Electronic Supplementary Information (ESI) for *New Journal of Chemistry*

Two Gd^{III} complexes derived from dicarboxylate ligands as cryogenic magnetorefrigerants

Sui-Jun Liu, *[a] Teng-Fei Zheng,[a] Jun Bao,[a] Piao-Ping Dong,[a] Jin-Sheng Liao,[a] Jing-Lin Chen,[a] He-Rui Wen,*[a] Jian Xu*[b] and Xian-He Bu[b]

[a]*School of Metallurgical and Chemical Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, Jiangxi Province, P.R. China*

[b]*Department of Chemistry, TKL of Metal- and Molecule-Based Material Chemistry and Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, P.R. China*

*Corresponding author. (S.-J. Liu) E-mail: liusuijun147@163.com, Tel: +86-797-8312204

(H.-R. Wen) E-mail: wenherui63@163.com, Tel: +86-797-8312553

(J. Xu) E-mail: jxu@nankai.edu.cn, Tel: +86-22-23502458.

Table S1. Comparison of $-\Delta S_m^{max}$ (larger than 37.0 J kg^{-1} K^{-1} with $\Delta H \leq 9$ T) among title complexes and Gd^{III} coordination polymers associated with potential molecular magnetorefrigerants.

Complex	M_W/N_{Gd}	Magnetic interaction (θ, K)	$-\Delta S_m^{max}$ [J kg^{-1} K^{-1}] (ΔH)	$-\Delta S_m^{max}$ [mJ cm^{-3} K^{-1}]
$[Gd(OH)CO_3]_\infty$[S1]	234.27	AF (−1.05)	66.4 (7 T)	355
$\{Gd(HCOO)_3\}_\infty$[S2]	292.30	AF (−0.3)	55.9 (7 T)	215.7
$[Gd_6]_\infty$[S3]	278.25	AF (−5.50)	46.6 (7 T)	206.81
$[Ln_4(SO_4)_4(\mu_3\text{-}OH)_4(H_2O)_4]_\infty$[S4]	288.34	AF (−1.57)	51.29 (7 T)	198.85
$[Gd_4(\mu_4\text{-}SO_4)_3(\mu_3\text{-}OH)_4(\mu_2\text{-}C_2O_4)(\mu_2\text{-}H_2O)(H_2O)_4]\cdot H_2O$[S5]	295.33	AF (−1.57)	51.49 (7 T)	190.46
$\{[Gd_6(OH)_8(suc)_5(H_2O)_2]\cdot 4H_2O\}_\infty$[S6]	294.67	AF (−2.15)	48 (7 T)	143.52
$[Gd(C_4O_4)(C_2O_2)_{0.5}(H_2O)_2]_\infty$[S7]	349.33	AF (−0.18)	44.0 (7 T)	127.6
$[Gd(HCOO)(C_8H_4O_4)]_\infty$[S8]	366.38	AF (−0.45)	47.0 (9 T)	125.11
$\{[Gd_2(OH)_2(suc)_2(H_2O)]\cdot 2H_2O\}_\infty$[S6]	317.36	AF (−2.78)	42.8 (7 T)	120.48
$[Gd_2(OH)_2(oda)_2(H_2O)_4]_\infty$ (**1**)	342.36	AF (−1.06)	43.3 (7 T)	116.6
$[Gd(cit)(H_2O)]_\infty$[S9]	363.36	F (1.13)	43.6 (7 T)	115.23
$[Gd(HCOO)(OAc)_2(H_2O)_2]_\infty$[S10]	356.38	AF	45.9 (7 T)	110.02
$[Gd(OAc)_3(H_2O)_{0.5}]_\infty$[S11]	343.39	AF (−0.22)	47.7 (7 T)	106.28
$[Gd(C_4O_4)(OH)(H_2O)_4]_\infty$[S12]	358.36	AF (−0.12)	43.8 (7 T)	104.59
$\{[Gd_2(IDA)_3]\cdot 2H_2O\}_\infty$[S13]	371.90	AF (−0.90)	40.6 (7 T)	100.69
$[Gd(OAc)_3(MeOH)]_\infty$[S11]	366.42	F (0.34)	45.0 (7 T)	96.71
$\{[Gd(fum)(ox)_{0.5}(H_2O)_2]\cdot 2H_2O\}_\infty$ (**2**)	387.38	F (0.93)	37.1 (7 T)	93.4
$[Gd_{36}]_\infty$[S14]	345.00	AF (−2.43)	39.66 (7 T)	91.34
$[Gd_2(piv)_5(\mu_3\text{-}OH)(H_2O)]_\infty$[S9]	427.57	AF (−0.86)	37.5 (7 T)	61.13

