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Supporting Information

High heat of hydrogen adsorption and guest-responsive magnetic modulation in a 3D porous pillared-layer coordination framework

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Experimental Section:

Materials: All the reagents and solvents employed were commercially available and used as supplied without further purification. $K_3[Cr(CN)_6]$, 4,4′-bipyridyl and $MnCl_2{\cdot}4H_2O$ were obtained from the Aldrich Chemical Co.

Synthesis of $\{[Mn_3(bipy)_3(H_2O)_4][Cr(CN)_6]_2{\cdot}2(bipy){\cdot}4(H_2O)\}_n$ (1): An aqueous solution (12.5 mL) of $K_3[Cr(CN)_6]$ (0.25 mmol, 0.0426 g) was added to an ethanolic solution (12.5 mL) of 4,4′-bipyridyl (0.25 mmol, 0.039 g) and stirred for 30 min. $MnCl_2{\cdot}4H_2O$ (0.25 mmol, 0.0494 g) was dissolved in 12.5 ml distilled water and 2.5 mL of this metal solution was carefully layered with the 2.5 mL of mixed 4,4′-bipyridyl and $K_3Cr(CN)_6$ solution using a ethanol : water buffer solution (1 mL, 1:1) in a crystal tube. After 15 days, transparent block crystals were appeared in the middle of the tube and separated and washed with ethanol (Yield ~ 60 %). The bulk amount of the sample was prepared by the direct mixing of the reagents in ethanol/water mixed solution with stirring for 24 h and the phase purity was checked with the PXRD and elemental analysis. This powdered sample was used for studying of different physical properties. IR: ν(C≡N) 2125, 2154 and 2170 cm^{-1}; ν(C=C): 1608 cm^{-1},

1536 cm^{-1}; ν(O-H): 3477 cm^{-1} and 3592 cm^{-1}. Anal. cald. for $C_{62}H_{56}Cr_2Mn_3N_{22}O_8$: C, 49.44; H, 3.75; N, 20.46. Found: C, 48.98; H, 3.31; N, 20.66%.

Preparation of {[Mn_3(bipy)$_3$][Cr(CN)$_6$]$_2$} (1a): Compound **1a** was prepared by heating **1** at 165 ºC under vacuum (< 10^{-1} Pa) for 72 hours. This powdered sample was used for characterization of different physical properties. IR: ν(C≡N) 2162 cm^{-1}; ν(C=C): 1603 cm^{-1}, 1531 cm^{-1}. Anal. cald. for $C_{42}H_{22}Cr_2Mn_3N_{18}$: C, 48.16; H, 2.12; N, 24.07. Found: C, 47.52; H, 1.92; N, 23.66%.

Preparation of {[Mn_3(bipy)$_3$][Cr(CN)$_6$]$_2$·8H_2O} (1b): Compound **1b** was prepared by exposing water vapour into **1a** for 6 days. Anal. cald. for $C_{42}H_{38}Cr_2Mn_3N_{18}O_8$: C, 42.33; H, 3.21; N, 21.16. Found: C, 41.92; H, 3.34; N, 20.96%

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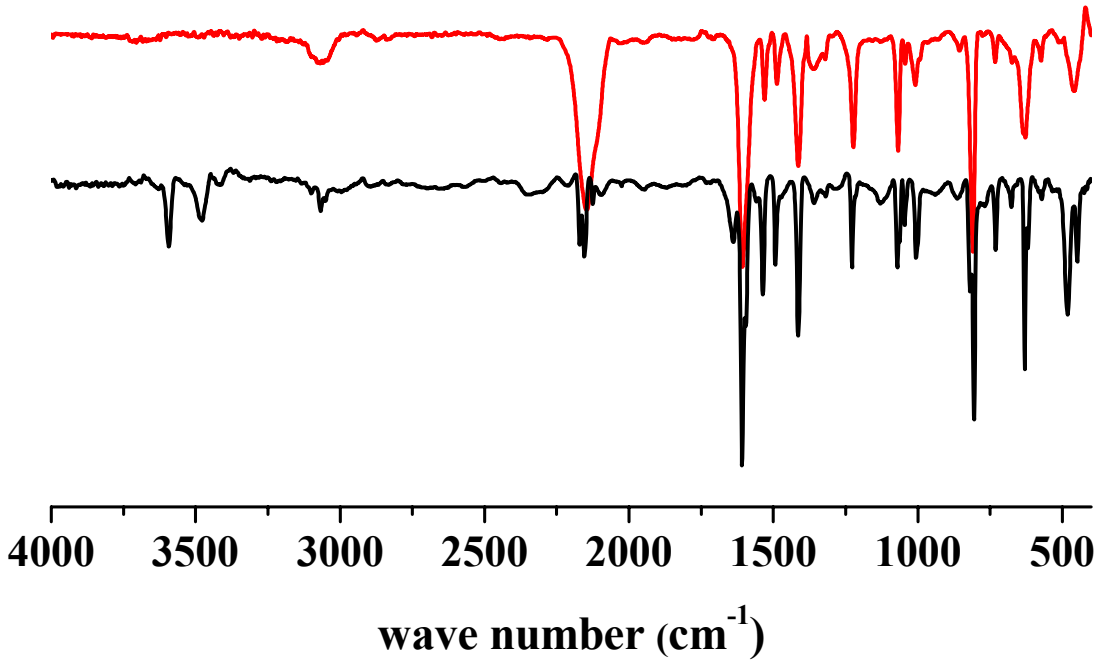

Fig. S1 IR spectra of **1** and **1a.**

Physical Measurements: The elemental analyses were carried out on a Thermo Fisher Flash 2000 Elemental Analyzer. Thermogravimetric analyses (TGA) was carried out with a METTLER TOLEDO TGA850 instrument under nitrogen atmosphere. IR spectra were recorded in the region 4000-400 cm^{-1} on a Bruker IFS 66v/S spectrophotometer with samples prepared in KBr pellets. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Discover instrument using Cu-*K*α radiation.

