

Electronic Supplementary Information (ESI)

Temperature- and vapor-induced reversible single-crystal-to-single-crystal transformations of three 2D/3D Gd^{III}-organic frameworks exhibiting significant magnetocaloric effects

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

Gd1—O1 ^{#2}	2.424(4)	Gd1—O1	2.519(3)
Gd1—O6	2.431(3)	Gd1—O4 ^{#2}	2.544(4)
Gd1—O2W	2.439(4)	Gd1—O2	2.585(4)
Gd1—O5 ^{#1}	2.446(4)	Gd1—O3 ^{#3}	2.650(4)
Gd1—O1W	2.477(4)	Gd1—O4 ^{#3}	2.477(4)
O1 ^{#2} —Gd1—O6	82.51(12)	O2—Gd1—O3 ^{#3}	69.84(12)
O1 ^{#2} —Gd1—O2W	84.50(13)	O4 ^{#3} —Gd1—O1	148.89(12)
O6—Gd1—O2W	138.42(13)	O1 ^{#2} —Gd1—O4 ^{#2}	66.06(12)
O1 ^{#2} —Gd1—O5 ^{#1}	71.85(13)	O6—Gd1—O4 ^{#2}	68.47(12)
O6—Gd1—O5 ^{#1}	66.84(12)	O2W—Gd1—O4 ^{#2}	70.14(13)
O2W—Gd1—O5 ^{#1}	143.32(13)	O5 ^{#1} —Gd1—O4 ^{#2}	121.08(12)
O1 ^{#2} —Gd1—O1W	137.26(13)	O1W—Gd1—O4 ^{#2}	125.54(12)
O6—Gd1—O1W	68.95(13)	O4 ^{#3} —Gd1—O4 ^{#2}	63.26(14)
O2W—Gd1—O1W	137.70(14)	O1—Gd1—O4 ^{#2}	115.54(12)
O5 ^{#1} —Gd1—O1W	67.97(13)	O1 ^{#2} —Gd1—O2	109.46(12)
O1 ^{#2} —Gd1—O4 ^{#3}	129.21(12)	O6—Gd1—O2	132.96(13)
O6—Gd1—O4 ^{#3}	76.52(12)	O2W—Gd1—O2	88.59(14)
O2W—Gd1—O4 ^{#3}	81.75(12)	O5 ^{#1} —Gd1—O2	74.07(13)
O5 ^{#1} —Gd1—O4 ^{#3}	134.93(12)	O1W—Gd1—O2	72.90(13)
O1W—Gd1—O4 ^{#3}	75.11(13)	O4 ^{#3} —Gd1—O2	118.75(12)
O1 ^{#2} —Gd1—O1	61.75(14)	O1—Gd1—O2	50.32(12)
O6—Gd1—O1	133.74(12)	O4 ^{#2} —Gd1—O2	158.41(13)
O2W—Gd1—O1	69.82(12)	O1 ^{#2} —Gd1—O3 ^{#3}	152.66(12)
O5 ^{#1} —Gd1—O1	74.32(12)	O6—Gd1—O3 ^{#3}	118.77(12)
O1W—Gd1—O1	118.23(12)	O2W—Gd1—O3 ^{#3}	68.20(13)
O1—Gd1—O3 ^{#3}	105.22(11)	O5 ^{#1} —Gd1—O3 ^{#3}	130.48(12)
O4 ^{#2} —Gd1—O3 ^{#3}	104.03(12)	O1W—Gd1—O3 ^{#3}	69.74(13)
O4 ^{#3} —Gd1—O3 ^{#3}	50.38(12)		

^aSymmetry codes: #1: $-x+1, -y+1, -z+1$; #2: $-x+1, -y+2, -z+1$; #3: $x+1, y, z$; #4: $x-1, y, z$.