$-\Delta S_m^{max}$ [mJ cm^{-3} K^{-1}] = $-\Delta S_m^{max}$ [J kg^{-1} K^{-1}]*ρ_{cald} [g cm^{-3}]

References

S1. Y.-C. Chen, L. Qin, Z.-S. Meng, D. Yang, C. Wu, Z. Fu, Y.-Z. Zheng, J.-L. Liu, R. Tarasenko, M. Orendáč, J. Prokleska, V. Sechovský and M.-L. Tong, *J. Mater. Chem. A*, 2014, **2**, 9851-9858.

S2. G. Lorusso, J. W. Sharples, E. Palacios, O. Roubeau, E. K. Brechin, R. Sessoli, A. Rossin, F. Tuna, E. J. L. McInnes, D. Collison and M. Evangelisti, *Adv. Mater.*, 2013, **25**, 4653-4656.

S3. Y.-L. Hou, G. Xiong, P.-F. Shi, R.-R. Cheng, J.-Z. Cui and B. Zhao, *Chem. Commun*., 2013, **49**, 6066-6068.

S4. S.-D. Han, X.-H. Miao, S.-J. Liu and X.-H. Bu, *Chem. Asian J*., 2014, **9**, 3116-3120.

S5. S.-D. Han, X.-H. Miao, S.-J. Liu and X.-H. Bu, *Inorg. Chem. Front.*, 2014, **1**, 549-552.

S6. Y.-C. Chen, F.-S. Guo, Y.-Z. Zheng, J.-L. Liu, J.-D. Leng, R. Tarasenko, M. Orendáč, J. Prokleška, V. Sechovský and M. L. Tong, *Chem. Eur. J*., 2013, **19**, 13504-13510.

S7. S. Biswas, H. S. Jena, A. Adhikary and S. Konar, *Inorg. Chem*., 2014, **53**, 3926-3928.

S8. R. Sibille, T. Mazet, B. Malaman and M. Francois, *Chem. Eur. J*., 2012, **18**, 12970-12973.

S9. S.-J. Liu, C.-C. Xie, J.-M. Jia, J.-P. Zhao, S.-D. Han, Y. Cui, Y. Li and X.-H. Bu, *Chem. Asian J*., 2014, **9**, 1116-1122.

S10. G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau and M. Evangelisti, *Chem. Commun*., 2012, **48**, 7592-7594.

S11. F.-S. Guo, J.-D. Leng, J. L. Liu, Z. S. Meng and M. L. Tong, *Inorg. Chem*., 2012, **51**, 405-413.

S12. S. Biswas, A. Adhikary, S. Goswami and S. Konar, *Dalton Trans*., 2013, **42**, 13331-13334.

S13. J.-M. Jia, S.-J. Liu, Y. Cui, S.-D. Han, T.-L. Hu and X.-H. Bu, *Cryst. Growth Des*., 2013, **13**, 4631- 4634.

S14. M. Wu, F. Jiang, X. Kong, D. Yuan, L. Long, S. A. Al-Thabaiti and M. Hong, *Chem. Sci*., 2013, **4**, 3104-3109.

Table S2. Selected bond lengths (Å) and angles (°) for **1**[a]