Adsorption Measurements: N_2, H_2 and CO_2 adsorption studies were carried out with the dehydrated samples of **1** (i.e. **1a**, prepared at 438 K under high vacuum ($<10^{-1}$ Pa) for 72 hours) by using QUANTACHROME QUADRASORB *SI* analyzer at 77 and 195 K, respectively. High-pressure hydrogen adsorption isotherm measurements at 77 and 87 K were carried out on a fully computer controlled volumetric BELSORP-HP, BEL JAPAN high pressure instrument. The hydrogen used for the high pressure measurements is of scientific/research grade with 99.999% purity. For the measurements, approximately 200 mg of sample was taken in a stainless-steel sample holder and degassed at 438 K for about 72 hours. Dead volume of the sample cell was measured using helium gas of 99.999% purity. Non-ideal correction for hydrogen gas was made by applying virial coefficients at the measurement temperature.

X-ray Single-Crystal Structure Determination:

Suitable single crystal of compound **1** was mounted on a thin glass fibre with commercially available super glue. X-Ray single crystal structural data was collected on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30 mA. The data was collected at 296 K. The program SAINT[1] was used for integration of diffraction profile and absorption correction was made with SADABS[2] program. The structure was

solved by SIR 92[3] and refined by full matrix least squares method using SHELXL-97.[4] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were fixed by HFIX command and placed in ideal positions (except for H_2O molecules which were located from Fourier map). Potential solvent accessible area or void space was calculated using the PLATON 99[5] multipurpose crystallographic software. The coordinates, anisotropic displacement parameters and torsion angles are available as ESI in CIF format. All crystallographic and structure refinement data of the compound **1** is summarized in Table S1. Selected bond distances and angles of **1** are given in Tables S2–S4, respectively. All calculations were carried out using SHELXL-97,[4] PLATON 99,[5] SHELXS-97[6] and WinGX system, Ver 1.70.01.[7]

References:

1. SAINT+, 6.02 ed.; Bruker AXS: Madison, WI, 1999.
2. G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*; University of Göttingen, Göttingen, Germany, 1997.
3. Altomare, G. Cascarano, C. Giacovazzo and A. Gualaradi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
4. G. M. Sheldrick, SHELXL 97, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1997.
5. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7.
6. G. M. Sheldrick, SHELXS 97, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, 1997.
7. L. J. Farrugia, WinGX - A Windows Program for Crystal Structure Analysis, *J. Appl. Crystallogr.*, 1999, **32**, 837.

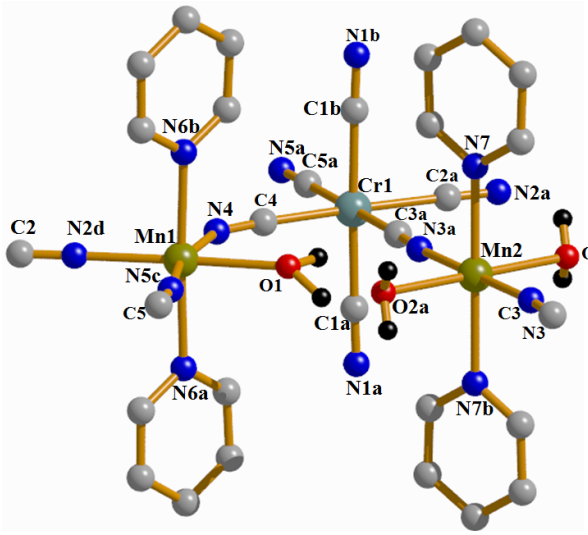

Fig. S2 View of coordination environment around Mn1, Mn2 and Cr1 in **1**. Symmetry codes: a = 2-x, 1-y, z; b = 2-x, 1-y, 1-z; c = 2.5-x, 0.5-y, 1-z; d = -0.5+x, 1.5-y, 1-z.

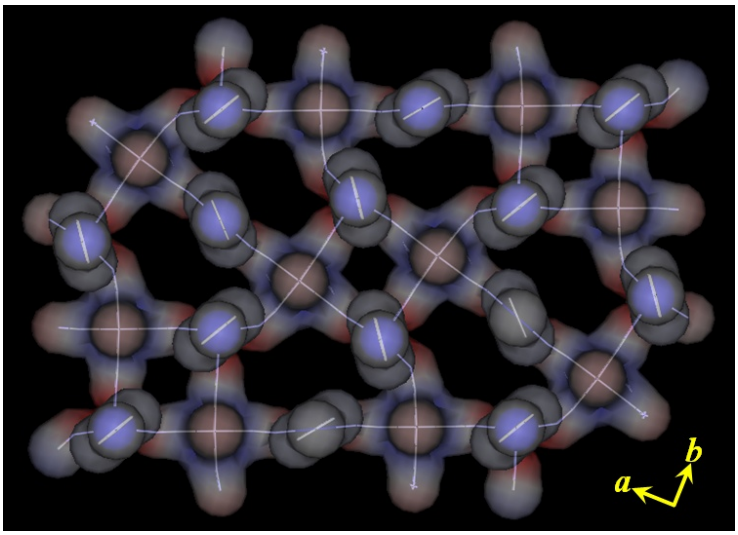

Fig. S3 View of two different kind of channels in **1** along *c* direction.

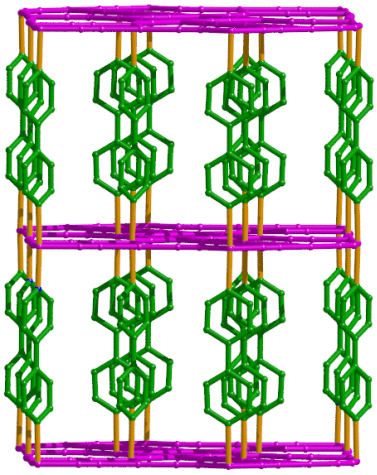

Fig. S4 Pillared-layer structure of **1**. The layers formed by $[Cr(CN)_6]^{3-}$ and Mn^{II} are shown in pink colour and the pillars (bipy) are shown in green colour.

