Supporting Information for

High-Performance Low-Temperature Magnetic Refrigerants Made of Gadolinium-Hydroxy-Chloride

Yanyan Wang,[a] Lei Qin,[a] Guo-jun Zhou,[a] Xinxin Ye,[b] Jiaqing He[b],* and Yan-Zhen Zheng[a],*

[a] Frontier Institute of Science and Technology (FIST), State Key Laboratory for Mechanical Behavior of Materials and MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710054, P. R. China.

[b] Shenzhen Key Laboratory of Thermoelectric Materials, Department of Physics, Southern University of Science and Technology , Shenzhen 518055, P. R. China

*To whom correspondence should be addressed. Email: zheng.yanzhen@xjtu.edu.cn, he.jq@sustc.edu.cn

Experimental

Synthetic procedures

The reagents and solvents employed in the synthesis were commercially available and used as received without further purification.

Synthesis of 1. The crystals of **1** were synthesized in the hydrothermal reaction system of $GdCl_3$-HCl-$NaOH$-H_2O. Typically, gadolinium (III) chloride hexahydrate ($GdCl_3·6H_2O$) was dispersed in a solution of hydrochloric acid (37 wt%) in water under vigorous stirring at room temperature. 2.5M NaOH solution was added to this mixture giving the pH value of about 6. After stirring for one hour, a homogeneous gel with an overall molar composition of $1.0 GdCl_3$: $1.2HCl$: $3.75NaOH$: $356H_2O$ was formed, which was heated under autogenous pressure in a 12 mL Teflon-lined stainless steel autoclave at 200 °C for 2 days. The obtained crystals were washed in distilled water and dried at room temperature overnight. The product was recovered with a yield about 88.2 % based on Gd. ICP analysis of the product gave (in wt.%) Gd: 72.6 (calcd. 73.3) and anion chromatography analysis gave (in wt.%) Cl: 5.45 (calcd. 5.52). That were consistent with the elemental contents calculated from the molecular formula of $[Gd_3(OH)_8Cl]_n$.

Synthesis of 2. The crystals of **2** were also synthesized in the hydrothermal reaction system of $GdCl_3$-HCl-$NaOH$-H_2O. Typically, gadolinium (III) chloride hexahydrate ($GdCl_3·6H_2O$) was dispersed in a solution of hydrochloric acid (37 wt%) in water under vigorous stirring at room temperature. 2.5M NaOH solution was added to this mixture giving the pH value of about 6. After stirring for one hour, a homogeneous gel with an overall molar composition of $1.0 GdCl_3$: $1.2HCl$: $2.5NaOH$: $356H_2O$ was formed, which was heated under autogenous pressure in a 12 mL Teflon-lined stainless steel autoclave at 200 °C for 2 days. The obtained crystals were washed in distilled water and dried at room temperature overnight. The product was recovered with a yield of more than 90 % based on Gd. ICP analysis of the product gave (in wt.%) Gd: 68.8 (calcd. 69.3) and anion chromatography analysis gave (in wt.%) Cl: 15.2 (calcd. 15.6). That were consistent with the elemental contents calculated from the molecular formula of $[Gd(OH)_2Cl]_n$.

Characterization Methods

Powder X-ray diffraction (PXRD) data were collected on a Rigaku Smartlab X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Anion chromatography analysis was performed on DX-500 Ion Chromatography (IC) System of Dionex. Thermogravimetric analysis (TGA) was carried out on a TA Q500 analyzer in nitrogen with a heating rate of 10°C min^{-1} from RT to 800°C. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Escalab 250 spectrometer with monochromatized Al Kα excitation. The crystal morphology was studied by field-emission scanning electron microscopy (HITACHI UHR FE-SEM SU-8010) using conventional sample preparation and imaging techniques.

Magnetic analyses

The magnetic measurements of the polycrystalline samples were performed using a SQUID magnetometer (Quantum Design MPMS XL-7). Diamagnetic corrections were made with Pascal's constants for all the constituent atoms and sample holder. The isothermal magnetization was measured in the temperature range of 2-10 K in applied field of 0-7 T. At each temperature, the M-H curves were measured isothermally from 0 to 7.0 T with step size of 0.25 T during 0–1.0 T

and 0.5 T during 1.0–7.0 T, then set the field to 0 T to begin another measurement.

Thermal conductivity

High-density SPS processed pellets were prepared by crashed samples into coins of $\phi \sim 9$ mm and thickness ~ 2 mm for measuring thermal diffusivity. The samples were coated with a thin layer of graphite to minimize errors from the emissivity of the materials. Thermal conductivity was calculated from $\kappa = \alpha \cdot c_p \cdot \rho$, where the thermal diffusivity coefficient (α) was measured using the laser-flash diffusivity method in a Netzsch LFA457, the specific heat capacity (c_p) was indirectly derived using a representative sample (Pyroceram 9606) between 248 and 373 K, and the density (ρ) could be obtained from their crystal structures, which is very close to the values determined by using the dimensions and mass of the sample. The thermal diffusivity data were analyzed using the Cowan model with pulse correction; heating and cooling cycles gave reproducible values for every individual sample. The uncertainty of the thermal conductivity is estimated to be within 5%, considering the uncertainties for α, c_p, and ρ. The combined uncertainty for all measurements involved in the calculation of ZT is about 15%.

Structural Determination

Suitable single crystal of **1** and **2** with dimension of $0.13 \times 0.08 \times 0.07$ mm^3 and $0.08 \times 0.03 \times 0.03$ mm^3 were selected for single-crystal X-ray diffraction analyses, respectively. The intensity data were collected on a Bruker Apex Ⅱ DUO area-detector diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at temperature of 23 ± 2 °C. Cell refinement and data reduction were accomplished with the SAINT processing program.[1] The structures of **1** and **2** were solved in the space group $C2/m$ and $P2_1/m$, respectively, by direct methods and refined by full matrix least-squares technique with the SHELXTL crystallographic software package.[2] The heaviest atoms of Gd, O and Cl could be unambiguously located and refined anisotropically. For **1**, H atoms were not added. For **2**, H atoms were located geometrically. Crystal data and refinement parameters for the structure determination are presented in Tables S1, S3. The selected bond distances and bond angles are listed in the Tables S2, S4.

References:

[1] SAINT, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711–5373, USA, 2000.

[2] SHELXTL, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711–5373, USA, 2000.

Table S1. Crystal data and structure refinement for **1**[a].