Gd1—O6	2.260(10)	Gd1—O1W	2.437(9)
Gd1—O6$^{\#1}$	2.284(9)	Gd1—O4	2.439(7)
Gd1—O2$^{\#2}$	2.377(9)	Gd1—O3	2.508(7)
Gd1—O1	2.416(8)	Gd1—O2W	2.520(8)
O6—Gd1—O6$^{\#1}$	66.2(3)	O2$^{\#2}$—Gd1—O4	78.3(3)
O6—Gd1—O2$^{\#2}$	83.0(4)	O1—Gd1—O4	126.6(2)
O6$^{\#1}$—Gd1—O2$^{\#2}$	115.5(4)	O1W—Gd1—O4	80.2(3)
O6—Gd1—O1	91.6(4)	O6—Gd1—O3	138.0(3)
O6$^{\#1}$—Gd1—O1	87.5(4)	O6$^{\#1}$—Gd1—O3	78.7(3)
O2$^{\#2}$—Gd1—O1	151.1(3)	O2$^{\#2}$—Gd1—O3	134.9(3)
O6—Gd1—O1W	145.7(3)	O1—Gd1—O3	63.6(2)
O6$^{\#1}$—Gd1—O1W	148.1(3)	O1W—Gd1—O3	71.6(3)
O2$^{\#2}$—Gd1—O1W	79.6(3)	O4—Gd1—O3	63.4(2)
O1—Gd1—O1W	89.7(3)	O6—Gd1—O2W	75.7(3)
O6—Gd1—O4	124.6(3)	O6$^{\#1}$—Gd1—O2W	138.2(3)
O6$^{\#1}$—Gd1—O4	76.1(3)	O2$^{\#2}$—Gd1—O2W	74.4(3)
O4—Gd1—O2W	143.4(3)	O1—Gd1—O2W	76.7(3)
O3—Gd1—O2W	124.6(3)	O1W—Gd1—O2W	71.3(3)

[a]Symmetry code: #1: −x+2, −y, −z+2; #2: x, y−1, z.

Table S3. Selected bond lengths (Å) and angles (°) for **2**[a]

Gd1—O1$^{\#1}$	2.352(3)	Gd1—O3	2.443(3)
Gd1—O2	2.474(3)	Gd1—O1W	2.472(3)
C2—O1—Gd1$^{\#1}$	156.1(3)	O1$^{\#2}$—Gd1—O2$^{\#3}$	107.32(11)
O1$^{\#2}$—Gd1—O1$^{\#1}$	144.99(14)	O1$^{\#1}$—Gd1—O2$^{\#3}$	83.81(11)
O1$^{\#2}$—Gd1—O3$^{\#3}$	140.53(9)	O3$^{\#3}$—Gd1—O2$^{\#3}$	70.71(10)
O1$^{\#1}$—Gd1—O3$^{\#3}$	74.40(9)	O3—Gd1—O2$^{\#3}$	78.62(10)
O1$^{\#2}$—Gd1—O3	74.40(9)	O1W$^{\#3}$—Gd1—O2$^{\#3}$	72.80(10)
O1$^{\#1}$—Gd1—O3	140.53(9)	O1W—Gd1—O2$^{\#3}$	143.61(10)
O3$^{\#3}$—Gd1—O3	66.50(12)	O2—Gd1—O2$^{\#3}$	143.22(14)
O1$^{\#2}$—Gd1—O1W$^{\#3}$	77.21(11)	O1$^{\#2}$—Gd1—O1W	74.68(11)
O1$^{\#1}$—Gd1—O1W$^{\#3}$	74.68(11)	O1$^{\#1}$—Gd1—O1W	77.21(11)
O3$^{\#3}$—Gd1—O1W$^{\#3}$	133.97(10)	O3$^{\#3}$—Gd1—O1W	130.96(10)
O3—Gd1—O1W$^{\#3}$	130.96(10)	O3—Gd1—O1W	133.97(10)
O3$^{\#3}$—Gd1—O2	78.62(10)	O1W$^{\#3}$—Gd1—O1W	72.37(14)
O3—Gd1—O2	70.71(10)	O1$^{\#2}$—Gd1—O2	83.81(11)
O1W$^{\#3}$—Gd1—O2	143.61(10)	O1$^{\#1}$—Gd1—O2	107.32(11)
O1W—Gd1—O2	72.80(10)		

[a]Symmetry code: #1: −x+3/2, −y+1/2, −z+1; #2: x−1/4, y−1/4, −z+1; #3: −x+5/4, −y+1/4, z.

Table S4. Hydrogen-Bonding Geometry (Å, °) for **1**

D–H···A	**D–H**	**H···A**	**D···A**	**D–H···A**
O1W–H1WA···O5	0.87	2.09	2.760(12)	133
O1W–H1WB···O5	0.87	1.89	2.699(12)	154
O2W --H2WB···O4	0.87	2.36	3.119(14)	146
O6–H6···O1	0.85(11)	2.47(10)	3.285(13)	162(12)
C2–H2A···O4	0.97	0.97	3.159(14)	131

