Electronic Supplementary Information

Solvent-induced formation of two gadolinium clusters demonstrated for strong magnetocaloric effects and ferroelectric properties

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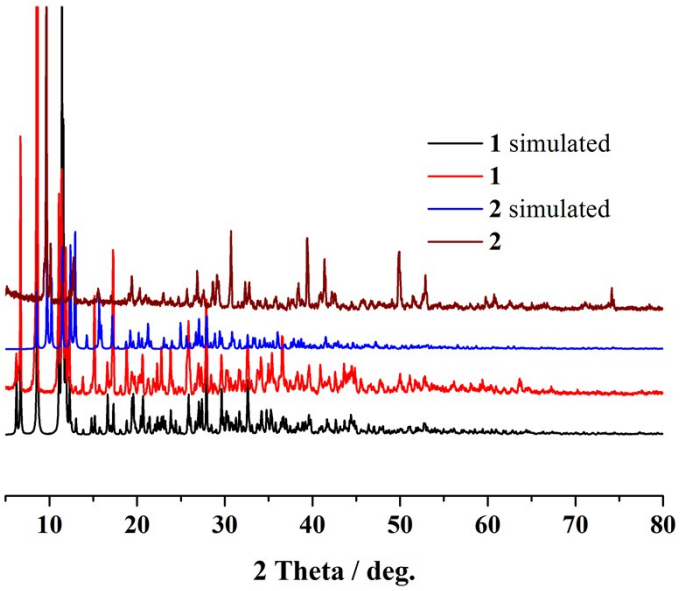

Figure S1. Simulated and experimental powder X-ray diffractions of **1** and **2**.

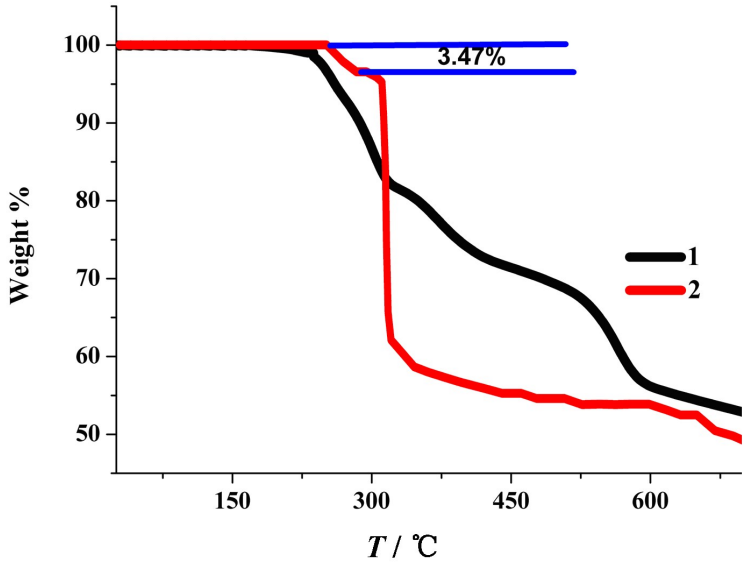

Figure S2. TGA curves of **1** (black) and **2** (red).

Table S1. Single-crystal parameters of **1** and **2_200 K**

	1	**2_200 K**	**2_293 K**	**2_353 K**	**2_383 K**
formula	$C_{20}H_{46}Gd_2N_6O_{14}^{2+}$, $2(NO_3^{1-})$	$C_{22}H_{49}Gd_3N_8O_{21}$	$C_{22}H_{49}Gd_3N_8O_{21}$	$C_{22}H_{49}Gd_3N_8O_{21}$	$C_{22}H_{49}Gd_3N_8O_{21}$
fw	1033.15	1233.42	1233.42	1233.42	1233.42
temp(K)	120(2)	200(2)	293(2)	353(2)	383(2)
Symmetry system	triclinic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
space group	*P*-1	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$
a (Å)	8.8005(8)	28.2783(6)	28.3822(6)	28.4536(7)	28.4960(6)
b (Å)	9.3882(13)	14.9386(3)	14.9641(3)	14.9700(3)	14.9727(3)
c (Å)	10.6360(6)	9.0311(2)	9.0770(2)	9.1074(2)	9.1211(2)
α (deg)	101.502(8)	90	90	90	90
β (deg)	96.239(6)	90	90	90	90
γ (deg)	97.956(9)	90	90	90	90
V (Å^3)	844.37(15)	3815.08(15)	3855.15(16)	3879.32(17)	3891.64(15)
Z	1	4	4	4	4
*D*c (g·cm^{-3})	2.032	2.147	2.125	2.125	2.125
μ (mm^{-1})	3.987	5.245	5.190	5.158	5.141
R_{int}	0.0597	0.0392	0.0409	0.0382	0.0262
GOOF	1.075	0.995	0.983	0.963	0.998
R_1	0.0593	0.0327	0.0360	0.0346	0.296
wR_2	0.1671	0.0538	0.0477	0.0487	0.0536
*Δρ*max (e Å^{-3})	2.0	1.07	0.63	0.7	0.7
*Δρ*min (eÅ^{-3})	-1.9	-0.74	-0.70	-0.5	-0.7
flack		-0.011(15)	-0.022(15)	-0.043(15)	-0.023(13)