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

Gd1—O1W	2.426(15)	Gd1—O3 ^{#5}	2.499(12)
Gd1—O5	2.451(13)	Gd1—O6 ^{#3}	2.500(14)
Gd1—O1 ^{#4}	2.484(16)	Gd1—O2 ^{#1}	2.514(14)
Gd1—O3 ^{#1}	2.489(13)	Gd1—O2	2.517(12)
Gd1—O1	2.867(15)	Gd1—O4 ^{#5}	2.583(16)
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O1W—Gd1—O5	140.9(5)	O1W—Gd1—O4 ^{#5}	70.4(6)
O1W—Gd1—O1 ^{#4}	134.6(5)	O5—Gd1—O4 ^{#5}	138.8(5)
O5—Gd1—O1 ^{#4}	71.3(5)	O1 ^{#4} —Gd1—O4 ^{#5}	68.4(5)
O1W—Gd1—O3 ^{#1}	71.6(5)	O3 ^{#1} —Gd1—O4 ^{#5}	104.0(5)
O5—Gd1—O3 ^{#1}	111.1(5)	O3 ^{#5} —Gd1—O4 ^{#5}	50.8(4)
O1 ^{#4} —Gd1—O3 ^{#1}	136.9(4)	O6 ^{#3} —Gd1—O4 ^{#5}	111.3(5)
O1W—Gd1—O3 ^{#5}	81.5(4)	O2 ^{#1} —Gd1—O4 ^{#5}	149.2(5)
O5—Gd1—O3 ^{#5}	135.3(4)	O2—Gd1—O4 ^{#5}	107.4(5)
O1 ^{#4} —Gd1—O3 ^{#5}	87.0(4)	O1W—Gd1—O1	82.2(5)
O3 ^{#1} —Gd1—O3 ^{#5}	60.5(5)	O5—Gd1—O1	88.1(5)
O1W—Gd1—O6 ^{#3}	140.1(5)	O1 ^{#4} —Gd1—O1	65.1(5)
O5—Gd1—O6 ^{#3}	64.5(4)	O3 ^{#1} —Gd1—O1	153.7(4)
O1 ^{#4} —Gd1—O6 ^{#3}	74.3(5)	O3 ^{#5} —Gd1—O1	118.1(4)
O3 ^{#1} —Gd1—O6 ^{#3}	69.4(4)	O6 ^{#3} —Gd1—O1	136.8(5)
O3 ^{#5} —Gd1—O6 ^{#3}	72.2(4)	O2 ^{#1} —Gd1—O1	108.1(4)
O1W—Gd1—O2 ^{#1}	78.9(5)	O2—Gd1—O1	48.1(4)
O5—Gd1—O2 ^{#1}	68.4(5)	O4 ^{#5} —Gd1—O1	67.5(4)
O1 ^{#4} —Gd1—O2 ^{#1}	139.4(5)	O5—Gd1—O2	74.0(5)
O3 ^{#1} —Gd1—O2 ^{#1}	65.8(4)	O1 ^{#4} —Gd1—O2	103.8(5)
O3 ^{#5} —Gd1—O2 ^{#1}	126.2(4)	O3 ^{#1} —Gd1—O2	118.5(4)
O6 ^{#3} —Gd1—O2 ^{#1}	92.8(5)	O3 ^{#5} —Gd1—O2	150.5(5)
O1W—Gd1—O2	71.4(5)	O6 ^{#3} —Gd1—O2	136.9(5)
O2 ^{#1} —Gd1—O2	60.1(5)		

^aSymmetry codes: #1: $-x, -y+1, -z+1$; #3: $-x+1, -y+1, -z+2$; #4: $-x+1, -y+1, -z+1$; #5: $x, y-1, z$.

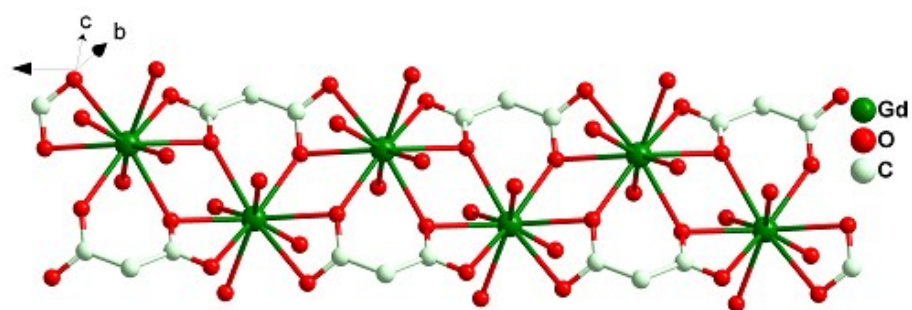
Table S3. Selected bond lengths (Å) and angles (°) for **1b^a**