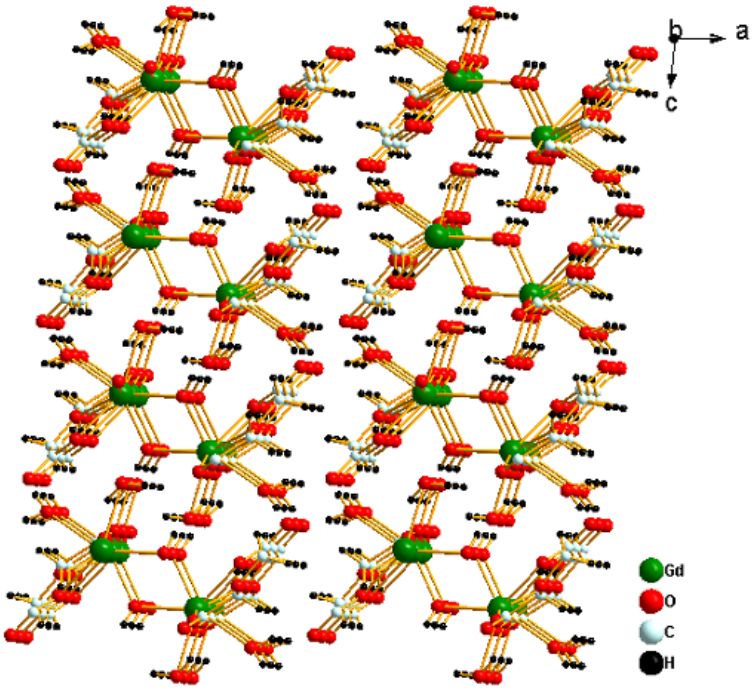


Fig. S1. View of the 3D packing structure of **1**.