Table S2. Continuous-shape measures calculations for the Gd^{3+} ion in **1** and **2**_200K.

1			
Structure [ML_9]	CSAPR-9 (C_{4v})	MFF-9 (C_s)	JCSAPR-9 (C_{4v})
Gd^{3+}in **1**	2.338	2.704	2.745
2_200K			
Structure [ML_9]	CSAPR-9 (C_{4v})	TCTPR-9 (D_{3h})	MFF-9 (C_s)
$Gd(1)^{3+}$ in **2**_200K	2.495	2.759	2.793
Structure [ML_8]	SAPR-8 (D_{4d})	TDD-8 (D_{2d})	BTPR-8 (C_{2v})
$Gd(2)^{3+}$ in **2**_200K	3.614	2.759	4.137
Structure [ML_9]	CSAPR-9 (C_{4v})	MFF-9 (C_s)	JCSAPR-9 (C_{4v})
$Gd(3)^{3+}$ in **2**_200K	2.551	2.798	3.222

CSAPR-9 = Spherical capped square antiprism, SAPR-8 = Square antiprism, MFF-9 = Muffin, JCSAPR-9 = Capped square antiprism J10, TCTPR-9 = Spherical tricapped trigonal prism, BTPR-8 = Biaugmented trigonal prism, TDD-8 = Triangular dodecahedron

Table S3. Selected bond lengths [Å] and angles [deg.] for **1** and **2**_200 K

1					
Gd(1)-O(2)#1	2.311(8)	Gd(1)-O(1)	2.382(9)	Gd(1)-N(2)	2.697(11)
Gd(1)-O(2)	2.345(9)	Gd(1)-O(4)	2.574(10)	Gd(1)-N(3)	2.921(12)
Gd(1)-O(3)	2.470(9)	Gd(1)-O(6)	2.499(9)	Gd(1)-Gd(1)#1	3.8572(12)
Gd(1)-O(5)	2.439(9)	Gd(1)-N(1)	2.641(10)		

O(2)#1-Gd(1)-O(2)	68.1(3)	O(2)-Gd(1)-O(3)	73.3(3)	O(3)-Gd(1)-O(6)	117.7(3)
O(2)#1-Gd(1)-O(1)	95.2(3)	O(1)-Gd(1)-O(3)	166.6(3)	O(2)#1-Gd(1)-O(4)	75.8(3)
O(2)-Gd(1)-O(1)	93.5(3)	O(5)-Gd(1)-O(3)	72.8(3)	O(2)-Gd(1)-O(4)	139.3(3)
O(2)#1-Gd(1)-O(5)	84.5(3)	O(2)#1-Gd(1)-O(6)	140.4(3)	O(1)-Gd(1)-O(4)	71.2(3)
O(2)-Gd(1)-O(5)	138.8(3)	O(2)-Gd(1)-O(6)	147.7(3)	O(5)-Gd(1)-O(4)	50.6(3)
O(1)-Gd(1)-O(5)	120.0(3)	O(1)-Gd(1)-O(6)	72.8(3)	O(3)-Gd(1)-O(4)	120.0(3)
O(2)#1-Gd(1)-O(3)	81.5(3)	O(5)-Gd(1)-O(6)	70.8(3)	O(6)-Gd(1)-O(4)	64.6(3)
O(2)#1-Gd(1)-N(1)	130.4(3)	O(6)-Gd(1)-N(3)	63.0(3)	O(1)-Gd(1)-N(2)	117.7(3)
O(2)-Gd(1)-N(1)	68.3(3)	O(4)-Gd(1)-N(3)	25.4(4)	O(5)-Gd(1)-N(2)	82.0(3)
O(1)-Gd(1)-N(1)	65.0(3)	N(1)-Gd(1)-N(3)	141.6(3)	O(3)-Gd(1)-N(2)	65.7(3)
O(5)-Gd(1)-N(1)	145.2(3)	N(2)-Gd(1)-N(3)	98.1(3)	O(6)-Gd(1)-N(2)	60.7(3)
O(3)-Gd(1)-N(1)	107.3(3)	O(2)#1-Gd(1)-N(3)	81.3(3)	O(4)-Gd(1)-N(2)	116.3(3)
O(6)-Gd(1)-N(1)	79.4(3)	O(2)-Gd(1)-N(3)	148.9(3)	N(1)-Gd(1)-N(2)	67.6(3)
O(4)-Gd(1)-N(1)	129.6(3)	O(1)-Gd(1)-N(3)	95.1(4)	O(3)-Gd(1)-N(3)	97.3(4)
O(2)#1-Gd(1)-N(2)	146.9(3)	O(5)-Gd(1)-N(3)	25.4(4)	O(2)-Gd(1)-N(2)	104.2(3)

