Electronic Supporting Information(ESI)

A triangle [Mn_3] cluster-based ferrimagnet with significant magnetic entropy change

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Table S1 Summary of the reported molecule-based magnetic coolants for T_{max} >3.0 K

Compounds	T_{max} (K)	$-\Delta S_m$ (J kg^{-1} K^{-1})	ΔH (T)	Ref.
Gd_4Ni_4	3.5	19.0	7	1
Gd_4Ni_8	3.6	22	7	2
$Gd_{24}Co_{16}$	3.8	26.0	7	3
Gd_6Co_4	4	22.3	7	4
Gd_5Ni_{12}	4	21.8	7	5
Gd_8Co_8	4	20.4	7	4
Gd_4Co_8	4	19.9	7	4
Mn_4	4	19.34	5	6
$Gd_4Mn^{III}_4$	4	19.0	7	7
$GdNi_2$	4	13.74	7	8
Co_5	4	13.23	8	9
Dy_5Zn	4	10.82	7	10
Gd_2Cr_2	4.1	11.4	9	11
$Mn^{III}_{12}Mn^{II}_7$-**1**	4.2	8.9	7	12
Gd_2Ni_2	4.5	34.4	7	13
$Cu_{12}Gd_6$	4.5	14.0	7	14
$TbNi_3$	4.5	13.54	7	15
YNi_3	4.5	10.83	7	15
$[Gd_2(fum)_3(H_2O)_4]_n \cdot 3nH_2O$	5	20.7	7.5	16
Co_3Dy	5	12.58	7	17
$Mn^{III}_{11}Mn^{II}_6$	5.2	13.3	9	12
$GdNi_3$	5.5	18.31	7	15
Gd_4Cu_8	5.6	14.6	7	2
$[Fe_{14}(C_2H_2N_3)_6O_6(OMe)_{18}Cl_6]$ (T_N= 3.4 K)	6	20.3	7	18
$[Fe_{14}(bta)_6O_6(OMe)_{18}Cl_6]$ (T_N= 1.87 K)	6	17.6	7	19
$Mn_{12}Gd_6$-**1**	6	15.8	7	20
Mn_4Gd_3	6	7.4	5	21
Mn_4Dy_3	6	3.7	5	21
Mn_{12} (T_B=3.0 K)	6.5	12.5	3	22
$Mn_{12}Gd_6$-**2**	7	17.0	7	20
$Fe_{14}(bta)_2$-Au	7	13.0	6	23

$Mn^{III}_{12}Mn^{II}_{7}$-**2**	7	9.0	7	24
$[Mn(glc)_2]_n$	≈7	6.9	7	25
$DyNi_3$	7.5	≈12.2	7	15
$HoNi_3$	7.5	≈11.5	7	15
$Mn^{III}_{11}Mn^{II}_{4}$	10	9.5	7	24
Co_4 (SMR+LRO)	≈10	2.4	5	26
$[Fe(pyrazole)_4]_2[Nb(CN)_8]\cdot 4H_2O\}_n$ (Ferrimagnet)	10.3	4.8	5	27
$[Na_2Mn_3(SO_4)_3(\mu_3\text{-}OH)_2(\mu_2\text{-}OH_2)_2]_n$ (this work)	13.5	14.4	7	
$Mn_3(OH)_2(C_6H_2O_4S)_2$ (T_N =17.7 K)	≈23	≈1.5	5	28
$[Mn^{II}(pydz)(H_2O)_2][Mn^{II}(H_2O)_2][Nb^{IV}(CN)_8]\cdot 3H_2O$ (Ferrimagnet)	43	8.95	5	29
$[Mn^{II}(pydz)(H_2O)_2][Mn^{II}(H_2O)_2][Nb^{IV}(CN)_8]\cdot 3H_2O$ (p=1.19 GPa)	52.5	4.63	5	29
$NiCr_{2/3}$ (Ferromagnet order)	68	6.6	7	30
$CsNi^{II}[Cr^{III}(CN)_6]\cdot H_2O$ (Ferromagnetic order)	≈90	6.6	7	31
CsNiCr (Ferromagnet order)	95	6.9	7	30
$Cr_3^{II}[Cr^{III}(CN)_6]_2\cdot 12H_2O$ (Ferrimagnet order)	≈230	0.93	7	31

Note: T_N: Antiferromagnetic temperature; T_B: Block temperature; SMR: Slow magnetic relaxtion; LRO: Long-range Order.