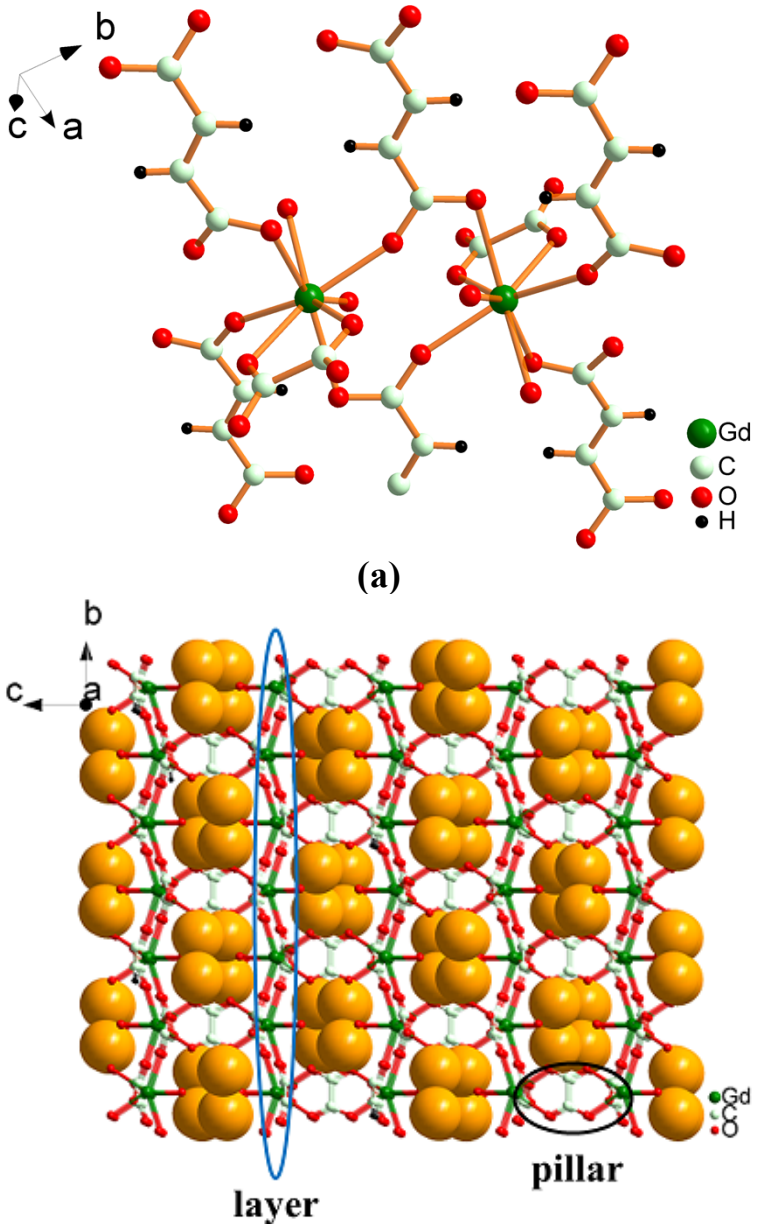
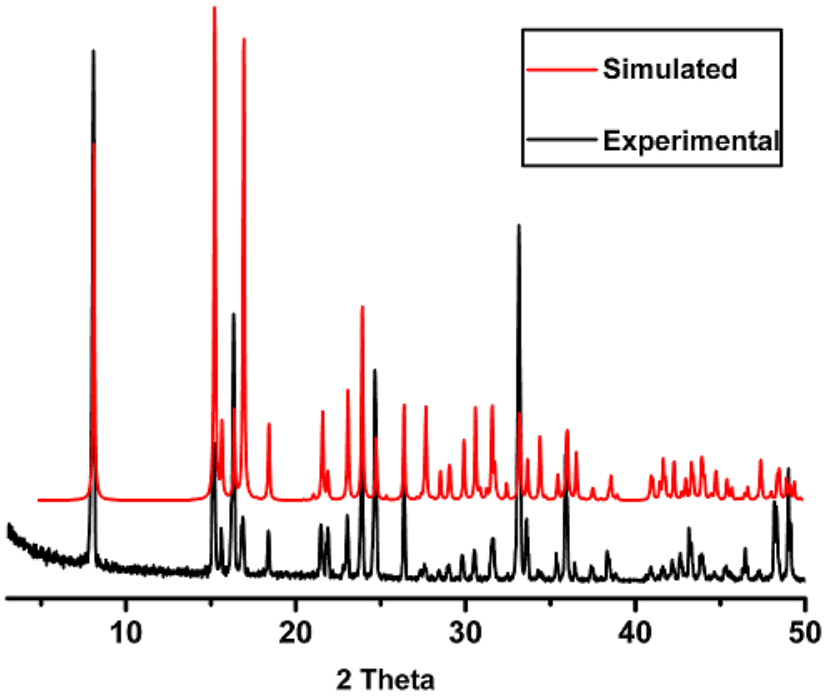
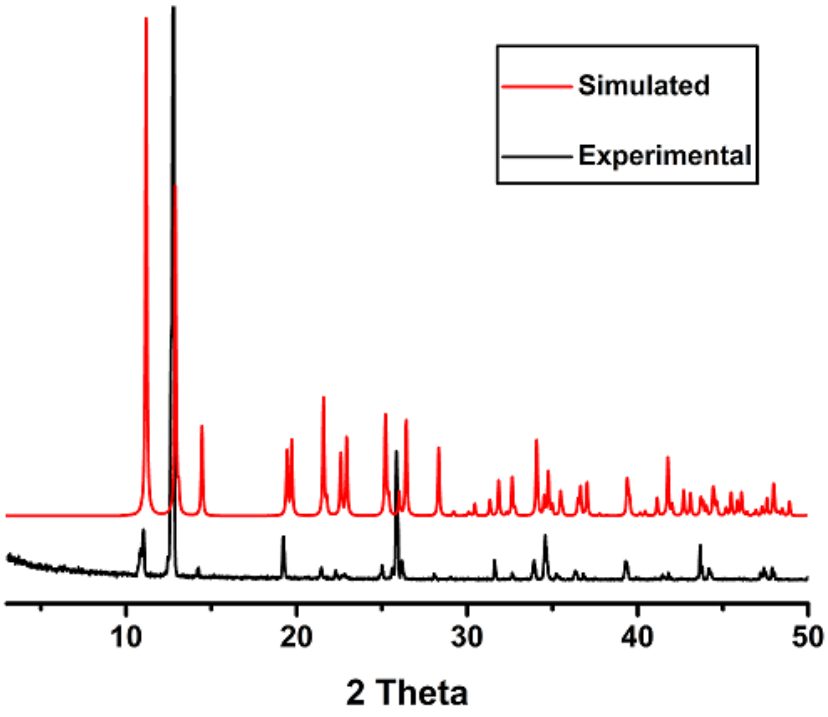


Fig. S2. (a) The coordination environment of Gd^{III} ions in **2**; (b) the 3D pillar-layer structure of **2**.

