Supporting Information

Mixed-anion templated cage-like Lanthanide clusters: Gd_{27} and Dy_{27}

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Table S1 Crystal data and details of data collection and refinement for complexes **1** and **2**.

Complex	**Gd_{27} (1)**	**Dy_{27} (2)**
formula	$C_{68}H_{310}Cl_{13}Gd_{27}O_{247}$	$C_{68}H_{310}Cl_{13}Dy_{27}O_{247}$
Formula weight	9787.76	9929.51
Temperature/K	123(2)	123(2)
Crystal system	triclinic	triclinic
Space group	P_{-1}	P_{-1}
a /Å	19.0866(5)	19.0141(5)
b /Å	20.1645(4)	20.0313(5)
c /Å	32.8057(7)	32.3892(9)
α/°	77.642(2)	77.671(2)
β/°	74.776(2)	74.878(2)
γ/°	69.343(2)	69.207(2)
V/Å^3	11296.2(4)	11033.1(5)
Z	2	2
Dc/g cm^{-3}	2.878	2.989
μ/mm^{-1}	8.107	9.329
Data/parameters	39691/2425	38832/2359
θ/°	2.9 – 25.00	2.9 – 25.00
Observed reflections	135113	87377
F (000)	9286.0	9394.0
GOF	1.016	0.954
$R_1[I > 2\sigma(I)]^a$	0.0647	0.0732
wR_2(All data)^b	0.1585	0.1943

^{a} $R_1 = \sum | |Fo| - |Fc| | / \sum |Fo|$ ^{b} $wR_2 = \{\sum [w (Fo^2 – Fc^2)^2] / \sum [w(Fo^2)^2]\}^{1/}$

Table S2. Selected bonds of **1**.

Gd1-O71	2.334(12)	Gd15-O78	2.363(7)
Gd1-O6	2.366(6)	Gd16-O2	2.306(7)
Gd2-O20	2.361(8)	Gd16-O86	2.365(8)
Gd2-O21	2.396(7)	Gd17-O39	2.327(8)
Gd3-O91	2.248(7)	Gd17-O90	2.379(8)
Gd3-O21	2.333(7)	Gd18-O33	2.339(9)
Gd4-O27	2.325(6)	Gd18-O51	2.344(8)
Gd4-O43	2.337(7)	Gd19-O46	2.296(7)
Gd5-O83	2.328(7)	Gd19-O16	2.354(7)
Gd5-O89	2.367(9)	Gd20-O11	2.359(7)
Gd6-O66	2.311(6)	Gd20-O7	2.369(7)
Gd6-O10	2.328(6)	Gd21-O56	2.315(7)
Gd7-O35	2.342(6)	Gd21-O26	2.362(6)
Gd7-O37	2.349(6)	Gd22-O44	2.343(7)
Gd8-O65	2.336(7)	Gd22-O2	2.371(7)
Gd8-O60	2.369(7)	Gd23-O31	2.354(8)
Gd9-O50	2.318(6)	Gd23-O24	2.373(7)
Gd9-O11	2.367(7)	Gd24-O49	2.297(11)
Gd10-O28	2.347(7)	Gd24-O4	2.373(7)
Gd10-O1	2.362(7)	Gd25-O92	2.353(8)
Gd11-O81	2.348(7)	Gd25-O32	2.366(7)
Gd11-O23	2.382(7)	Gd26-O11	2.378(7)
Gd12-O79	2.345(8)	Gd26-O16	2.390(7)
Gd12-O31	2.368(7)	Gd27-O12	2.353(7)
Gd13-O25	2.350(6)	Gd27-O31	2.396(8)
Gd13-O17	2.394(7)	Gd27-O15	2.435(8)
Gd14-O20	2.365(8)	Gd27-O27W	2.445(9)
Gd14-O22	2.416(6)	Gd27-O5W	2.451(13)
Gd15-O87	2.357(7)	Gd27-O7W	2.451(11)

Table S3. Selected bonds of **2**.