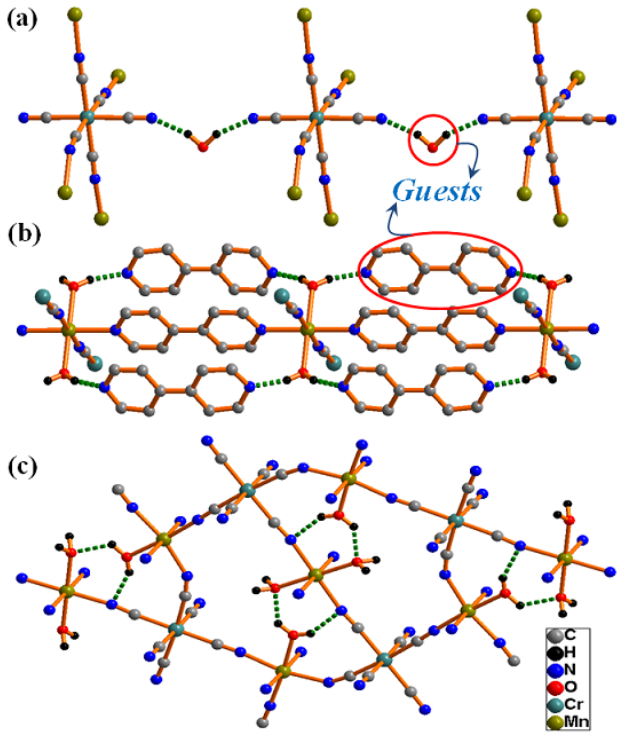

Fig. S5 The supramolecular interaction in **1**; (a) Two neighbouring Cr1 centres interact via N-H-O hydrogen bonding of coordinated CN and guest H_2O molecule, (b) Two Mn2 centres interact via hydrogen bonding of coordinated H_2O and guest bipy molecule, (c) In the 2D layer, coordinated water molecules are involved in H-bonding with each other and also with the CN groups.

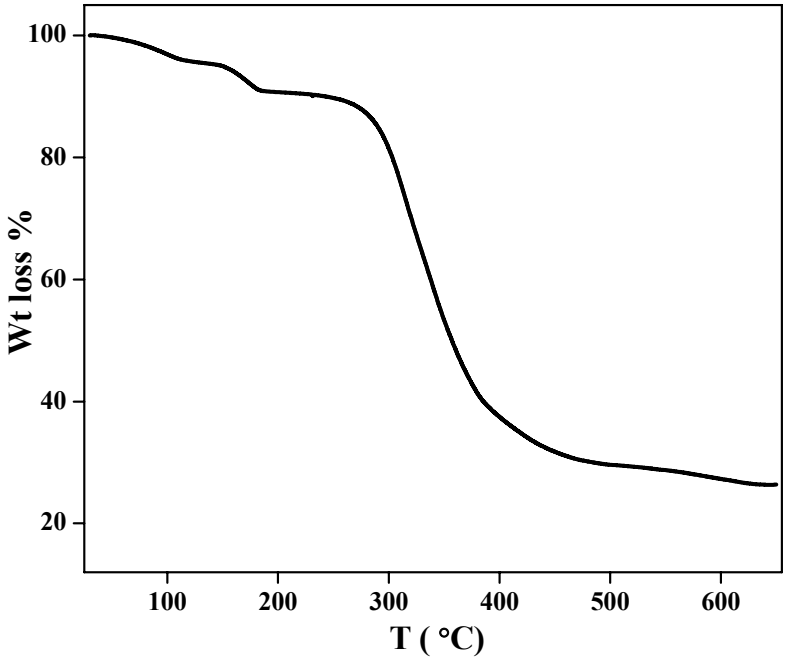

Fig. S6 TGA of **1** recorded under N_2 atmosphere in the temperature range 30 – 650 ºC.

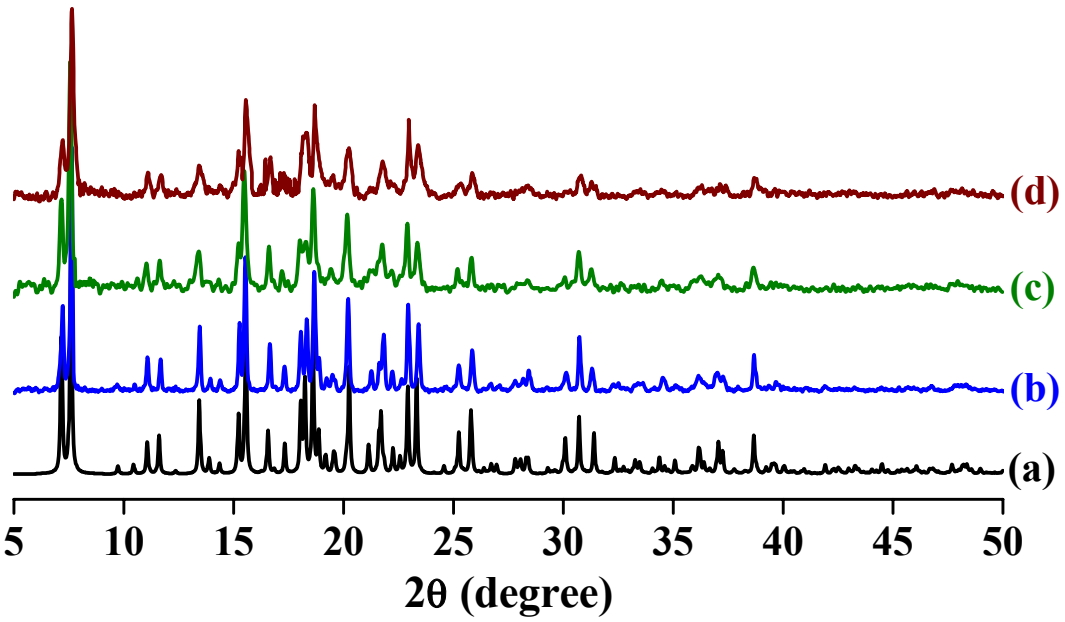

Fig. S7 PXRD plot of **1** at different states: (a) simulated; (b) assynthesized; (c) heated at 165 ºC under vacuum for 72 hrs and (d) rehydrated.