Gd1—O5	2.305(15)	Gd1—O1 ^{#5}	2.451(16)
Gd1—O6 ^{#1}	2.364(16)	Gd1—O2	2.470(15)
Gd1—O3 ^{#4}	2.423(18)	Gd1—O2 ^{#3}	2.472(16)
Gd1—O4 ^{#4}	2.517(17)	Gd1—O4 ^{#3}	2.492(17)
Gd1—O1	2.664(15)		
O5—Gd1—O6 ^{#1}	68.8(5)	O3 ^{#4} —Gd1—O4 ^{#4}	52.6(5)
O5—Gd1—O3 ^{#4}	131.5(5)	O1 ^{#5} —Gd1—O4 ^{#4}	75.7(5)
O6 ^{#1} —Gd1—O3 ^{#4}	142.7(6)	O2—Gd1—O4 ^{#4}	134.9(5)
O5—Gd1—O1 ^{#5}	79.4(5)	O2 ^{#3} —Gd1—O4 ^{#4}	128.6(5)
O6 ^{#1} —Gd1—O1 ^{#5}	77.6(6)	O4 ^{#3} —Gd1—O4 ^{#4}	64.6(6)
O3 ^{#4} —Gd1—O1 ^{#5}	77.2(5)	O5—Gd1—O1	131.3(5)
O5—Gd1—O2	143.1(5)	O6 ^{#1} —Gd1—O1	72.8(5)
O6 ^{#1} —Gd1—O2	80.4(5)	O3 ^{#4} —Gd1—O1	71.5(5)
O3 ^{#4} —Gd1—O2	85.4(5)	O1 ^{#5} —Gd1—O1	63.8(5)
O1 ^{#5} —Gd1—O2	114.1(5)	O2—Gd1—O1	50.4(5)
O5—Gd1—O2 ^{#3}	83.2(5)	O2 ^{#3} —Gd1—O1	110.7(5)
O6 ^{#1} —Gd1—O2 ^{#3}	70.1(6)	O4 ^{#3} —Gd1—O1	144.8(5)
O3 ^{#4} —Gd1—O2 ^{#3}	133.9(5)	O4 ^{#4} —Gd1—O1	116.5(5)
O1 ^{#5} —Gd1—O2 ^{#3}	147.1(5)	O1 ^{#5} —Gd1—O4 ^{#3}	138.9(5)
O2—Gd1—O2 ^{#3}	67.0(6)	O2—Gd1—O4 ^{#3}	101.8(5)
O5—Gd1—O4 ^{#3}	83.8(5)	O2 ^{#3} —Gd1—O4 ^{#3}	65.3(6)
O6 ^{#1} —Gd1—O4 ^{#3}	129.8(6)	O5—Gd1—O4 ^{#4}	80.8(5)
O3 ^{#4} —Gd1—O4 ^{#3}	86.8(6)	O6 ^{#1} —Gd1—O4 ^{#4}	142.5(5)

