Electronic supplementary information (ESI)

Large magnetocaloric effect in two hybrid Gd-complexes: the synergy of inorganic and organic ligands towards excellent cryo-magnetic coolants

Jin-Hua Li, Ai-Ju Liu, Yu-Juan Ma, Song-De Han*, Ji-Xiang Hu and Guo-Ming Wang*

College of Chemistry and Chemical Engineering, Qingdao University, Shandong 266071, P. R. China.

*Author to whom correspondence should be addressed. E-mail: hansongde@yeah.net; gmwang_pub@163.com

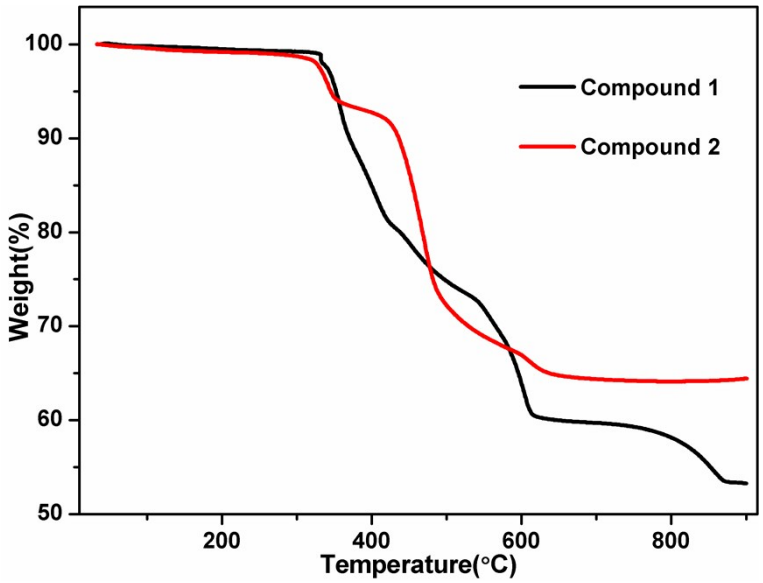

Fig. S1 TG plot of **1** and **2**.

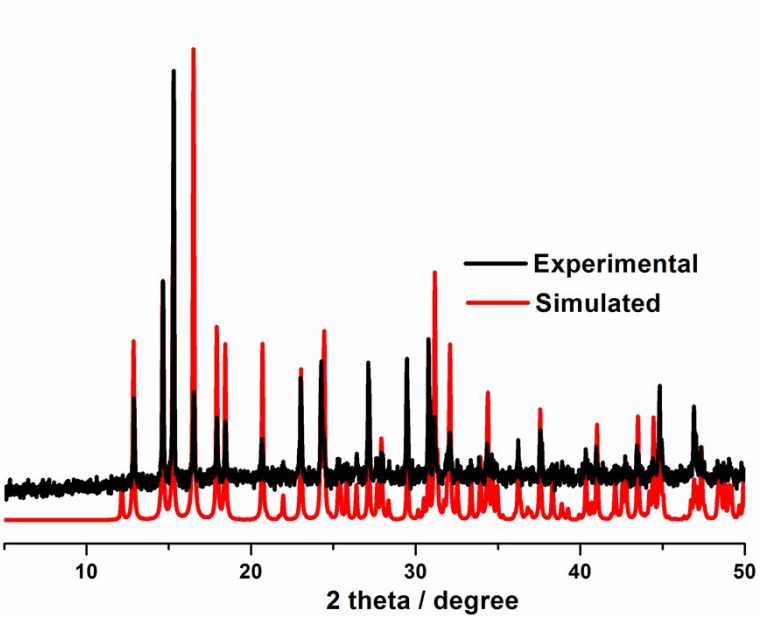

Fig. S2 PXRD plot of **1**.

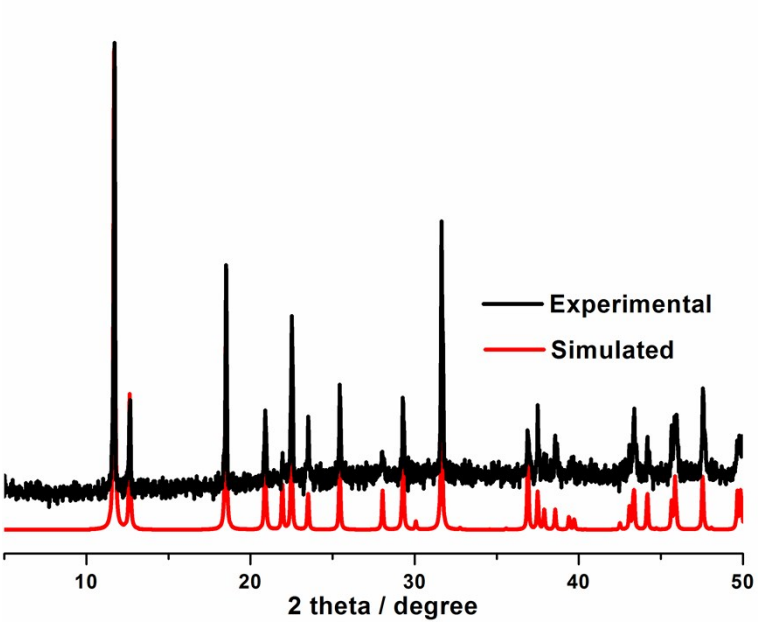

Fig. S3 PXRD plot of **2**.