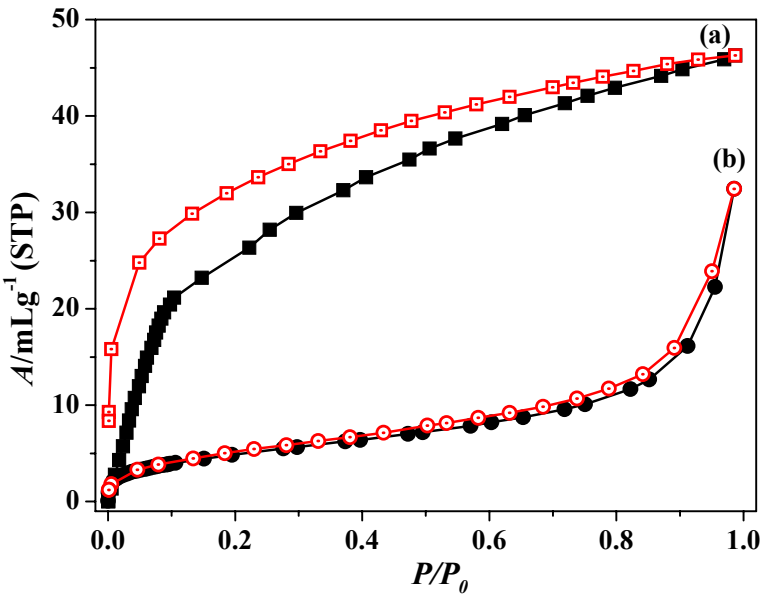

Fig. S8 Gas adsorption isotherms of **1a**: (a) H_2 and (b) N_2 at 77 K (P_0 is the saturated vapour pressure of the corresponding adsorbates at the measurement temperature).

Analysis of Gas Adsorption Isotherms: Hydrogen adsorption isotherms were fitted to the Langmuir-Freundlich[8] equation instead of the more commonly used Langmuir equation.[9] An accurate fit was obtained by using this equation which results a precise prediction over the quantity of hydrogen adsorbed at saturation. A variant of the Clausius-Clapeyron equation was used to calculate enthalpy of adsorption.

$$ln\left(\frac{P_1}{P_2}\right) = \Delta H_{ads} \times \left(\frac{T_2 - T_1}{R \times T_2 T_1}\right)$$

Where, P_n is = Pressure for isotherm n

T_n = Temperature for isotherm n

R = Universal Gas constant = 8.314 J mol^{-1} K^{-1}

Pressure as a function of amount of adsorption was determined by using the Langmuir-Freundlich fit for each isotherm.

$$\frac{Q}{Q_m} = \frac{B \times P^{\left(\frac{1}{t}\right)}}{1 + \left(B \times P^{\left(\frac{1}{t}\right)}\right)}$$

Where, Q = moles adsorbed

Q_m = moles adsorbed at saturation

P = Pressure

B and t = constant

By rearranging this equation we get

$$P = \left(\frac{\frac{Q}{Q_m}}{B - \left(B \times \frac{Q}{Q_m}\right)}\right)^t$$

Substituting this into Clausius-Clapeyron equation we get

$$\Delta H_{ads} = \frac{R \times T_1 \times T_2}{T_2 - T_1} \ln \frac{\left(\frac{\frac{Q}{Q_{m1}}}{B_1 - \left(B_1 \times \frac{Q}{Q_{m1}}\right)}\right)^{t_1}}{\left(\frac{\frac{Q}{Q_{m2}}}{B_2 - \left(B_2 \times \frac{Q}{Q_{m2}}\right)}\right)^{t_2}}$$

Where, the subscript 1 and 2 are representing the data corresponding to 77 and 87 K respectively.

References:

8. R. T. Yang, *Gas Separation by Adsorption Processes*; Butterworth:Boston, 1997.
9. F. Roquerol, J. Rouquerol, K. Sing, *Adsorption by Powders and Solids:Principles, Methodology, and Applications*; Academic Press: London,1999.

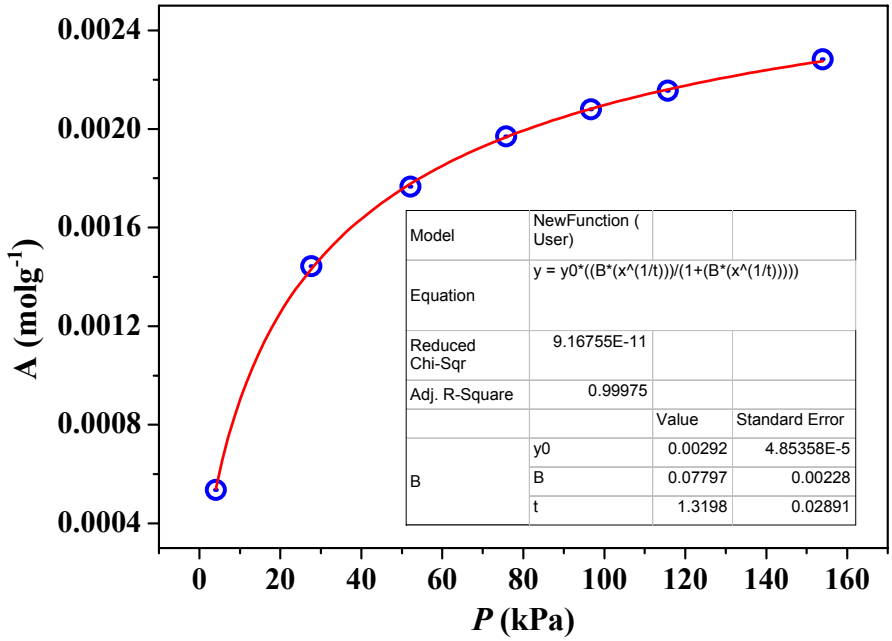

Fig. S9 H_2 adsorption isotherm for **1a** at 77 K. The solid line represents the best fit to the data using the Langmuir-Freundlich equation, as described above.