Table S2 Crystal data and structure refinement for **1**

Empirical formula	$Na_2Mn_3S_3O_{16}H_6$
Crystal system	orthorhombic
Space group	$Cmc2_1$
a/Å	18.0718(6)
b/Å	7.8465(3)
c/Å	9.9048(3)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume / Å^3	1404.51(9)
Z	8
ρ_{calc} mg/mm^3	2.681
m/mm-1	3.250
F(000)	1108.0
Radiation	Mo Kα (λ = 0.71073)
2θ range for data collection	7 to 52°
Index ranges	-19 ≤ h ≤ 22, -5 ≤ k ≤ 9, -11 ≤ l ≤ 12
Reflections collected	1784
Independent reflections	1193 [R_{int} = 0.0280, R_{sigma} = 0.0487]
Goodness-of-fit on F2	1.081
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0841
Final R indexes [all data]	R_1 = 0.0348, wR_2 = 0.0858
$^a R1 = \sum \left\|F_O\right\| - \left\|F_C\right\| / \sum \left\|F_O\right\|$	$^b wR2 = \left[\sum w\left(F_O^2 - F_C^2\right)^2 / \sum wF_O^4\right]^{1/2}$

Table S3. Some selected bond lengths (Å) and angles (degree) for compound **1**

Mn(1)-O(2)#2	2.170(4)	O(2)#1-Mn(1)-O(9)	87.41(18)	O(3)#4-Mn(2)-O(4)	84.17(13)
Mn(1)-O(6)	2.115(4)	O(5)-Mn(1)-O(8)#3	81.18(16)	O(4)-Mn(2)-O(1)#5	89.42(14)
Mn(1)-O(8)#3	2.168(4)	O(5)-Mn(1)-O(9)	95.1(2)	O(5)-Mn(2)-O(4)	91.11(14)
Mn(1)-O(9)	2.182(5)	O(5)-Mn(1)-O(10)	88.4(19)	O(5)-Mn(2)-O(8)	83.8(2)
Mn(1)-O(10)	2.203(5)	O(6)-Mn(1)-O(8)#3	167.2(2)	O(5)-Mn(2)-O(3)#4	106.6(2)
Mn(1)-O(5)	2.163(4)	O(6)-Mn(1)-O(9)	83.25(19)	O(8)-Mn(2)-O(1)#5	90.9(2)
Mn(2)-O(1)#4	2.231(7)	O(6)-Mn(1)-O(10)	92.88(18)	O(8)-Mn(2)-O(3)#4	169.6(2)
Mn(2)-O(3)#5	2.185(6)	O(6)-Mn(1)-O(5)	92.99(18)	O(8)-Mn(2)-O(4)	95.84(12)
Mn(2)-O(4)	2.188(4)	O(8)#3-Mn(1)-O(2)#1	98.65(17)	Mn(1)-O(10)-Na(1)#9	119.49(18)
Mn(2)-O(8)	2.175(6)	O(8)#3-Mn(1)-O(9)	85.9(2)	Mn(1)-O(6)-Na(1)	104.25(17)
Mn(2)#8-O(3)	2.185(6)	O(8)#3-Mn(1)-O(10)	98.3(2)	Mn(1) -O(5)- Mn(1)#2	96.3(2)
Mn(2)-O(5)	2.142(5)	O(9)-Mn(1)-O(10)	174.95(18)	Mn(1)#5-O(8)-Mn(2)	119.8(2)
Mn(2)#3-O(1)	2.231(7)	O(3)#4-Mn(2)-O(1)#5	78.7(2)	Mn(2)-O(5)-Mn(1)	128.36(14)