Table S1. Selected bond lengths (Å) and angles (°) for **1**

C(1)-O(4)	1.239(7)	Gd(1)-O(9)	2.416(4)
C(1)-O(3)	1.246(7)	Gd(1)-O(3)	2.426(4)
C(1)-C(2)	1.538(9)	Gd(1)-O(4)#3	2.428(4)
C(2)-O(2)	1.246(7)	Gd(1)-O(1)	2.438(4)
C(2)-O(1)	1.256(7)	O(5)-S(1)	1.468(5)
Gd(1)-O(7)#1	2.338(4)	O(6)-S(1)	1.452(5)
Gd(1)-O(5)	2.345(5)	O(7)-S(1)	1.478(4)
Gd(1)-O(8)#2	2.353(5)	O(8)-S(1)	1.462(5)
Gd(1)-O(2)#3	2.414(4)		
O(7)#1-Gd(1)-O(5)	79.24(15)	O(9)-Gd(1)-O(3)	82.85(16)
O(7)#1-Gd(1)-O(8)#2	75.87(15)	O(7)#1-Gd(1)-O(4)#3	89.49(15)
O(5)-Gd(1)-O(8)#2	130.76(19)	O(5)-Gd(1)-O(4)#3	75.88(17)
O(7)#1-Gd(1)-O(2)#3	84.52(15)	O(8)#2-Gd(1)-O(4)#3	144.32(15)
O(5)-Gd(1)-O(2)#3	139.71(16)	O(2)#3-Gd(1)-O(4)#3	67.29(13)
O(8)#2-Gd(1)-O(2)#3	78.89(16)	O(9)-Gd(1)-O(4)#3	144.88(15)
O(7)#1-Gd(1)-O(9)	100.68(15)	O(3)-Gd(1)-O(4)#3	106.74(15)
O(5)-Gd(1)-O(9)	73.23(17)	O(7)#1-Gd(1)-O(1)	147.71(15)
O(8)#2-Gd(1)-O(9)	70.63(16)	O(5)-Gd(1)-O(1)	70.74(15)
O(2)#3-Gd(1)-O(9)	146.54(15)	O(8)#2-Gd(1)-O(1)	133.60(14)
O(7)#1-Gd(1)-O(3)	146.59(16)	O(2)#3-Gd(1)-O(1)	110.90(14)
O(5)-Gd(1)-O(3)	132.45(15)	O(9)-Gd(1)-O(1)	82.13(15)
O(8)#2-Gd(1)-O(3)	74.09(15)	O(3)-Gd(1)-O(1)	65.63(14)
O(2)#3-Gd(1)-O(3)	75.69(15)	O(4)#3-Gd(1)-O(1)	72.16(14)

Symmetry codes: #1: -x, -y+1, -z+2; #2: x+1, y, z; #3: -x+1/2, y+1/2, -z+3/2; #4: -x+1/2, y-1/2, -z+3/2; #5: x-1, y, z.