Compound	1
Empirical formula	$H_8ClGd_3O_8$
Formula weight	643.26
Temperature	296(2) K
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $C2/m$
Unit cell dimensions	
a (Å)	34.635(3)
b (Å)	7.3106(7)
c (Å)	6.5139(6)
α (°)	90
β (°)	90.186(2)
γ (°)	90
Volume ($Å^{-3}$)	1649.3(3)
Z, calculated density (kg m^{-3})	8, 5.181
Absorption coefficient (mm^{-1})	24.176
$F(000)$	2248
Crystal size (mm^3)	$0.13 \times 0.08 \times 0.07$
θ range (°) for data collection	1.18 − 27.65
Limiting indices	$-44 \le h \le 44, -9 \le k \le 9, -8 \le l \le 8$
Reflections collected/unique	12272/2057, [$R_{int} = 0.0356$]
Completeness to θ (%)	27.65, 99.0
Absorption correction	Semi-empirical from equivalents
Max and min transmission	0.2824 and 0.1452
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2057/31/107
Goodness-of-fit on F^2	1.176
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0526, wR_2 = 0.1411$
R indices (all data)	$R_1 = 0.0609, wR_2 = 0.1531$
Largest diff. peak and hole (e Å^{-3})	6.119 and −6.390

[a] $R_1 = \sum(\Delta F / \sum(F_o))$, $wR_2 = (\sum[w(F_o^2 - F_c^2)]) / \sum[w(F_o^2)^2]^{1/2}$ and $w = 1/\sigma^2(F_o^2)$.

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

Gd(1)-O(1)#1	2.322(9)	O(5)-Gd(3)-O(7)	75.5(4)
Gd(1)-O(1)#2	2.322(9)	O(4)-Gd(3)-O(7)	68.8(4)
Gd(1)-O(2)	2.304(13)	O(6)-Gd(3)-O(7)	76.0(4)
Gd(1)-O(1)	2.354(10)	O(8)-Gd(3)-O(1)	69.9(4)
Gd(1)-O(1)#3	2.354(10)	O(2)-Gd(3)-O(1)	66.0(4)
Gd(1)-O(3)#1	2.346(13)	O(4)-Gd(3)-O(1)	74.6(4)
Gd(1)-Cl(2)	2.762(6)	O(3)-Gd(3)-O(1)	67.7(4)
Gd(2)-O(7)#3	2.466(10)	O(7)#8-Gd(4)-O(7)	95.2(5)
Gd(2)-O(7)	2.466(10)	O(7)-Gd(4)-O(10)	73.1(4)
Gd(2)-O(10)	2.461(10)	O(7)#8-Gd(4)-O(10)#8	73.1(4)
Gd(2)-O(10)#3	2.461(10)	O(10)-Gd(4)-O(10)#8	96.8(5)
Gd(2)-O(12)	2.478(11)	O(7)-Gd(4)-O(12)#3	70.1(4)
Gd(2)-O(12)#3	2.478(11)	O(10)-Gd(4)-O(12)#3	70.0(4)
Gd(2)-O(6)#5	2.534(16)	O(7)#8-Gd(4)-O(12)#9	70.1(4)
Gd(2)-O(8)	2.437(15)	O(10)#8-Gd(4)-O(12)#9	70.0(4)
Gd(2)-O(11)	2.581(17)	O(12)#3-Gd(4)-O(12)#9	94.9(5)
Gd(3)-O(8)	2.449(10)	O(10)-Gd(4)-O(5)#5	68.2(4)
Gd(3)-O(2)	2.448(9)	O(10)#8-Gd(4)-O(5)#5	68.2(4)
Gd(3)-O(5)	2.430(9)	O(12)#3-Gd(4)-O(5)#5	71.4(4)
Gd(3)-O(4)	2.476(10)	O(12)#9-Gd(4)-O(5)#5	71.4(4)
Gd(3)-O(3)	2.472(9)	O(7)#8-Gd(4)-O(4)	68.9(3)
Gd(3)-O(6)	2.456(10)	O(7)-Gd(4)-O(4)	68.9(3)
Gd(3)-O(10)#7	2.525(13)	O(10)-Gd(4)-O(4)	75.6(4)
Gd(3)-O(7)	2.464(11)	O(10)#8-Gd(4)-O(4)	75.6(4)
Gd(3)-O(1)	2.623(9)	O(7)#8-Gd(4)-O(9)	72.6(4)
Gd(4)-O(7)#8	2.454(10)	O(7)-Gd(4)-O(9)	72.6(4)
Gd(4)-O(7)	2.454(10)	O(12)#3-Gd(4)-O(9)	65.8(4)
Gd(4)-O(10)	2.439(10)	O(12)#9-Gd(4)-O(9)	65.8(4)
Gd(4)-O(10)#8	2.439(10)	O(9)#6-Gd(5)-O(12)	74.4(6)
Gd(4)-O(12)#3	2.468(11)	O(11)-Gd(5)-O(12)	74.1(5)
Gd(4)-O(12)#9	2.468(11)	O(9)#6-Gd(5)-O(9)#11	70.4(8)
Gd(4)-O(5)#5	2.547(15)	O(12)#10-Gd(5)-O(9)#11	73.2(5)
Gd(4)-O(4)	2.478(15)	O(12)-Gd(5)-O(9)#11	94.1(5)
Gd(4)-O(9)	2.650(18)	O(11)-Gd(5)-O(11)#11	73.0(7)
Gd(5)-O(9)#6	2.118(9)	O(12)#10-Gd(5)-O(11)#11	72.6(5)
Gd(5)-O(11)	2.156(9)	O(12)-Gd(5)-O(11)#11	95.1(5)
Gd(5)-O(12)#10	2.240(13)	O(9)#11-Gd(5)-O(11)#11	95.2(5)
Gd(5)-O(12)	2.466(13)	Gd(1)#1-O(1)-Gd(1)	106.2(4)
Gd(5)-O(9)#11	2.454(13)	Gd(1)#1-O(1)-Gd(3)	105.4(4)
Gd(5)-O(11)#11	2.498(13)	Gd(1)-O(1)-Gd(3)	106.3(4)
Gd(5)-Cl(1)	2.8523(16)	Gd(1)-O(2)-Gd(3)	114.0(4)
		Gd(1)-O(2)-Gd(3)#3	114.0(4)
O(1)#1-Gd(1)-O(1)	73.8(4)	Gd(3)-O(2)-Gd(3)#3	96.3(5)
O(2)-Gd(1)-O(1)	72.8(3)	Gd(3)#8-O(4)-Gd(3)	95.4(5)
O(1)#2-Gd(1)-O(1)#3	73.8(4)	Gd(3)#8-O(4)-Gd(4)	110.5(4)
O(2)-Gd(1)-O(1)#3	72.8(3)	Gd(3)-O(4)-Gd(4)	110.5(4)
O(1)-Gd(1)-O(1)#3	88.0(5)	Gd(1)#1-O(3)-Gd(3)#8	109.6(4)
O(1)#1-Gd(1)-O(3)#1	75.0(3)	Gd(1)#1-O(3)-Gd(3)	109.6(4)

