0(8)
C16[1]-N2-C13[1]	111.0(4)	C6-C5-C4	111.0(8)
C16[1]-N2-C13	111.3(4)	C22-N3-C22[2]	119.9(13)
C16[1]-N2-C16	106.4(7)	C19[2]-N3-C22[2]	111.3(6)
C7-N1-C1	107.2(5)	C19[2]-N3-C22	106.8(7)
C10-N1-C1	108.8(5)	C19-N3-C22[2]	106.8(7)
C10-N1-C7	110.5(5)	C19-N3-C22	111.3(6)
C4-N1-C1	111.8(5)	C19-N3-C19[2]	98.8(11)
C4-N1-C7	109.2(5)	C23-C22-N3[2]	133.7(10)
C4-N1-C10	109.2(5)	C22-C23-C24	126.6(11)
C2-C1-N1	118.1(6)	C19-C20-C21	111.6(11)
C14-C13-N2[1]	115.0(6)	C20-C19-N3[2]	133.4(11)

Symmetry codes: [1]3/2 - *x*, +*y*, -*z*; [2]3/2-*x*, +*y*, 1-*z*.

Table S3. Bond lengths [Å] and bond angles [°] of the hydrogen bond in **1** at 298 K

D-H···A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C1-H1a···Br2[1]	0.9700	2.824(7)	3.749(7)	159.69(14)
C7-H7a···Br4[2]	0.9700	2.956(7)	3.840(7)	152.12(14)
C10-H10b···Br4	0.9700	3.067(7)	3.897(7)	144.43(14)
C8-H8a···Br2[1]	0.9700	2.930(9)	3.835(9)	155.63(18)
C9-H9b···Br1[2]	0.9600	3.50(6)	3.838(10)	104(4)
C9-H9c···Br1[2]	0.9600	3.55(6)	3.838(10)	100(4)
C15-H15c···Br[3]	0.9600	3.35(5)	3.878(9)	117(4)
C21-H21c···Br2[1]	0.9600	2.985(16)	3.780(12)	141.0(13)
C20-H20b···Br2[1]	0.9700	3.078(15)	3.815(15)	133.9(2)

Symmetry codes: [1]3/2 - *x*,1/2 - *y*,1/2 - *z*; [2]1-*x*, -1/2+*y*,1/2-*z*; [3]1/2+*x*, -*y*, +*z*.

Table S4. Hirshfeld surface analysis of **1**.

Surface Property	Range(Å)	Globularity	Asphericity	Volume (Å^3)	Area (Å^2)
d_i	1.0031- 3.1260	0.624	0.351	1162.87	856.81
d_e	1.0037- 2.9812	0.624	0.351	1162.87	856.81
d_{norm}	-0.1522- 1.5863	0.624	0.351	1162.87	856.81
Shape index	-1.0000-1.0000	0.624	0.351	1162.87	856.81
Curvedness	-4.0000-0.4000	0.624	0.351	1162.87	856.81

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

$$\Delta S = \int_{T_1}^{T_2} \frac{Q}{T} dT \approx \frac{\Delta H}{T_c} = \frac{35.54\, J \cdot g^{-1} \times\ 747.278\, g \cdot mol^{-1}}{400\ K} = \frac{26558.26\, J \cdot mol^{-1}}{400\ K} \approx$$

$$K^{-1}$$

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

$$N = \exp\left(\frac{\Delta S}{R}\right) = \exp\left(\frac{67.08\, J \cdot mol^{-1} \cdot K^{-1}}{8.314\, J \cdot mol^{-1} \cdot K^{-1}}\right) = 3197.1$$