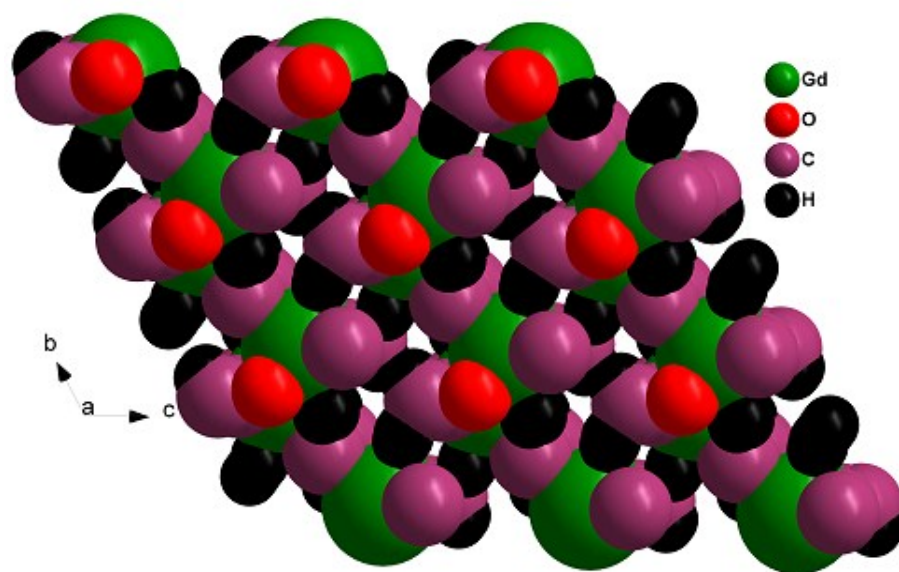
^aSymmetry codes: #1: -x, -y+1, -z+3; #2: x, y+1, z; #3: -x+1, -y+1, -z+2; #4: x, y-1, z; #5: -x, -y+1, -z+2.

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

D–H···A	D–H	H···A	D···A	D–H···A
O2W–H2WA···O5	0.85	2.02	2.8223	157
O2W–H2WB···O6	0.85	2.02	2.8230	157
O1W–H1WB···O3	0.85	1.89	2.7202	166
O1W–H1WA···O2	0.85	2.00	2.7320	143
C2–H2A···O3	0.97	2.60	3.5371	163

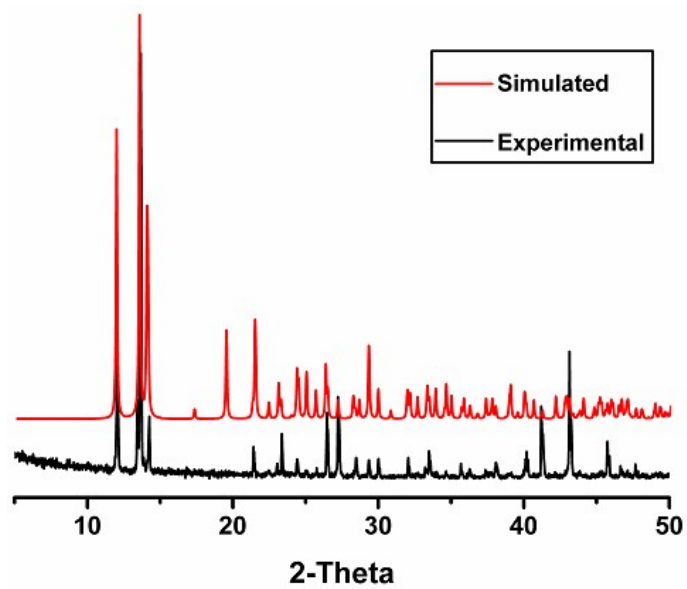


(a)

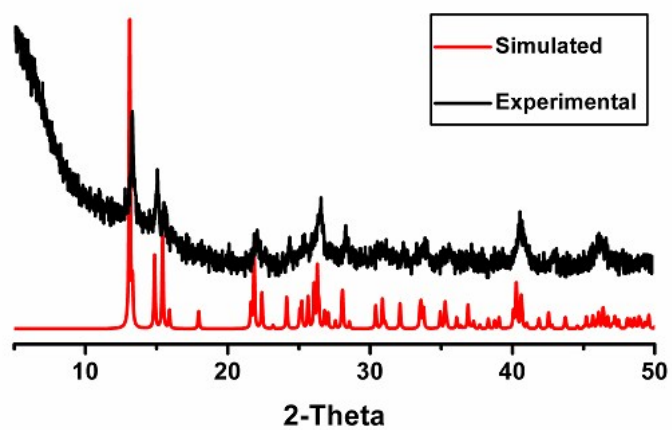


(b)