O(1)#2-Gd(1)-O(3)#1	75.0(3)	Gd(3)#8-O(3)-Gd(3)	95.7(4)
O(1)-Gd(1)-O(3)#1	96.1(3)	Gd(5)#3-O(11)-Gd(5)	116.1(8)
O(1)#3-Gd(1)-O(3)#1	96.1(3)	Gd(5)-O(11)-Gd(5)#11	107.0(7)
O(7)#3-Gd(2)-O(7)	96.8(5)	Gd(5)#3-O(11)-Gd(5)#10	107.0(7)
O(7)-Gd(2)-O(10)	72.6(4)	Gd(5)#11-O(11)-Gd(5)#10	94.1(6)
O(7)#3-Gd(2)-O(10)#3	72.6(4)	Gd(5)#3-O(11)-Gd(2)	111.6(5)
O(10)-Gd(2)-O(10)#3	96.2(5)	Gd(5)-O(11)-Gd(2)	111.6(5)
O(7)#3-Gd(2)-O(12)	69.7(4)	Gd(5)#11-O(11)-Gd(2)	103.3(5)
O(10)#3-Gd(2)-O(12)	69.5(4)	Gd(5)#10-O(11)-Gd(2)	103.3(5)
O(7)-Gd(2)-O(12)#3	69.7(4)	Gd(5)#3-O(9)-Gd(5)#9	119.2(8)
O(10)-Gd(2)-O(12)#3	69.5(4)	Gd(5)#3-O(9)-Gd(5)#14	109.6(8)
O(12)-Gd(2)-O(12)#3	95.7(5)	Gd(5)#9-O(9)-Gd(5)#11	109.6(8)
O(10)-Gd(2)-O(6)#5	68.3(4)	Gd(5)#14-O(9)-Gd(5)#11	96.2(7)
O(10)#3-Gd(2)-O(6)#5	68.3(4)	Gd(5)#3-O(9)-Gd(4)	111.0(5)
O(12)-Gd(2)-O(6)#5	70.7(4)	Gd(5)#9-O(9)-Gd(4)	111.0(5)
O(12)#3-Gd(2)-O(6)#5	70.7(4)	Gd(5)#14-O(9)-Gd(4)	103.1(6)
O(7)#3-Gd(2)-O(8)	68.3(3)	Gd(5)#11-O(9)-Gd(4)	103.1(6)
O(7)-Gd(2)-O(8)	68.3(3)	Gd(3)#8-O(5)-Gd(3)	97.9(5)
O(10)-Gd(2)-O(8)	76.3(4)	Gd(3)#8-O(5)-Gd(4)#7	111.3(4)
O(10)#3-Gd(2)-O(8)	76.3(4)	Gd(3)-O(5)-Gd(4)#7	111.3(4)
O(7)#3-Gd(2)-O(11)	72.6(4)	Gd(4)-O(10)-Gd(2)	96.5(4)
O(7)-Gd(2)-O(11)	72.6(4)	Gd(4)-O(10)-Gd(3)#5	111.8(4)
O(12)-Gd(2)-O(11)	67.0(4)	Gd(2)-O(10)-Gd(3)#5	111.7(4)
O(12)#3-Gd(2)-O(11)	67.0(4)	Gd(3)-O(6)-Gd(3)#3	95.8(5)
O(8)-Gd(3)-O(2)	71.5(4)	Gd(3)-O(6)-Gd(2)#7	111.5(4)
O(8)-Gd(3)-O(4)	95.8(4)	Gd(3)#3-O(6)-Gd(2)#7	111.5(4)
O(5)-Gd(3)-O(4)	72.7(4)	Gd(5)#10-O(12)-Gd(4)#6	117.5(5)
O(2)-Gd(3)-O(3)	96.2(3)	Gd(5)-O(12)-Gd(4)#6	106.0(5)
O(5)-Gd(3)-O(3)	71.2(4)	Gd(5)#10-O(12)-Gd(2)	116.5(5)
O(4)-Gd(3)-O(3)	67.4(4)	Gd(5)-O(12)-Gd(2)	105.1(5)
O(8)-Gd(3)-O(6)	72.3(4)	Gd(4)#6-O(12)-Gd(2)	95.3(4)
O(2)-Gd(3)-O(6)	68.3(4)	Gd(4)-O(7)-Gd(2)	96.0(4)
O(5)-Gd(3)-O(6)	96.9(4)	Gd(4)-O(7)-Gd(3)	111.8(4)
O(2)-Gd(3)-O(10)#7	69.2(4)	Gd(2)-O(7)-Gd(3)	111.0(4)
O(5)-Gd(3)-O(10)#7	68.7(4)	Gd(3)-O(8)-Gd(3)#3	96.2(5)
O(3)-Gd(3)-O(10)#7	73.8(4)	Gd(3)-O(8)-Gd(2)	112.5(4)
O(6)-Gd(3)-O(10)#7	68.5(4)	Gd(3)#3-O(8)-Gd(2)	112.5(4)
O(8)-Gd(3)-O(7)	68.2(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1/2,-y+1/2,-z+1   #2 -x+1/2,y+1/2,-z+1   #3 x,-y+1,z   #4 -x+1/2,-y+3/2,-z+1   #5 x,y,z-1   #6 x,y+1,z   #7 x,y,z+1   #8 x,-y,z   #9 x,y-1,z   #10 -x+1,y,-z   #11 -x+1,-y+1,-z   #12 x,-y+2,z   #13 -x+1,-y+2,-z   #14 -x+1,y-1,-z   #15 -x+1,y,-z+1

Table S3. Crystal data and structure refinement for **2**[a].

Compound	2
Empirical formula	H_2ClGdO_2
Formula weight	226.72
Temperature	293(2) K
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/m$
Unit cell dimensions	
a (Å)	6.180(7)
b (Å)	3.757(4)
c (Å)	6.734(7)
α (°)	90
β (°)	111.075(17)
γ (°)	90
Volume (Å^{-3})	145.9(3)
Z, calculated density (kg m^{-3})	2, 5.161
Absorption coefficient (mm^{-1})	23.365
$F(000)$	198
Crystal size (mm^3)	$0.08 \times 0.03 \times 0.03$
θ range (°) for data collection	3.24 – 25.49
Limiting indices	$-7 \leq h \leq 7, -4 \leq k \leq 4, -7 \leq l \leq 8$
Reflections collected/unique	894/302, [$R_{int} = 0.0354$]
Completeness to θ (%)	25.49, 95.6
Absorption correction	Semi-empirical from equivalents
Max and min transmission	0.5408 and 0.2565
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	302/7/25
Goodness-of-fit on F^2	1.118
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0342, wR_2 = 0.0858$
R indices (all data)	$R_1 = 0.0379, wR_2 = 0.0882$
Largest diff. peak and hole (e Å^{-3})	4.076 and -1.921

[a] $R_1 = \sum(\Delta F/\sum(F_o))$, $wR_2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$ and $w = 1/\sigma^2(F_o^2)$.