Dy1-O4	2.326(9)	Dy15-O78	2.337(10)
Dy1-O6	2.356(10)	Dy16-O2	2.297(9)
Dy2-O1	2.412(9)	Dy16-O86	2.335(10)
Dy2-O18	2.457(10)	Dy17-O39	2.315(12)
Dy3-O18	2.357(10)	Dy17-O2	2.355(9)
Dy3-O21	2.306(9)	Dy18-O33	2.312(12)
Dy4-O3	2.357(8)	Dy18-O14	2.329(10)
Dy4-O9	2.328(9)	Dy19-O46	2.244(9)
Dy5-O6	2.346(10)	Dy19-O16	2.261(11)
Dy5-O8	2.415(10)	Dy20-O24	2.342(10)
Dy6-O4	2.351(9)	Dy20-O11	2.343(10)
Dy6-O6	2.453(9)	Dy21-O56	2.306(10)
Dy7-O1	2.406(9)	Dy21-O26	2.324(9)
Dy7-O5	2.376(9)	Dy22-O44	2.331(8)
Dy8-O3	2.441(9)	Dy22-O2	2.348(11)
Dy8-O5	2.365(9)	Dy23-O31	2.338(12)
Dy9-O7	2.488(9)	Dy23-O24	2.343(10)
Dy9-O11	2.303(10)	Dy24-O29	2.254(15)
Dy10-O1	2.368(8)	Dy24-O53	2.332(12)
Dy10-O22	2.403(10)	Dy25-O29	2.289(11)
Dy11-O23	2.329(8)	Dy25-O92	2.293(10)
Dy11-O57	2.335(10)	Dy26-O11	2.337(10)
Dy12-O79	2.280(10)	Dy26-O3W	2.340(3)
Dy12-O76	2.313(9)	Dy27-O12	2.322(10)
Dy13-O25	2.291(9)	Dy27-O33W	3.25(14)
Dy13-O17	2.363(9)	Dy27-O31	2.341(11)
Dy14-O20	2.276(10)	Dy27-O15	2.354(10)
Dy14-O22	2.379(9)	Dy27-O27W	2.382(12)
Dy15-O87	2.332(10)	Dy27-O77	2.412(17)

Table S4. Selected bond angles of **1**.

O71-Gd1-O6	145.6(3)	O87-Gd15-O3	142.1(3)
O71-Gd1-O4	74.4(3)	O2-Gd16-O86	139.8(3)
O20-Gd2-O21	76.7(2)	O2-Gd16-O13	71.5(2)
O21-Gd2-O1	136.0(2)	O39-Gd17-O90	82.8(3)
O91-Gd3-O21	89.4(3)	O90-Gd17-O2	140.4(3)
O30-Gd3-O18	134.3(2)	O33-Gd18-O51	81.6(4)
O27-Gd4-O43	145.8(2)	O51-Gd18-O14	76.6(3)
O27-Gd4-O9	71.2(2)	O46-Gd19-O16	139.9(3)
O83-Gd5-O89	146.0(3)	O46-Gd19-O42	82.6(2)
O83-Gd5-O6	75.7(2)	O11-Gd20-O7	71.8(3)
O66-Gd6-O10	89.9(2)	O11-Gd20-O24	139.9(3)
O10-Gd6-O38	142.1(2)	O56-Gd21-O26	80.1(2)
O35-Gd7-O37	94.2(2)	O56-Gd21-O12	139.6(2)
O37-Gd7-O47	147.7(2)	O44-Gd22-O2	85.5(2)
O65-Gd8-O60	147.9(3)	O44-Gd22-O29	141.2(3)
O65-Gd8-O27	74.3(2)	O31-Gd23-O24	138.6(2)
O50-Gd9-O11	85.4(2)	O24-Gd23-O26	72.6(3)
O11-Gd9-O61	139.4(3)	O49-Gd24-O4	78.1(4)
O28-Gd10-O1	73.3(2)	O49-Gd24-O53	113.9(5)
O1-Gd10-O22	141.8(2)	O92-Gd25-O32	77.2(3)
O81-Gd11-O23	75.7(2)	O92-Gd25-O13	142.3(2)
O81-Gd11-O57	137.7(2)	O11-Gd26-O16	72.7(3)
O79-Gd12-O31	88.7(3)	O11-Gd26-O4W	140.2(3)
O31-Gd12-O45	139.5(2)	O12-Gd27-O31	73.2(2)
O25-Gd13-O17	161.6(3)	O12-Gd27-O15	68.5(2)
O25-Gd13-O36W	81.1(3)	O31-Gd27-O15	66.6(2)
O20-Gd14-O22	76.5(2)	O12-Gd27-O27W	140.3(3)
O22-Gd14-O21	137.3(3)	O31-Gd27-O27W	86.6(3)
O87-Gd15-O78	97.6(3)	O15-Gd27-O27W	72.2(3)