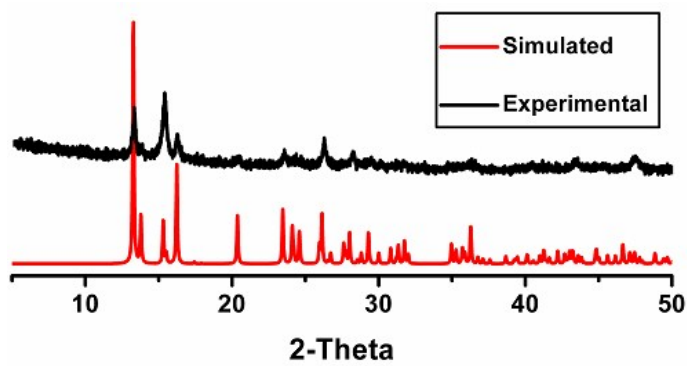
Fig. S1. View of (a) the 1D $[\text{Gd}(\text{pda})]_n$ chain in **1**; (b) the 3D packing structure of **1**.



(a)



(b)



(c)

Fig. S2. XRPD patterns of **1** (a), **1a** (b) and **1b** (c).

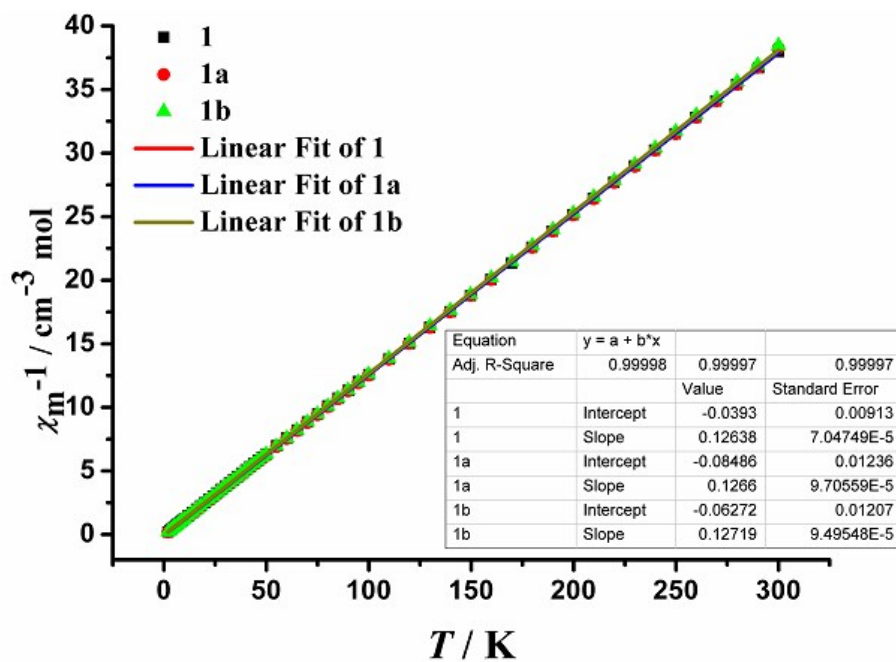


Fig. S3. The plots of χ_m^{-1} vs. T and the corresponding Curie-Weiss fitting curves for **1**, **1a** and **1b**.