Table S4. Selected Bond lengths [Å] and Angles [deg] for **2**.

Bond lengths		Angles	
Gd(1)-O(2)#1	2.365(10)	O(2)#1-Gd(1)-O(1)	77.2(3)
Gd(1)-O(1)#2	2.383(10)	O(1)#2-Gd(1)-O(1)	68.4(3)
Gd(1)-O(1)	2.418(6)	O(2)#1-Gd(1)-O(1)#3	77.2(3)
Gd(1)-O(1)#3	2.418(6)	O(1)#2-Gd(1)-O(1)#3	68.4(3)
Gd(1)-O(2)#3	2.442(6)	O(1)-Gd(1)-O(1)#3	101.9(3)
Gd(1)-O(2)	2.442(6)	O(2)#1-Gd(1)-O(2)#3	70.7(3)
Gd(1)-Cl(1)	2.927(3)	O(1)#3-Gd(1)-O(2)#3	69.6(3)
Gd(1)-Cl(1)#4	2.927(3)	O(2)#1-Gd(1)-O(2)	70.7(3)
		O(1)-Gd(1)-O(2)	69.6(3)
		O(2)#3-Gd(1)-O(2)	100.6(4)
		Gd(1)#2-O(1)-Gd(1)	111.6(3)
		Gd(1)#2-O(1)-Gd(1)#4	111.6(3)
		Gd(1)-O(1)-Gd(1)#4	101.9(3)
		Gd(1)#1-O(2)-Gd(1)#4	109.3(3)
		Gd(1)#1-O(2)-Gd(1)	109.3(3)
		Gd(1)#4-O(2)-Gd(1)	100.6(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z   #2 -x,-y,-z   #3 x,y+1,z   #4 x,y-1,z

(a)

(b)
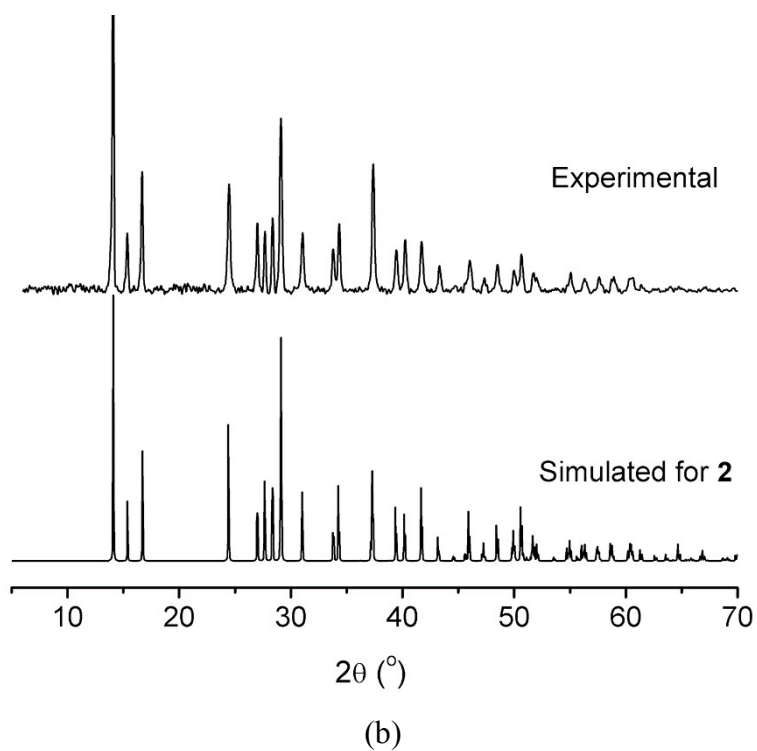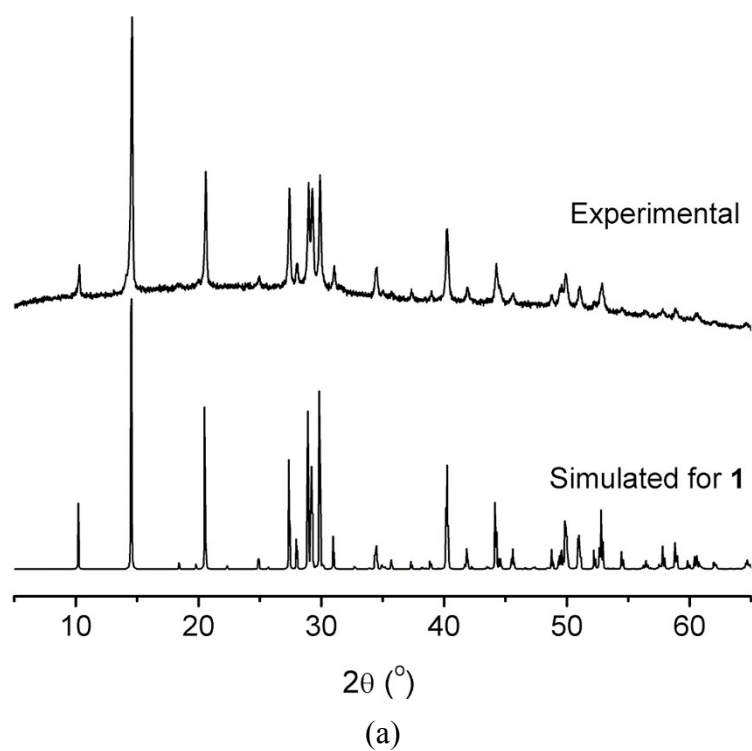
Figure S1 Experimental PXRD patterns of (a) **1** and (b) **2** comparing with the simulated one.
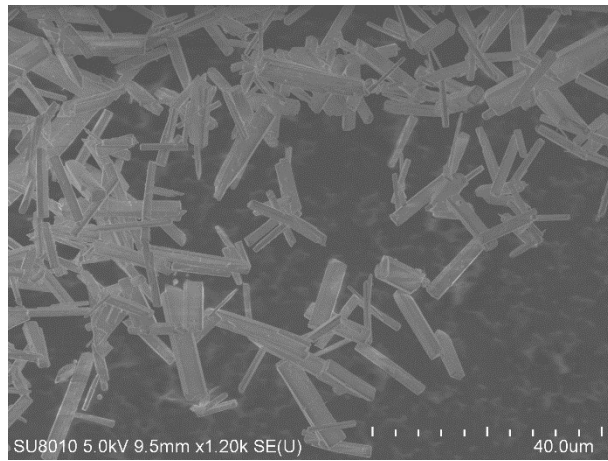
(a)
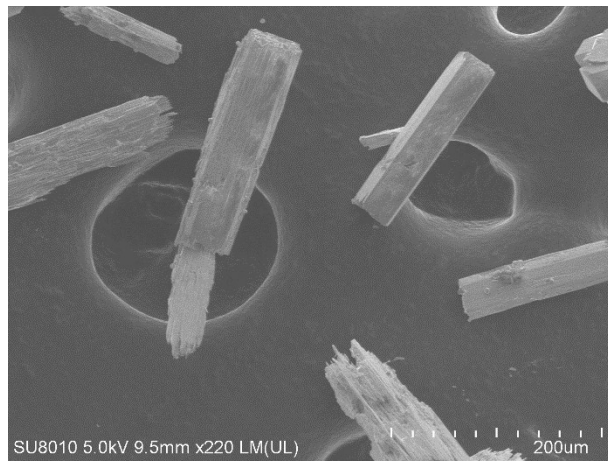
(b)