Table S5. Selected bond angles of **2**.

O71-Dy1-O4	74.9(4)	O87-Dy15-O3	142.5(4)
O71-Dy1-O6	144.9(4)	O2-Dy16-O86	141.4(4)
O21-Dy2-O1	136.7(3)	O86-Dy16-O73	72.6(4)
O21-Dy2-O20	75.0(3)	O39-Dy17-O2	84.5(3)
O91-Dy3-O21	90.8(4)	O2-Dy17-O90	140.7(3)
O91-Dy3-O30	82.8(3)	O33-Dy18-O14	86.5(4)
O27-Dy4-O23	132.1(3)	O33-Dy18-O51	79.8(5)
O27-Dy4-O9	70.6(3)	O46-Dy19-O16	140.9(4)
O10-Dy5-O6	71.1(3)	O46-Dy19-O42	84.1(3)
O10-Dy5-O83	140.8(3)	O24-Dy20-O11	140.2(4)
O66-Dy6-O10	90.4(3)	O24-Dy20-O84	73.7(4)
O66-Dy6-O38	98.4(3)	O56-Dy21-O26	80.9(3)
O35-Dy7-O37	93.9(3)	O26-Dy21-O95	144.5(3)
O37-Dy7-O47	147.0(4)	O44-Dy22-O2	86.9(3)
O65-Dy8-O60	145.7(3)	O44-Dy22-O29	140.4(3)
O65-Dy8-O27	76.2(3)	O31-Dy23-O24	139.3(3)
O50-Dy9-O11	85.7(3)	O24-Dy23-O93	77.5(4)
O50-Dy9-O74	144.7(4)	O49-Dy24-O53	107.2(6)
O28-Dy10-O1	74.2(3)	O53-Dy24-O10	81.2(4)
O1-Dy10-O22	143.1(3)	O29-Dy25-O92	84.5(4)
O23-Dy11-O57	143.0(3)	O29-Dy25-O26W	145.6(6)
O23-Dy11-O81	77.1(3)	O11-Dy26-O3W	146.9(8)
O79-Dy12-O76	145.3(4)	O11-Dy26-O19	68.5(3)
O79-Dy12-O45	97.2(3)	O12-Dy27-O33W	86.5(4)
O25-Dy13-O17	165.3(3)	O12-Dy27-O31	72.4(3)
O25-Dy13-O69	69.3(4)	O33W-Dy27-O31	143.5(5)
O20-Dy14-O22	76.0(3)	O31-Dy27-O15	68.3(4)
O20-Dy14-O21	77.7(3)	O12-Dy27-O27W	142.6(4)
O87-Dy15-O78	94.7(4)	O31-Dy27-O27W	90.1(4)

Table S6 Summary of the reported lanthanide-exclusive cluster-based magnetic coolers

Complex	$-\Delta S_{max}$ (J kg^{-1} K^{-1})	$-\Delta S_{max}$ (mJ cm^{-3} K^{-1})	ΔH (T)
Gd_2[1]	40.6	82.8	7
Gd_4[2]	51.2	198.8	7
Gd_4[3]	51.4	190.4	7
Gd_5[4]	34.0	60.6	7
Gd_7[5]	23.0	41.3	7
Gd_8[5]	32.3	45.1	7
Gd_{10}[6]	37.4	43.0	7
Gd_{10}[7]	31.2	68.8	7
Gd_{24}[8]	46.1	90.0	7
Gd_{27}[This work]	41.8	120.4	**7**
Gd_{38}[9]	37.9	102.0	7
Gd_{48}[9]	43.6	120.7	7
Gd_{104}[10]	46.6	137.2	7