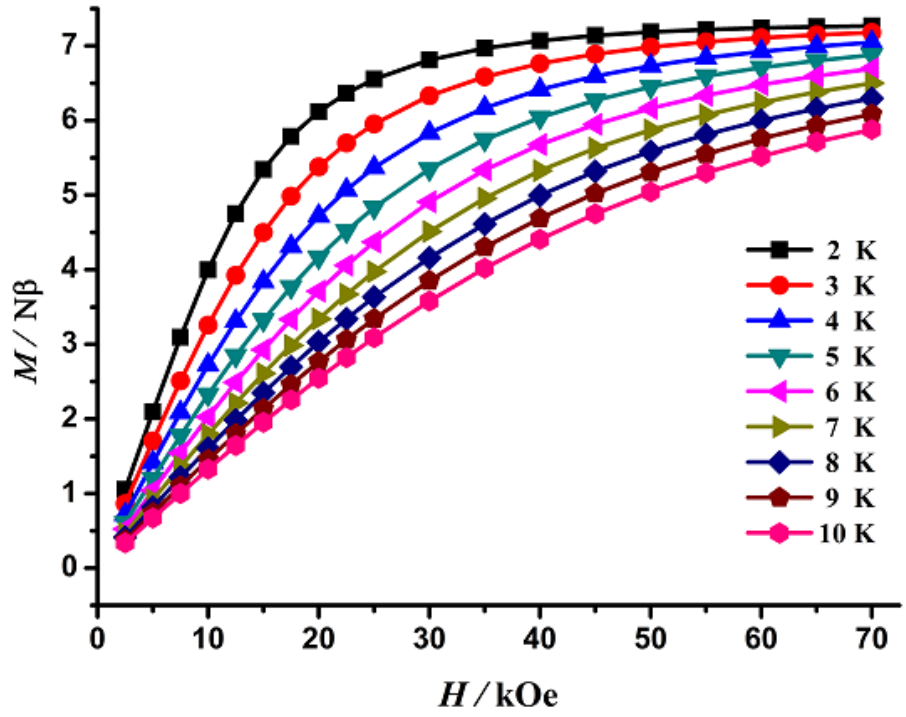


(a)

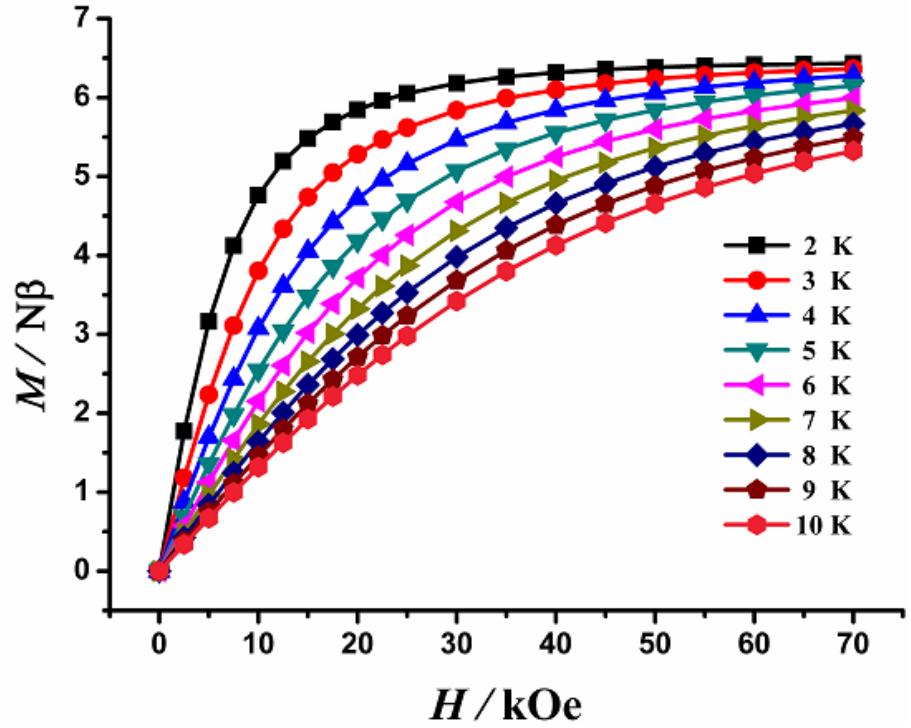


(b)

Fig. S3. PXRD patterns of **1** (a) and **2** (b).