Figure S2 SEM analyses of (a) **1** and (b) **2** showing the rod-like morphologies of them.
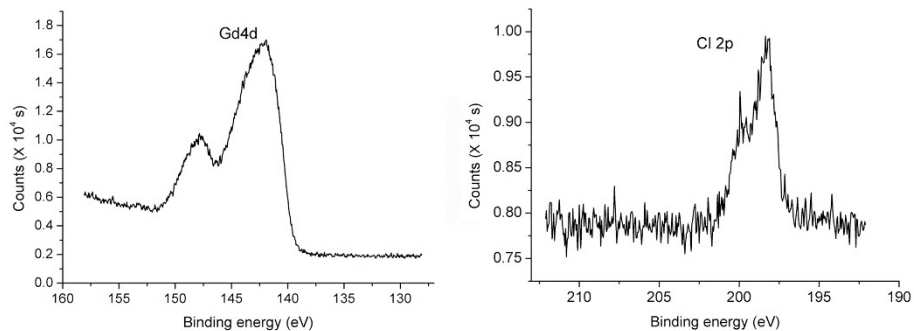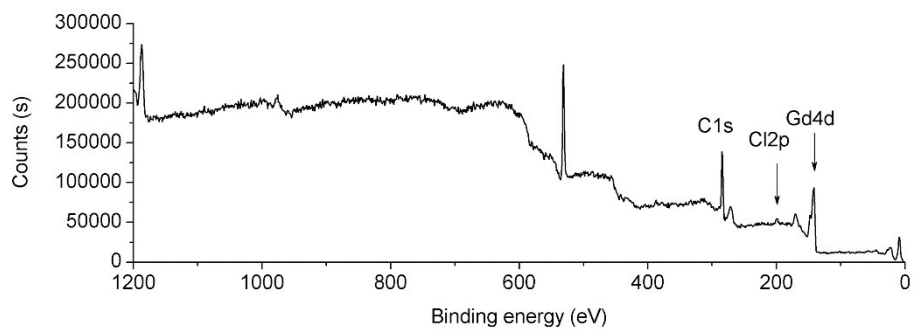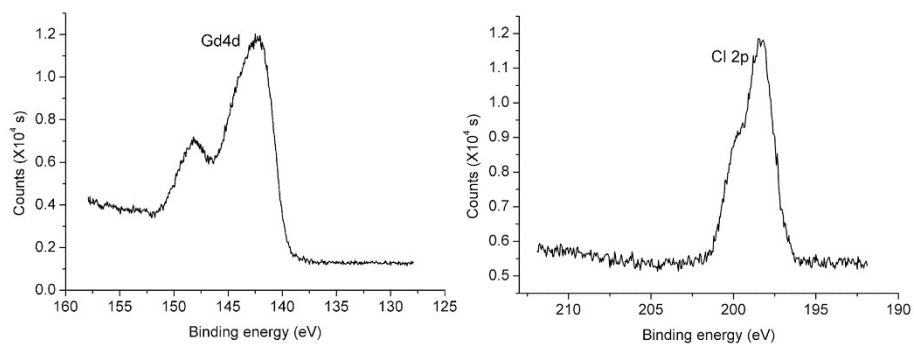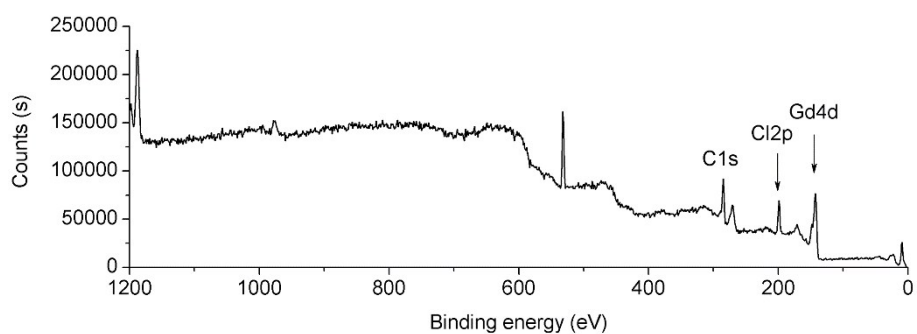
Figure S3 (a) XPS spectra of **1** with survey spectrum (up), XPS spectrum of Gd 4*d* (left) and spectrum of Cl 2*p* (right), the content ratio of Gd/Cl close to 3; (b) XPS spectra of **2** with survey spectrum, XPS spectrum of Gd 4*d* (left) and spectrum of Cl 2*p* (right), the content ratio of Gd/Cl close to 1.
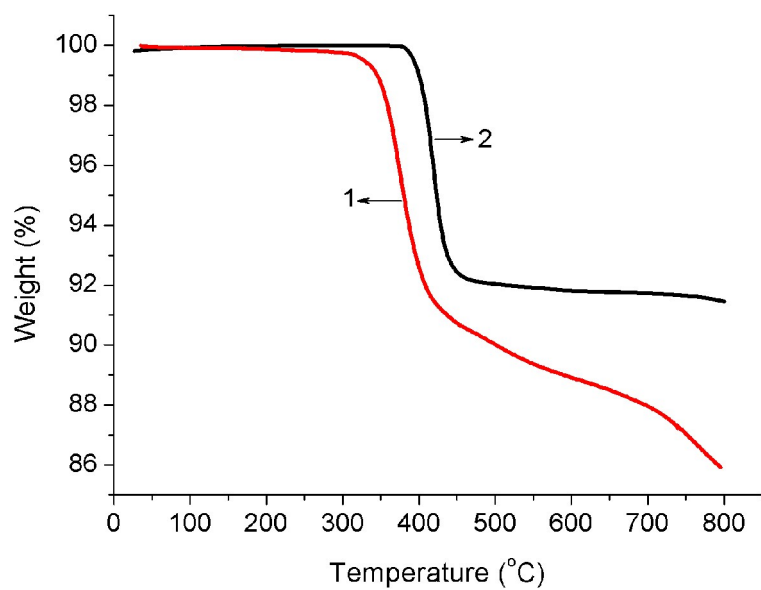
Figure S4 TG analyses of **1** and **2** in nitrogen with a heating rate of 10°C min^{-1} from RT to 800°C.
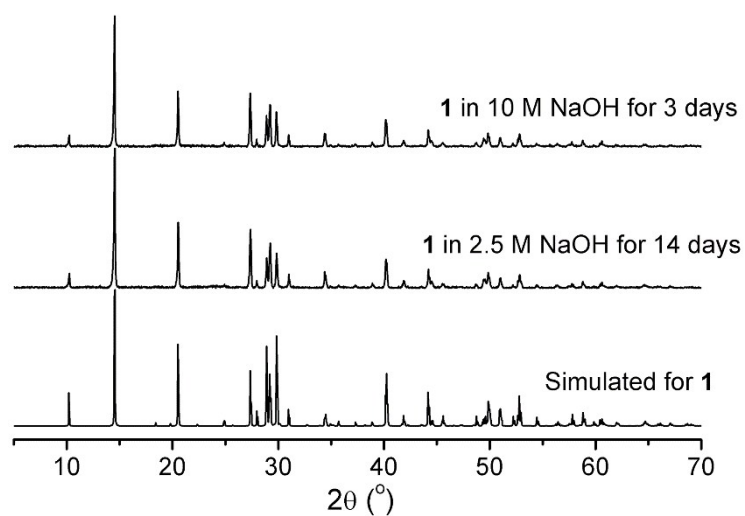
(a)
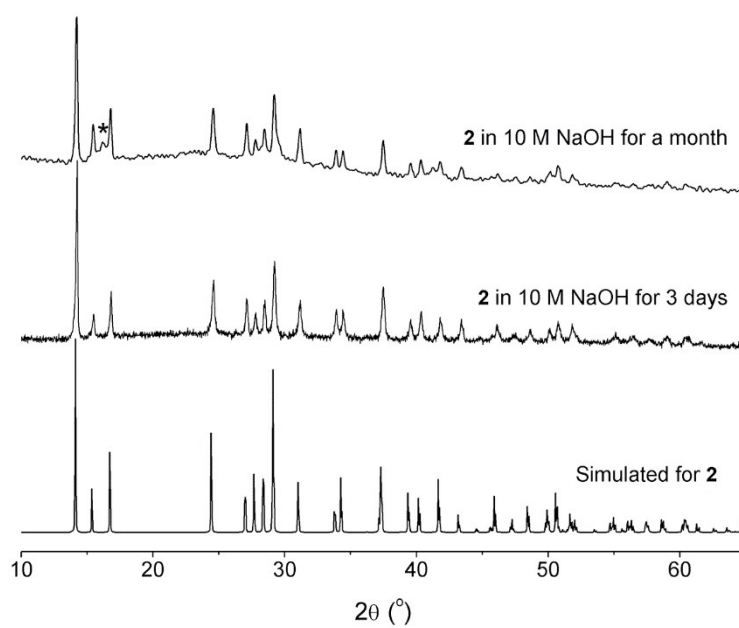
(b)