Symmetry transformations used to generate equivalent atoms for band length: #2 +X, 1-Y, 1/2+Z; #3 -X, 1-Y, 1/2+Z; #4 -X, 1-Y, -1/2+Z; #5 +X, -1+Y, +Z; #6 1/2-X, 1/2+Y, +Z; #8 +X, 1+Y, +Z;
Symmetry transformations used to generate equivalent atoms for band angles: #1 +X, 1-Y, 1/2+Z; #2 –X, +Y, +Z; #3 -X, 1-Y, 1/2+Z; #4 +X, -1+Y, +Z; #5 -X, 1-Y, -1/2+Z; #7 +X, 1-Y, -1/2+Z; #9 1/2-X, -1/2+Y, +Z

Table S4. Geometrical parameters of strong hydrogen bonds for compound **1**

Donor --- H....Acceptor	D - H	H...A	D...A	D - H...A
O(10) --H(10A) ..O(7)	0.84	1.94	2.7414	161
O(10) --H(10B) ..O(3)	0.84	2.25	3.0250	154

Table S5. The determination of oxidation state for Mn in **1**[32]

	Bond length	Bond valences(s)		Bond length	Bond valences(*s*)
Mn1-O2	2.17	0.33468	Mn2-O1	2.231	0.28381
Mn1-O5	2.163	0.34107	Mn2-O3	2.185	0.32138
Mn1-O6	2.115	0.38831	Mn2-O4	2.188	0.31878
Mn1-O8	2.168	0.33649	Mn2-O4A	2.188	0.31878
Mn1-O9	2.182	0.324	Mn2-O5	2.142	0.36098
Mn1-O10	2.203	0.30612	Mn2-O8	2.175	0.33018

Thorp pointed out that the oxidation state of metal ions could be given via the bond valence sum. Bond valence $s = \exp[(r_0-r)/B]$, where B=0.37, r_0 values base on crystallographically characterized model complexes, r represents the metal-ligand bond lengths, namely, the bond distances of Mn-O in our work, and then 2.03 and 1.93 are gained for Mn1 and Mn2, respectively, indicating the oxidation state of Mn is +2.

Thermogravimetric Analysis (TGA)

To confirm the thermal stability of coordination polymer **1**, thermogravimetric analysis (TGA) has been measured. The result indicates that this compound exhibits high thermal stability. The framework is stable up to about 240 °C, which is indicative of no solvent molecules and strong hydrogen bonded interactions existing in **1**. Further heating, the framework starts to collapse due to the appearance of a gradual weight loss.

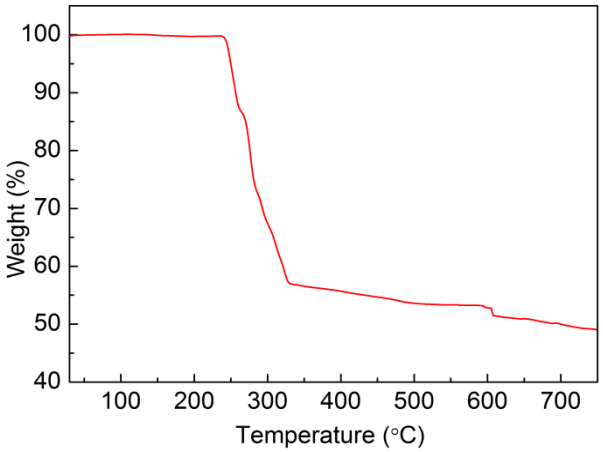

Fig. S1 The thermogravimetric analysis curve for coordination polymer **1**.

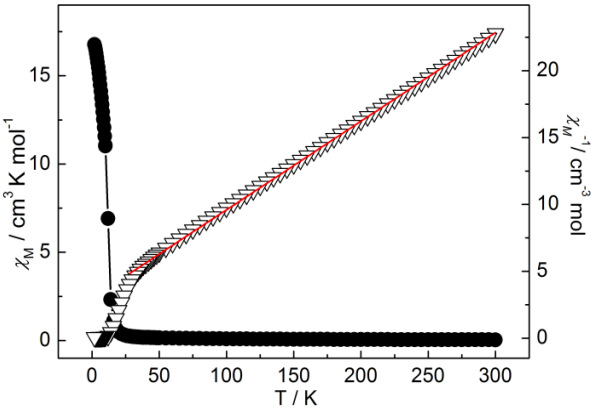

Fig. S2 The plots of χ_M *vs.* *T* and χ_M^{-1} *vs.* *T* for **1** at *H*=1000 Oe from 2 to 300K. The solid line is the best fit according to the Curie-Weiss law (28-300 K).