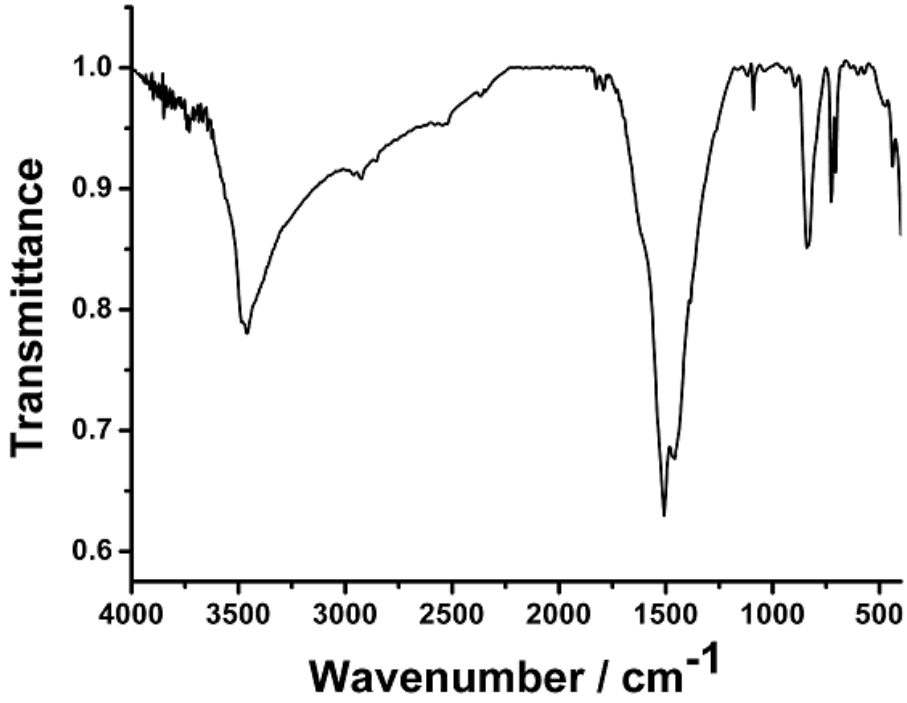


(a)

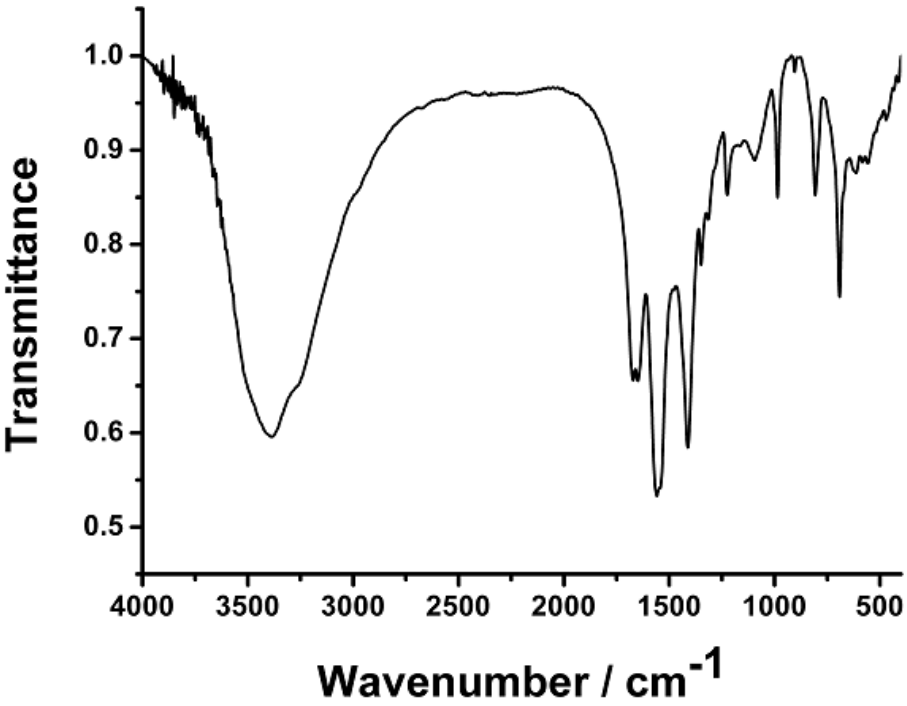


(b)

Fig. S4. The *M vs. H* curves of **1** (a) and **2** (b) at T = 2–10 K and H = 2.5–70 kOe



(a)



(b)

Fig. S5. IR spectra of **1** (a) and **2** (b).