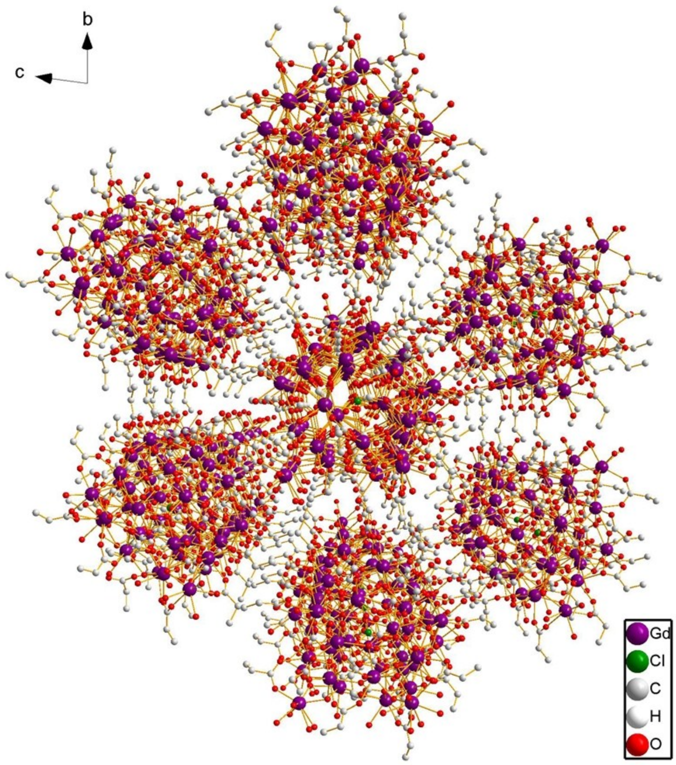

Figure S1. The packing mode of **1** along *a*-axis.

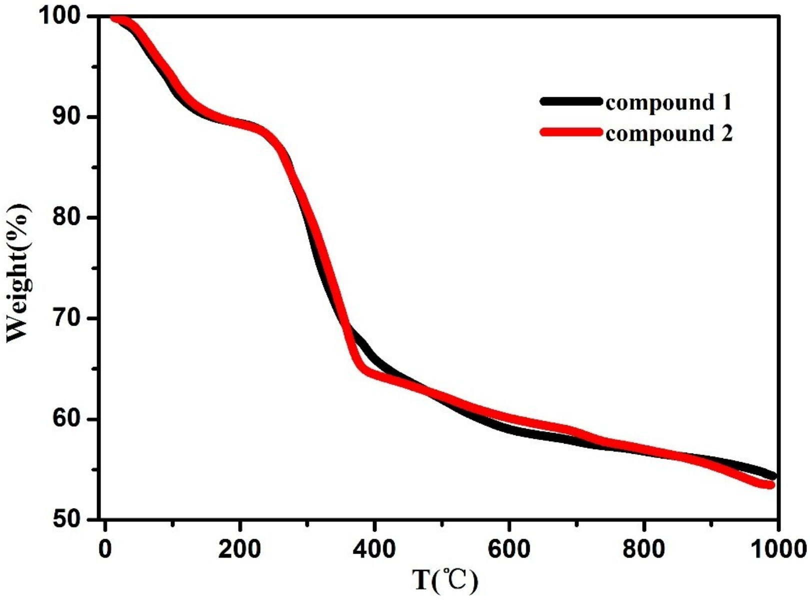

Figure S2. TG Curves for complexes **1** and **2**.

As shown **Fig S2**, the thermal analyses of the two compounds were investigated under atmosphere, which almost had the same curve. The TGA trace indicated a slight mass loss of ~10% at 120 ^{o}C, likely due to partial loss of guest water molecular. On further hearting, the mass loss of ~15% at 250 ^{o}C, which can be attributed to the loss of coordinated water. As temperature increasing, ligands decomposed gradually and the framework completely collapsed.