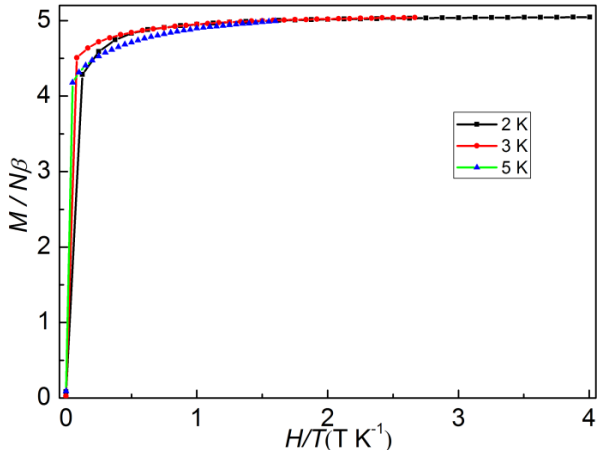

Fig. S3 *M vs. H/T* curves under the temperatures of 2, 3 and 5 K for **1**

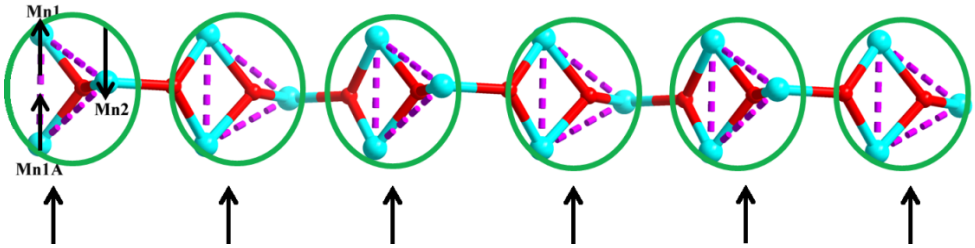

Fig. S4 The spin sketch map of magnetic interaction for per [Mn_3] cluster and the corresponding chain.

The simulation of magnetic data were carried out based on the Lippard's work (*J. Am. Chem. Soc*., 1987, **109**, 4244), in which one equicrural triangular [M_3] model when each M ion has s = 5/2 (high-spin), and the χ_M is expressed as depicted $\chi_M = (Ng^2\beta^2/4kT)*(F/G)$,[33]

where F=F_2+F_3+10*(A^3)*(F_6-F_5)+35*(A^8)*(1+F_6)+84*(A^15)*F_6+165*(A^24)*(F_6-F_1)+286*(A^35)*(F_3+F_4+F_5)+455*(A^48)*(F_4+F_5)+680*(A^63)*F_5

G=F_2+F_3+2*(A^3)*(F_6-F_5)+3*(A^8)*(1+F_6)+4*(A^15)*F_6+5*(A^24)*(F_6-F_1)+6*(A^35)*(F_3+F_4+F_5)+7*(A^48)*(F_4+F_5)+8*(A^63)*F_5

A=exp(P_2/(0.695*T))

B=exp((P_1-P_2)/(0.695*T))

F_1=B^2

F_2=B^6

F_3=B^12

F_4=B^20

F_5=B^30

F_6=F_1+F_2+F_3+F_4+F_5

χ_M = 0.09375*(P_3^2)*F/(G*T)

With the introduction of an intercluster interaction zJ', χ_M is expressed as shown

χ_M=χ_M /(1-2*P_4*χ_M /(0.26*(P_3^2))), and χ_M T=T*χ_M /(1-2*P_4*χ_M /(0.26*(P_3^2)))

P_1 and P_2 refer to the J_1 (the Mn1···Mn1A interaction) and J_2 (the interactions between Mn1···Mn2 and Mn1A···Mn2), P_3 refers to *g*-factor, P_4 refers to zJ' (the intercluster exchange interaction).

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