Figure S5 Experimental PXRD patterns of (a) **1** and (b) **2** after immersing in aqueous solutions of NaOH. It shows the PXRD of the **1** immersing in different aqueous solutions of NaOH corresponds well with the simulated one. The PXRD of **2** in 10M NaOH for 3 days did not change comparing with the synthesized one; after immersing 10M NaOH for a month, an extra peak that is the signal of $Gd(OH)_3$ will appear.
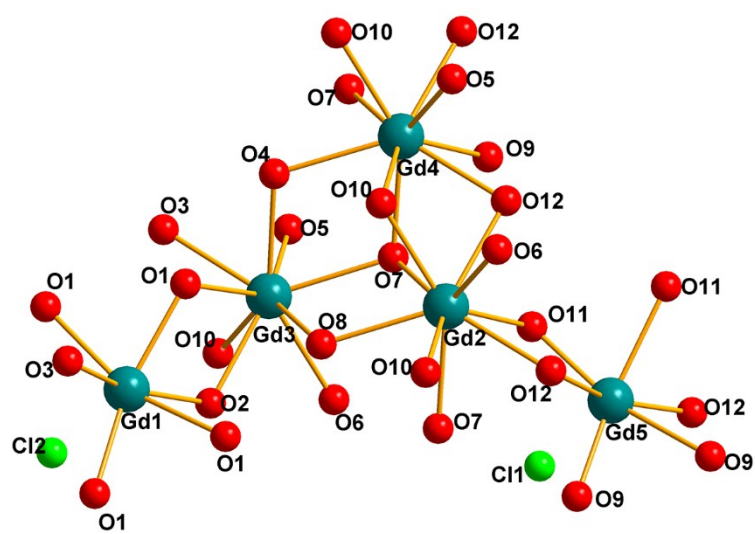
(a)
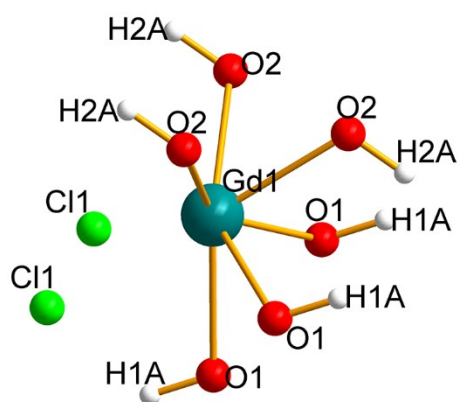
(b)