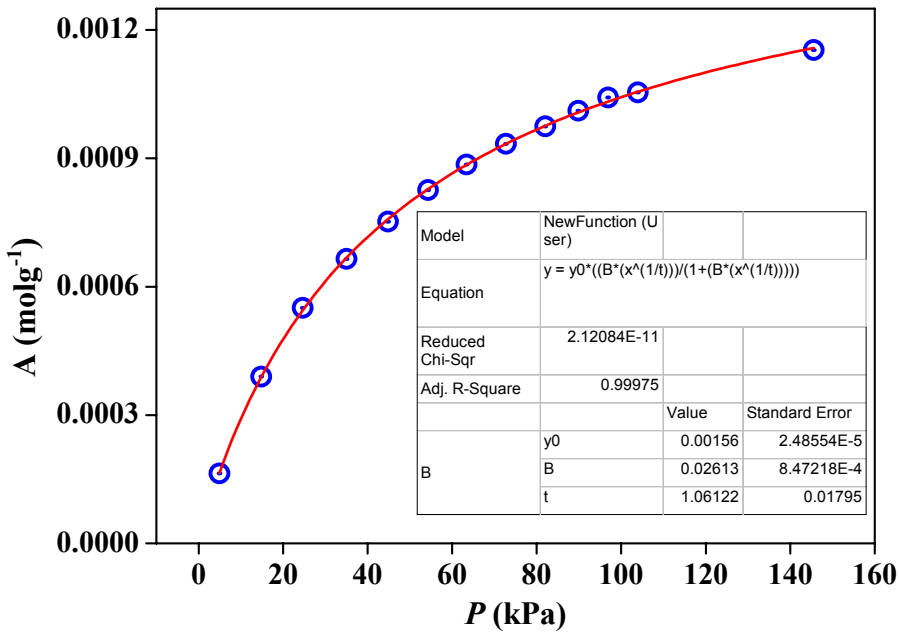

Fig. S10 H_2 adsorption isotherm for **1a** at 87 K. The solid line represents the best fit to the data using the Langmuir-Freundlich equation, as described above.

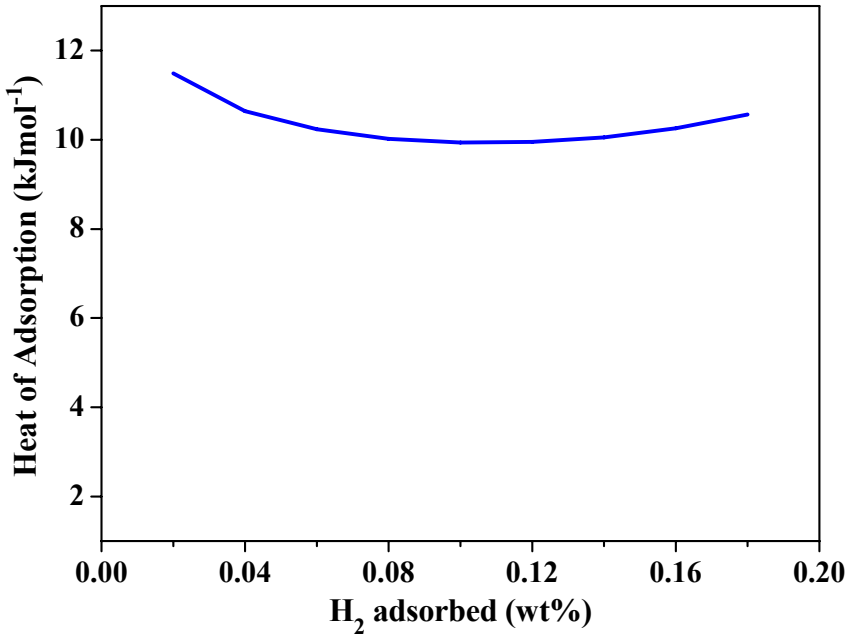

Fig. S11 Enthalpy of H_2 adsorption for **1a** calculated using Clasius-Clapeyron equation.

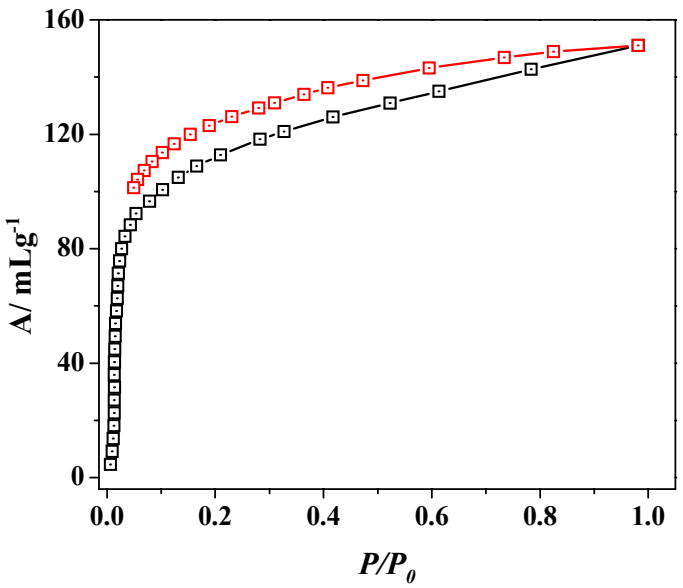

Fig. S12 H_2O adsorption isotherm of **1a** measured at 298 K (P_0 is the saturated vapour pressure of H_2O at 298 K).