Table S2. Selected bond lengths (Å) and angles (°) for **2**

Gd(1)-O(1)#1	2.416(5)	Gd(1)-O(2)#1	2.467(3)
Gd(1)-O(1)	2.416(5)	Gd(1)-O(2)#4 Gd(1)-	2.467(3)
Gd(1)-O(4)	2.422(9)	O(2)#5	2.467(3)
Gd(1)-O(3)#2	2.431(3)	O(1)-C(1)	1.252(8)
Gd(1)-O(3)#1	2.431(3)	O(2)-C(2)	1.28(2)
Gd(1)-O(3)#3	2.431(3)	O(3)-C(2)	1.266(9)
Gd(1)-O(3)	2.431(3)	O(3)-C(2)#6	1.266(9)
Gd(1)-O(2)	2.467(3)	C(1)-C(1)#7	1.53(2)
O(1)#1-Gd(1)-O(1)	66.9(3)	O(3)#3-Gd(1)-O(2)	113.6(3)
O(1)#1-Gd(1)-O(4)	146.56(13)	O(3)-Gd(1)-O(2)	52.4(3)
O(1)-Gd(1)-O(4)	146.56(13)	O(1)#1-Gd(1)-O(2)#1	76.5(3)
O(1)#1-Gd(1)-O(3)#2	77.01(11)	O(1)-Gd(1)-O(2)#1	88.1(3)
O(1)-Gd(1)-O(3)#2	132.00(11)	O(4)-Gd(1)-O(2)#1	99.2(3)
O(4)-Gd(1)-O(3)#2	74.56(2)	O(3)#2-Gd(1)-O(2)#1	113.6(3)
O(1)#1-Gd(1)-O(3)#1	77.01(11)	O(3)#1-Gd(1)-O(2)#1	52.4(3)
O(1)-Gd(1)-O(3)#1	132.00(11)	O(3)#3-Gd(1)-O(2)#1	134.0(3)
O(4)-Gd(1)-O(3)#1	74.56(2)	O(3)-Gd(1)-O(2)#1	71.6(3)
O(3)#2-Gd(1)-O(3)#1	62.7(2)	O(1)#1-Gd(1)-O(2)#4	76.5(3)
O(1)#1-Gd(1)-O(3)#3	132.01(11)	O(1)-Gd(1)-O(2)#4	88.1(3)
O(1)-Gd(1)-O(3)#3	77.01(11)	O(4)-Gd(1)-O(2)#4	99.2(3)
O(4)-Gd(1)-O(3)#3	74.56(2)	O(3)#2-Gd(1)-O(2)#4	52.4(3)
O(3)#2-Gd(1)-O(3)#3	108.4(2)	O(3)#1-Gd(1)-O(2)#4	113.6(3)
O(3)#1-Gd(1)-O(3)#3	149.12(5)	O(3)#3-Gd(1)-O(2)#4	71.6(3)
O(1)#1-Gd(1)-O(3)	132.01(11)	O(3)-Gd(1)-O(2)#4	134.0(3)
O(1)-Gd(1)-O(3)	77.01(11)	O(2)-Gd(1)-O(2)#4	161.6(6)
O(4)-Gd(1)-O(3)	74.56(2)	O(2)#1-Gd(1)-O(2)#4	152.0(6)
O(3)#2-Gd(1)-O(3)	149.12(5)	O(1)#1-Gd(1)-O(2)#5	88.1(3)
O(3)#1-Gd(1)-O(3)	108.4(2)	O(1)-Gd(1)-O(2)#5	76.5(3)
O(3)#3-Gd(1)-O(3)	62.7(2)	O(4)-Gd(1)-O(2)#5	99.2(3)
O(1)#1-Gd(1)-O(2)	88.1(3)	O(3)#2-Gd(1)-O(2)#5	71.6(3)
O(1)-Gd(1)-O(2)	76.5(3)	O(3)#1-Gd(1)-O(2)#5	134.0(3)
O(4)-Gd(1)-O(2)	99.2(3)	O(3)#3-Gd(1)-O(2)#5	52.4(3)
O(3)#2-Gd(1)-O(2)	134.0(3)	O(3)-Gd(1)-O(2)#5	113.6(3)
O(3)#1-Gd(1)-O(2)	71.6(3)	O(2)#1-Gd(1)-O(2)#5	161.6(6)

Symmetry codes: #1: -x+1, y, z; #2: x+1/2, -y+1/2, -z+1; #3: -x+1/2, -y+1/2, -z+1; #4: -x+1, y, z+1; #5: x, y, z+1; #6: -x+1/2, -y+1/2, -z; #7: -x+1, -y, -z+1; #8: x, y, z-1; #9: x, -y, -z+1.

Table S3. Comparison of $-\Delta S_m^{max}$ (larger than 40.0 J kg^{-1} K^{-1}) between **2** and some selected Gd-complexes fabricated by organic ligands

Complex	D	$-\Delta S_m^{max}$	
		[J kg^{-1} K^{-1}]	[mJ cm^{-3} K^{-1}]
$[Gd(HCOO)_3]$[1]	3D	55.9	216
2 in this work	3D	50.7	165
$[Gd(HCOO)(SO_4)(H_2O)]$[2]	3D	49.9	190
$[Gd(C_2O_4)(H_2O)_3Cl]$[3]	2D	48.0	144
$[Gd(OAc)_3(H_2O)_{0.5}]$[4]	1D	47.7	106
$[Gd_7(CDA)_6(HCOO)_3(\mu_3\text{-}OH)_6(H_2O)_8]_n$[5]	2D	47.3	129
$[Gd(HCOO)(C_8H_4O_4)]$[6]	2D	47.0	125
$[Gd_2(C_2O_4)_3(H_2O)_6\cdot 0.6H_2O]$[7]	2D	46.6	118
$[Gd_{24}(dmc)_{36}(\mu_4\text{-}CO_3)_{18}(\mu_3\text{-}H_2O)_2]\cdot 6H_2O$[8]	0D	46.1	90
$[Gd(HCOO)(OAc)_2(H_2O)_2]$[9]	1D	45.9	110
$[Gd(OAc)_3(MeOH)]$[4]	1D	45.0	97
$[Gd_2(oda)_2(ox)(H_2O)_6]_n$[10]	1D	44.6	120
$[Gd(C_4O_4)(C_2O_4)_{0.5}(H_2O)_2]$[11]	3D	44.0	128
$[Gd(cit)(H_2O)]$[12]	2D	43.6	115
$\{[Gd(OAc)_3(H_2O)_2]\}_2\cdot 4H_2O$[13]	0D	41.6	83
$\{[Gd_2(IDA)_3]\cdot 2H_2O\}$[14]	3D	40.6	101

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

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