Figure S6 The coordination environment of Gd^{3+} in (a) **1** and (b) **2**.
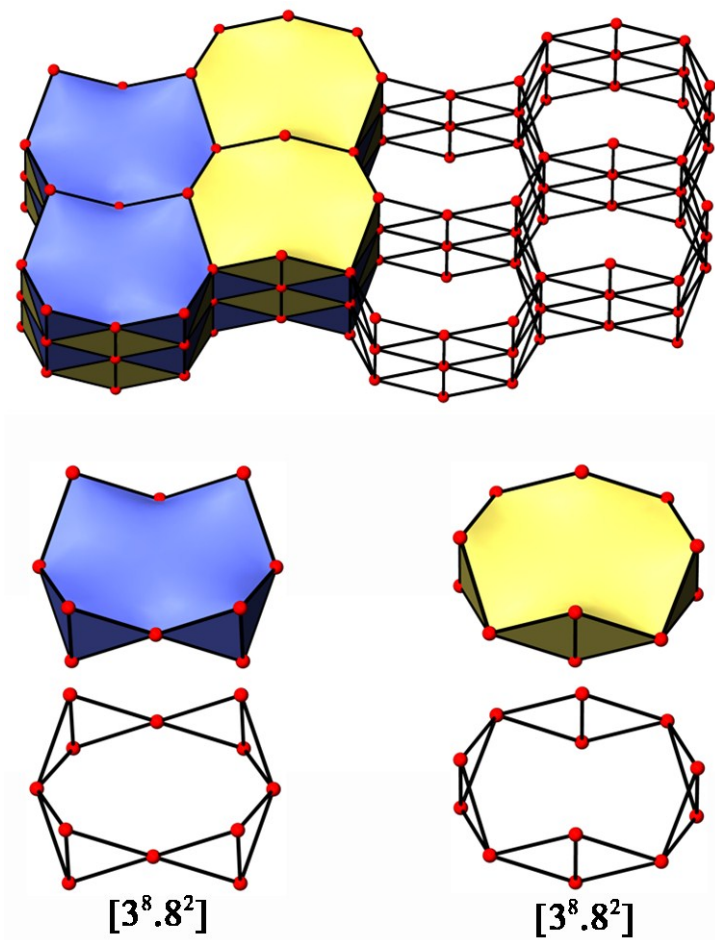
Figure S7 Structural features of **1** displayed by tiles, showing the 8-ring channels. The face symbols for blue and yellow tiles are both $[3^8.8^2]$.
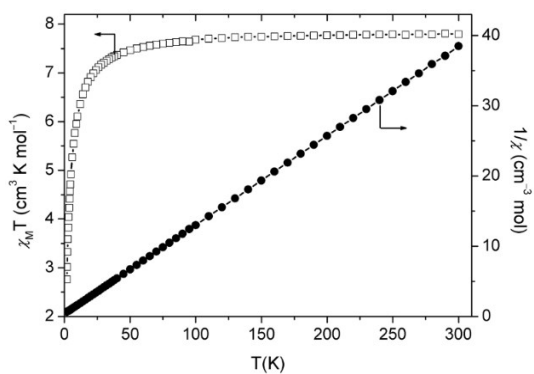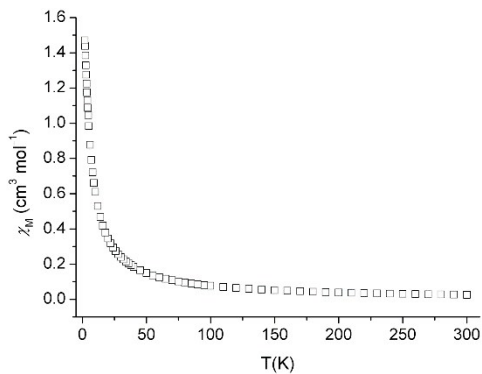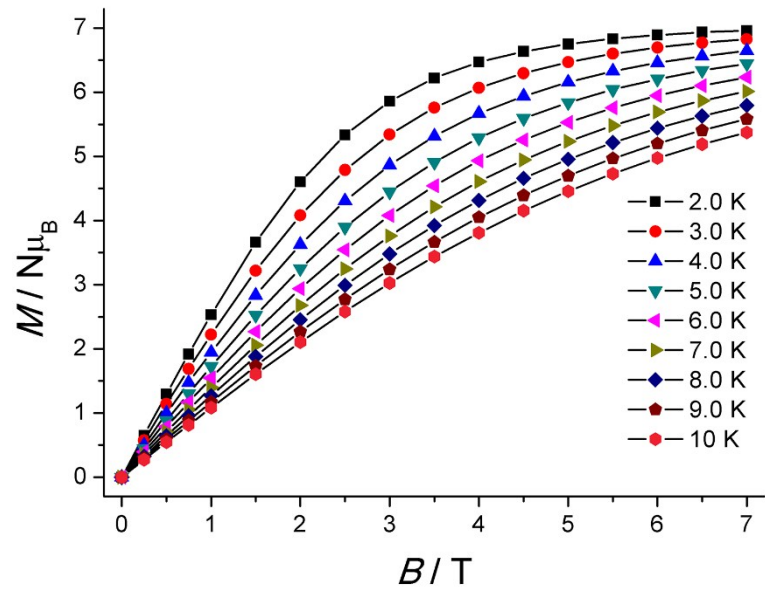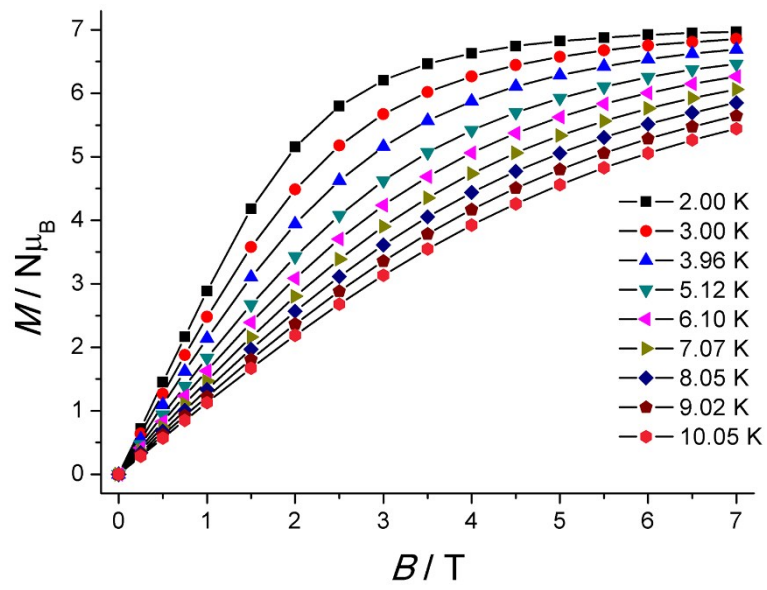
(a)
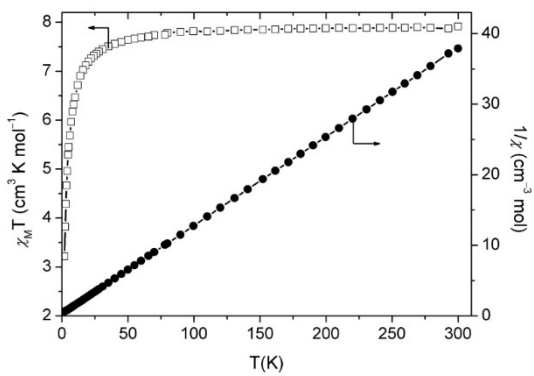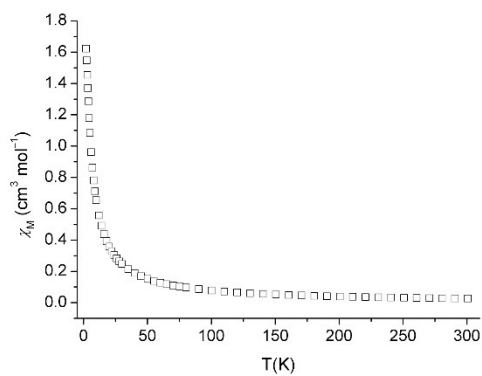
(b)