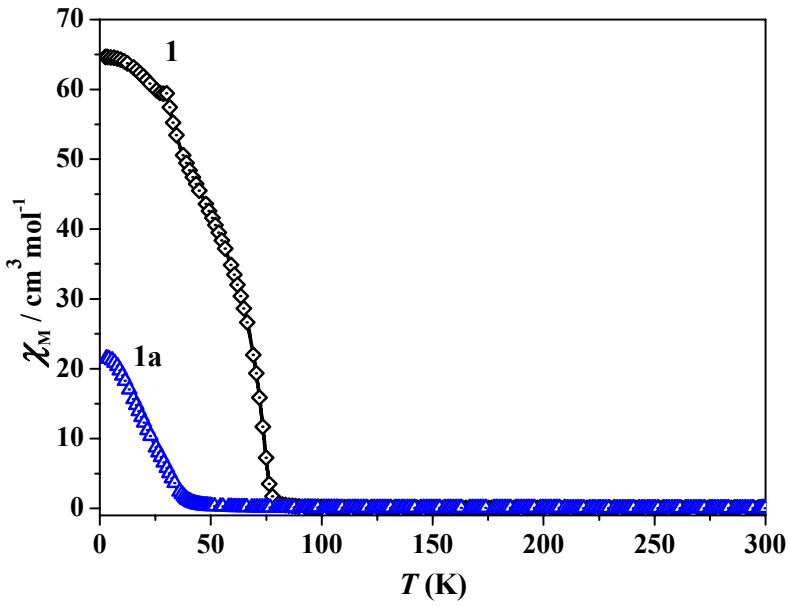

Fig. S13 Temperature dependence of the magnetic susceptibility (χ_M) of **1** and **1a** in an applied field of 500 Oe under zero field cooled condition.

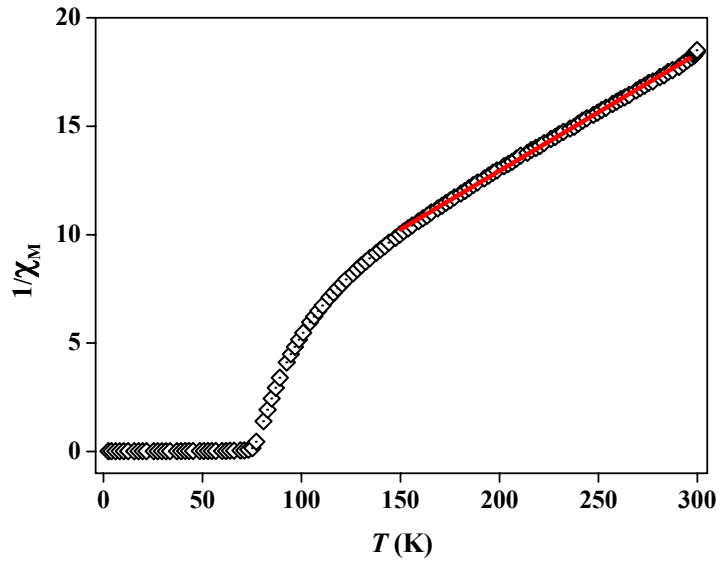

Fig. S14 Curie–Weiss fitting of **1** above 150 K with C = 18.50 cm^{3}K mol^{-1}, and θ = -39.3 K.