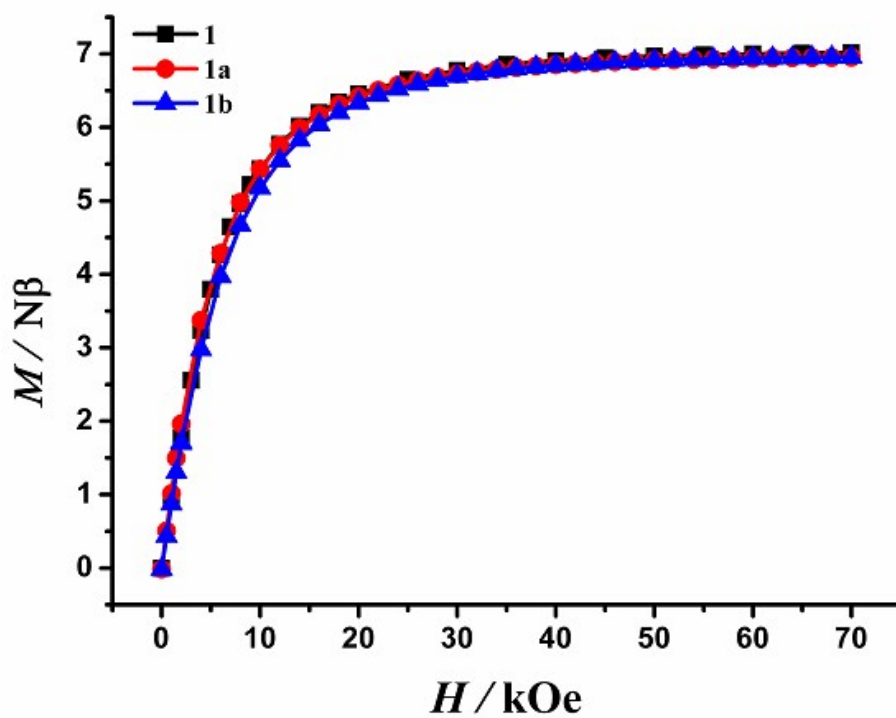
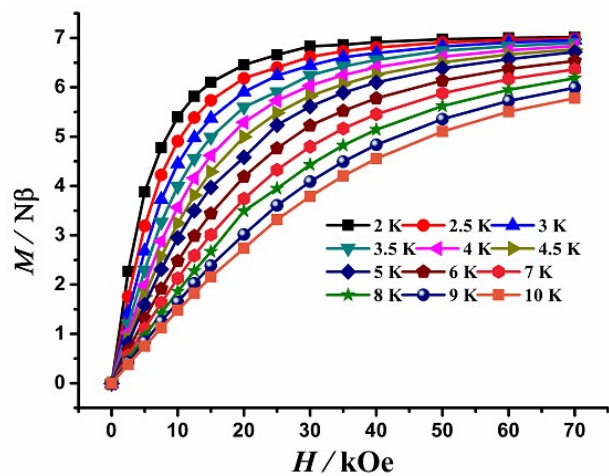
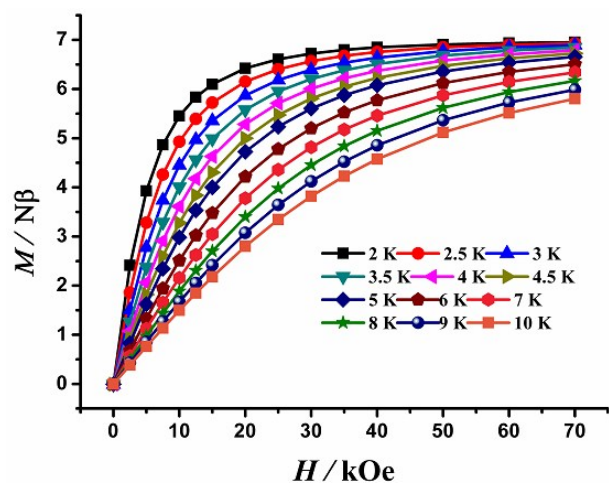


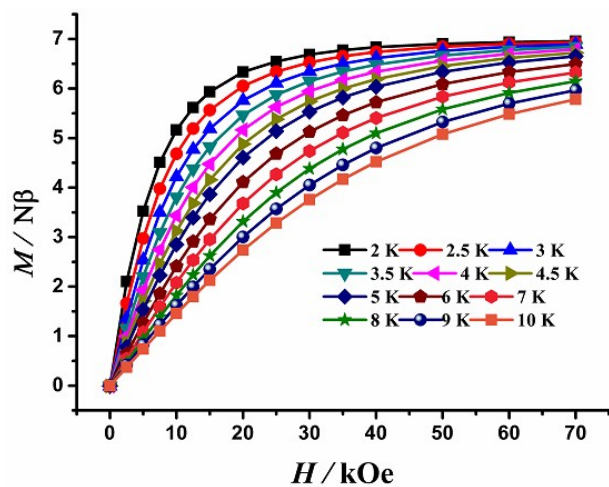
Fig. S4. The M vs. H curves at 2.0 K of **1**, **1a** and **1b**.



(a)



(b)



(c)

Fig. S5. The M vs. H plots of **1** (a), **1a** (b) and **1b** (c) at the indicated temperatures