2					
Gd(1)-Gd(2)	3.5290(7)	Gd(1)-O(16)	2.470(8)	Gd(2)-O(13)	2.531(8)
Gd(1)-Gd(3)	3.9255(7)	Gd(2)-Gd(3)	3.5600(7)	Gd(3)-N(3)	2.680(7)
Gd(1)-N(1)	2.584(9)	Gd(2)-N(5)	2.879(11)	Gd(3)-N(4)	2.601(9)
Gd(1)-N(2)	2.667(8)	Gd(2)-N(6)	2.934(11)	Gd(3)-N(8)	2.969(11)
Gd(1)-N(7)	2.921(11)	Gd(2)-O(1)	2.377(7)	Gd(3)-O(1)	2.503(7)
Gd(1)-O(1)	2.486(6)	Gd(2)-O(2)	2.455(7)	Gd(3)-O(2)	2.420(6)
Gd(1)-O(2)	2.417(7)	Gd(2)-O(3)	2.231(6)	Gd(3)-O(4)	2.307(7)

Gd(1)-O(3)	2.312(7)	Gd(2)-O(4)	2.245(6)	Gd(3)-O(7)	2.325(7)
Gd(1)-O(5)	2.530(7)	Gd(2)-O(9)	2.466(8)	Gd(3)-O(8)	2.476(7)
Gd(1)-O(6)	2.322(7)	Gd(2)-O(10)	2.471(8)	Gd(3)-O(18)	2.538(8)
Gd(1)-O(15)	2.550(8)	Gd(2)-O(12)	2.451(9)	Gd(3)-O(19)	2.596(8)
Gd(2)-Gd(1)-Gd(3)	56.754(13)	O(1)-Gd(2)-Gd(1)	44.72(15)	O(3)-Gd(2)-Gd(1)	39.87(17)
O(1)-Gd(1)-Gd(2)	42.27(17)	O(1)-Gd(2)-Gd(3)	44.56(17)	O(3)-Gd(2)-Gd(3)	106.35(17)
O(1)-Gd(1)-Gd(3)	38.27(17)	O(1)-Gd(2)-O(2)	59.8(2)	O(3)-Gd(2)-O(1)	79.7(2)
O(2)-Gd(1)-Gd(2)	44.01(16)	O(2)-Gd(2)-Gd(1)	43.17(15)	O(3)-Gd(2)-O(2)	71.6(2)
O(2)-Gd(1)-Gd(3)	35.78(16)	O(2)-Gd(2)-Gd(3)	42.71(15)	Gd(2)-Gd(3)-Gd(1)	55.999(13)
O(2)-Gd(1)-O(1)	58.8(2)	O(2)-Gd(3)-Gd(2)	43.47(16)	O(1)-Gd(3)-Gd(1)	37.97(14)
Gd(2)-O(3)-Gd(1)	101.9(2)	O(2)-Gd(3)-O(1)	58.5(2)	O(1)-Gd(3)-Gd(2)	41.78(17)
O(2)-Gd(3)-Gd(1)	35.74(17)				

[a]Symmetry transformations used to generate equivalent atoms: #1 −*x* + 1, −y, −z + 1