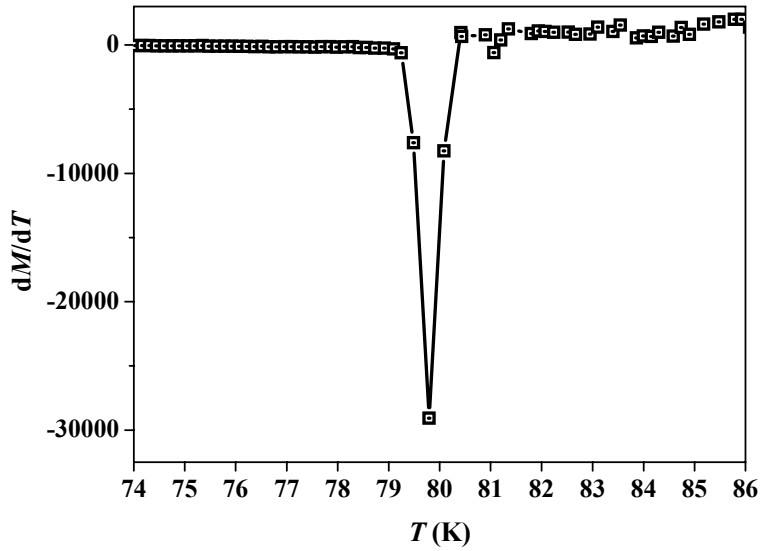

Fig. S15 d*M*/d*T* plot for **1.**

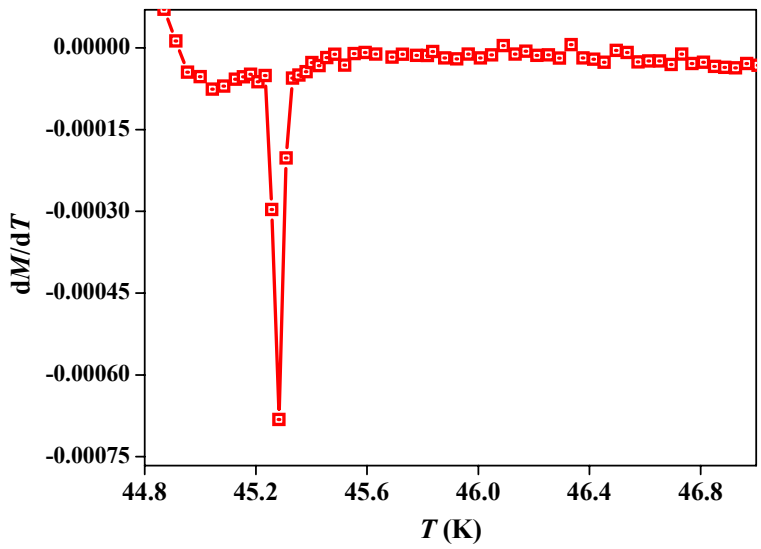

Fig. S16 d*M*/d*T* plot for **1a.**

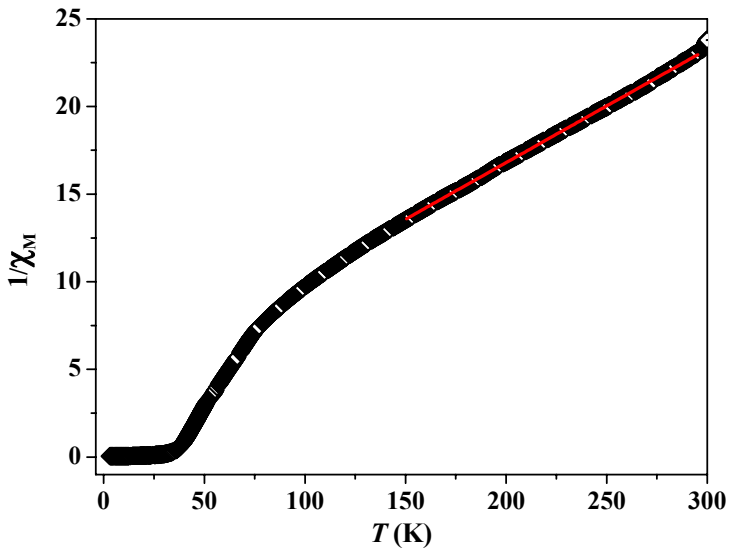

Fig. S17 Curie–Weiss fitting of **1a** above 150 K with C = 15.46 cm^{3}K mol^{-1}, and θ = -59.8 K.

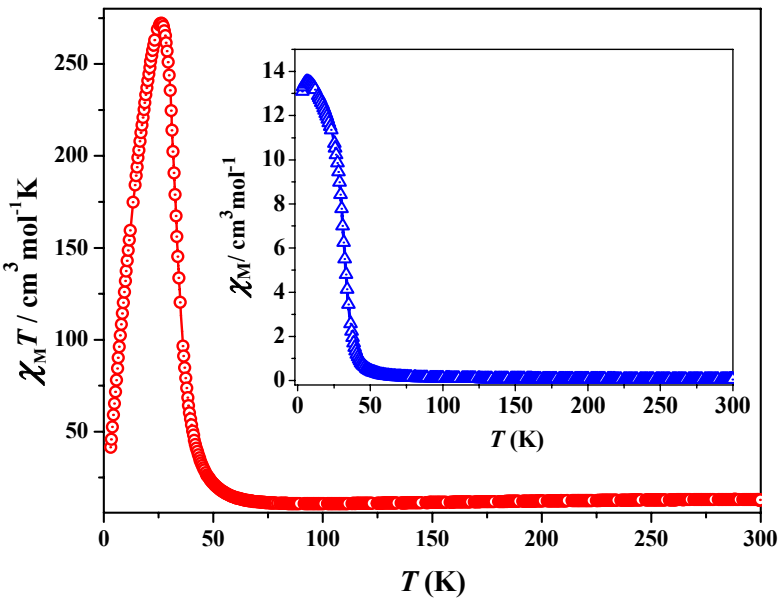

Fig. S18 Temperature dependence of the magnetic susceptibility ($\chi_M T$) of **1b** in an applied field of 500 Oe under zero field cooled condition. Inset shows the χ_M vs T plot for **1b** measured at 500 Oe under zero filed cooled condition.

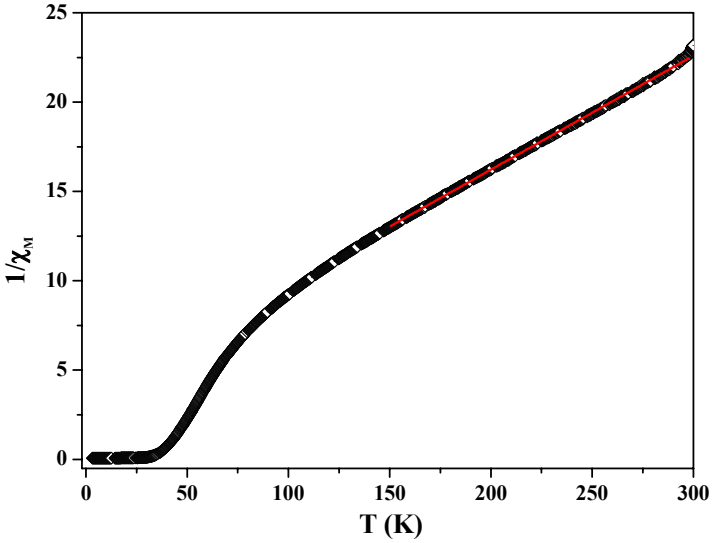

Fig. S19 Curie–Weiss fitting of **1b** above 150 K with C = 15.68 cm^{3}K mol^{-1}, and θ = -54.5 K.