Figure S8 Temperature-dependencies of the magnetic susceptibility product, χ, $\chi_M T$ and $1/\chi$ at 2－300 K with dc field of 2 kOe for (a) **1** and (b) **2**, denoting predominant antiferromagnetic interactions.

(a)

(b)

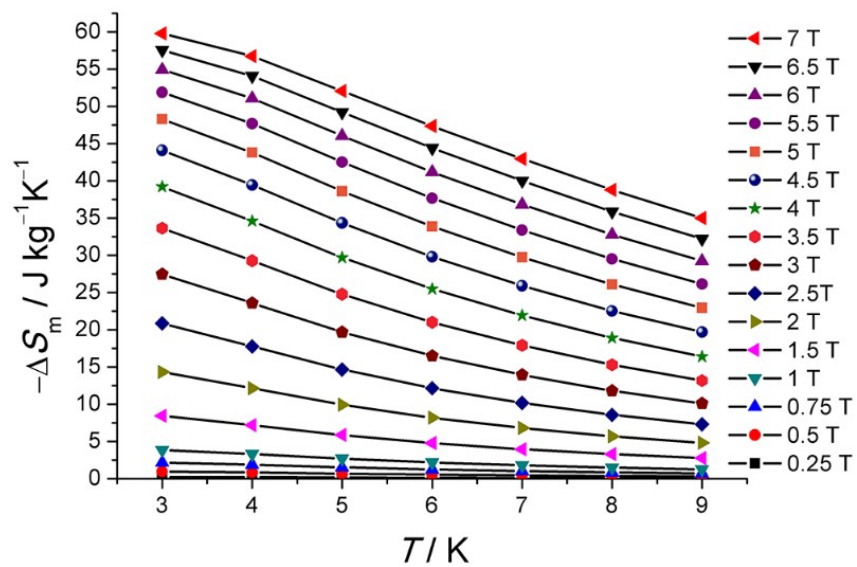**Figure S9** M-B curve for (a) **1** and (c) **2** from 2.0 K to 10 K.

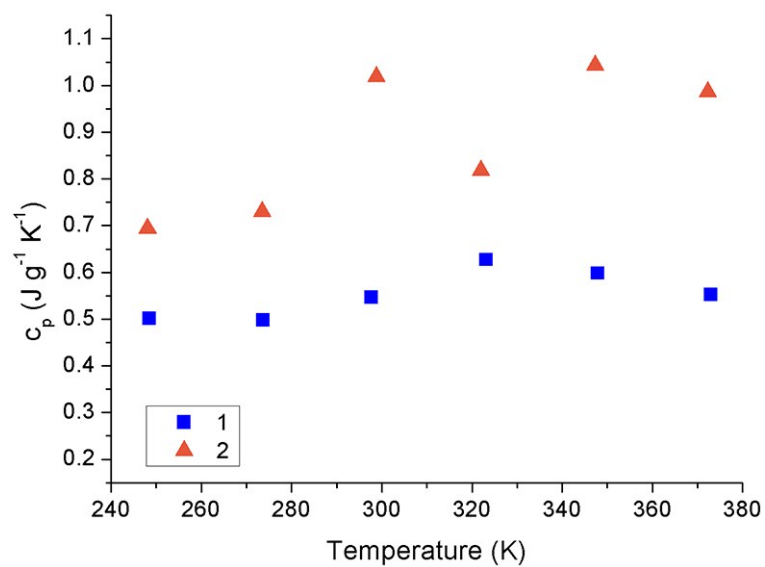**Figure S10** $-\Delta S_m$ calculated by using the magnetization data of **1** at different fields and temperatures.

Figure S11 Specific heat capacity at indicated temperatures for compounds **1** and **2**.
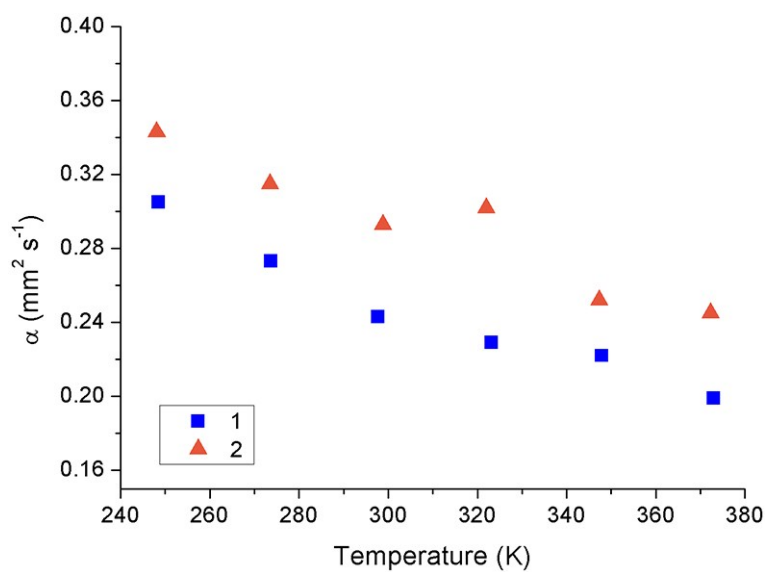

Figure S12 The thermal diffusion coefficient of **1** and **2** between 248 and 373K.