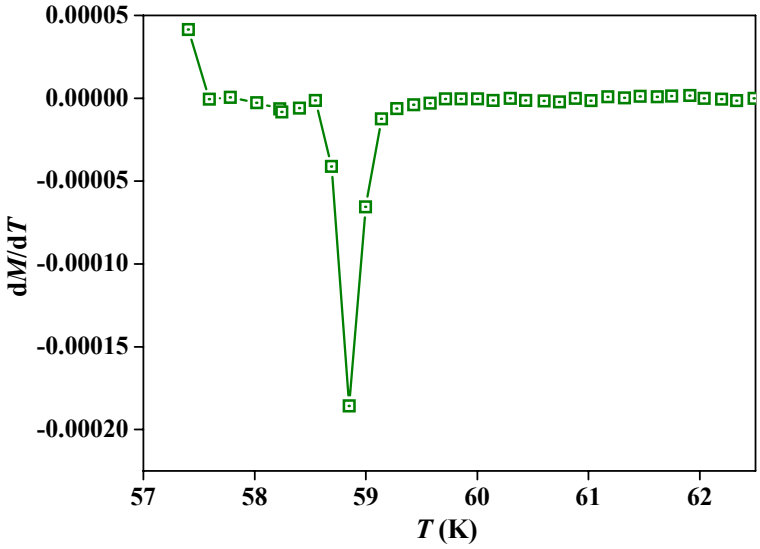

Fig. S20 dM/dT plot for **1b.**

Table S1: Crystal data and structure refinement parameters for compound 1

Parameter	Compound 1
Formula	$C_{62}H_{56}Cr_2Mn_3N_{22}O_8$
M	1506.06
crystal system	Orthorhombic
space group	*P*bam
a [Å]	16.7961(4)
b [Å]	18.1575(4)
c [Å]	11.6335(2)
α [º]	90
β [º]	90
γ [º]	90
V [Å^3]	3547.93(13)
Z	2
T[K]	296
μ[mm^{-1}]	0.883
ρ_c [g/cm^3]	1.405
F (000)	1528
reflections [$I>2\sigma(I)$]	3380
Unique reflections	3815
measured reflections	33673
GOF	1.35
$R_1[I>2\sigma(I)]$[a]	0.0947
$R_w[I>2\sigma(I)]$[b]	0.2279
$\Delta\rho$ max/min [e Å^{-3}]	0.092/-1.17

Table S2: Selected Bond Angles [deg] for 1:

Mn1-O1	2.219(8)	Mn1-N5	2.194(9)
Mn1-N6	2.270(6)	N6-C10	1.324(11)
Mn1-N2_a	2.168(9)	Mn1-N4_c	2.204(8)
Mn1-N6_j	2.270(6)	Mn2-O2	2.261(7)
Mn2-N3	2.191(9)	Mn2-N7	2.272(10)
Mn2-O2_b	2.261(7)	Mn2-N3_b	2.191(9)
Mn2-N7_h	2.272(10)	Cr1-C1	2.082(8)
Cr1-C2	2.073(11)	Cr1-C3	2.063(10)
Cr1-C4	2.056(9)	Cr1-C5	2.047(10)
Cr1-C1_j	2.082(8)		

Symmetry codes: a= -x, -y, z; b= 1-x, -y, z; c= -1/2+x, 1/2-y, 1-z; h= 1-x,-y,1-z; j= x, y, 1-z.

Table S3: Selected Bond Distances [Å] for 1

O1-Mn1-N5	82.7(3)	O2_b-Mn2-N7_h	90.00
O1-Mn1-N6	88.57(15)	N3_b-Mn2-N7_h	90.00
O1-Mn1-N2_a	175.7(3)	C1-Cr1-C2	89.6(2)
O1-Mn1-N4_c	83.7(3)	C1-Cr1-C3	89.1(2)
O1-Mn1-N6_j	88.57(15)	C1-Cr1-C4	90.4(2)
N5-Mn1-N6	89.74(17)	C1-Cr1-C5	90.9(2)
N2_a-Mn1-N5	93.0(3)	C1-Cr1-C1_j	178.0(3)
N4_c-Mn1-N5	166.4(3)	C2-Cr1-C3	88.1(4)
N5-Mn1-N6_j	89.74(17)	C2-Cr1-C4	175.9(4)
N2_a-Mn1-N6	91.42(14)	C2-Cr1-C5	92.4(4)
N4_c-Mn1-N6	89.92(17)	C1_j-Cr1-C2	89.6(2)
N6-Mn1-N6_j	177.1(2)	C3-Cr1-C4	87.8(4)
N2_a-Mn1-N4_c	100.6(3)	C3-Cr1-C5	179.6(4)
N2_a-Mn1-N6_j	91.42(14)	C1_j-Cr1-C3	89.1(2)
N4_c-Mn1-N6_j	89.92(17)	C4-Cr1-C5	91.8(4)
O2-Mn2-N3	94.8(3)	C1_j-Cr1-C4	90.4(2)
O2-Mn2-N7	90.00	C1_j-Cr1-C5	90.9(2)
O2-Mn2-O2_b	180.00	O2-Mn2-N3_b	85.2(3)
O2-Mn2-N7_h	90.00	Mn1-O1-H1A	119.00
N3-Mn2-N7	90.00	Mn1-O1-H1B	142.00
O2_b-Mn2-N3	85.2(3)	Mn1-O1-H1B_j	142.00
N3-Mn2-N3_b	180.00	N3-Mn2-N7_h	90.00
Mn2-O2-H2A_j	126.00	O2_b-Mn2-N7	90.00
N3_b-Mn2-N7	90.00	Mn2-O2-H2	126.00
N7-Mn2-N7_h	180.00	O2_b-Mn2-N3_b	94.8(3)
Mn1_a-N2-C2	177.8(8)	Mn2-N-C3	170.9(9)
Mn1_d-N4-C4	145.5(7)	Mn1-N5-C5	173.0(8)
Mn1-N6-C6	122.4(5)	Mn1-N6-C10	119.9(5)
Mn2-N7-C11	122.5(6)	Mn2-N7-C11_b	122.5(6)
Cr1-C1-N1	178.6(7)	Cr1-C2-N2	177.3(9)
Cr1-C3-N3	175.6(9)	Cr1-C4-N4	171.8(8)
Cr1-C5-N5	178.8(9)		

Symmetry codes: a= -x, -y, z; b= 1-x, -y, z; c= -1/2+x, 1/2-y, 1-z; h= 1-x,-y,1-z; j= x, y, 1-z.

Table S4: Table 4: Hydrogen Bonding (Å, °) in 1

D-H···A	**D-H**	**H···A**	**D···A**	**<D-H..A>**
O1W--H1WA...N1	0.9600	2.0000	2.926(9)	160.00
O1--H1A...N3[i]	0.8600	2.1700	2.944(12)	150.00 3
O2--H2A...N8	0.9300	1.8200	2.715(8)	162.00
C7-- H7...O1W[ii]	0.9300	2.5300	3.451(12)	169.00 3

Symmetry codes: i = -1/2+x, 1/2-y, 1-z; ii = -1/2+x, 1/2-y, -z.