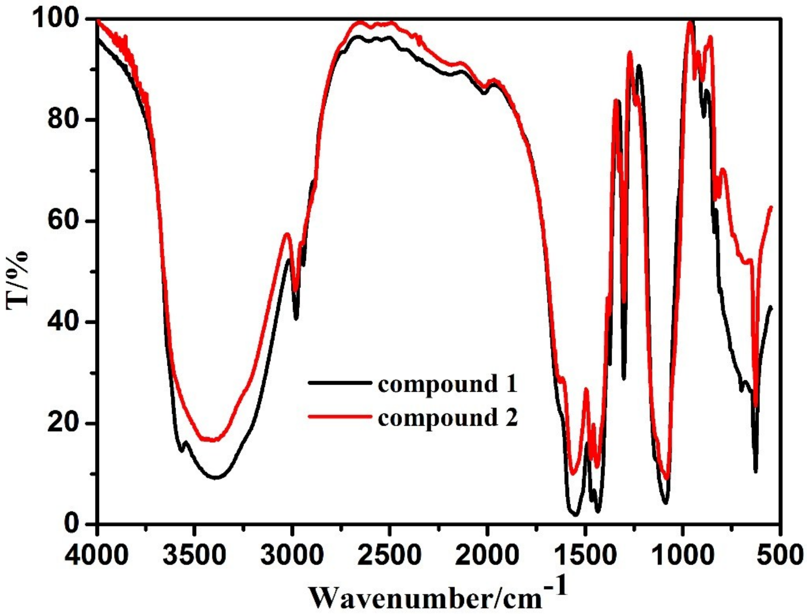

Figure S3. IR spectra in 500-4000 cm^{-1} for complexes **1** and **2**.

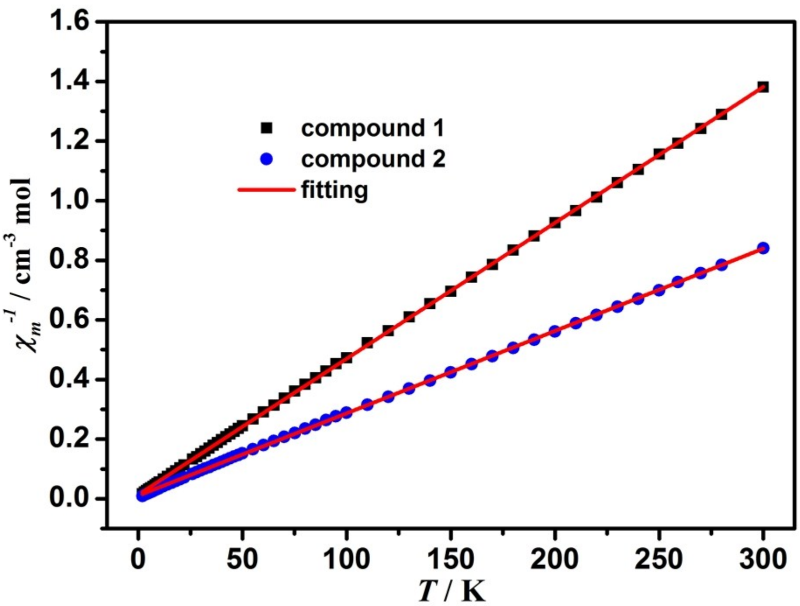

Figure S4. The χ_M^{-1} *vs* T and the Curie-Weiss linear fit for **1** and **2**.

The temperature dependence of magnetic susceptibilities of **1** and **2** were measured in the range of 2 K and 300 K, which is fitted well by Curie-Weiss law, with Curie constant C = 219.3 cm^3 K mol^{-1} and Weiss constant θ = -3.0 K for **1**. The negative θ demonstrated the antiferromagnetic interactions between the Gd^{3+} ions. For **2**, the Curie constant C = 362.3 cm^3 K mol^{-1} and Weiss constant θ = -3.7 K by fitting the temperature dependence of magnetic susceptibilities. The profile of the $\chi_M T$ value versus T may be attribute to the presence of strong spin–orbit coupling and the thermal depopulation of excited Stark sublevels of Dy^{3+}.[11,12]

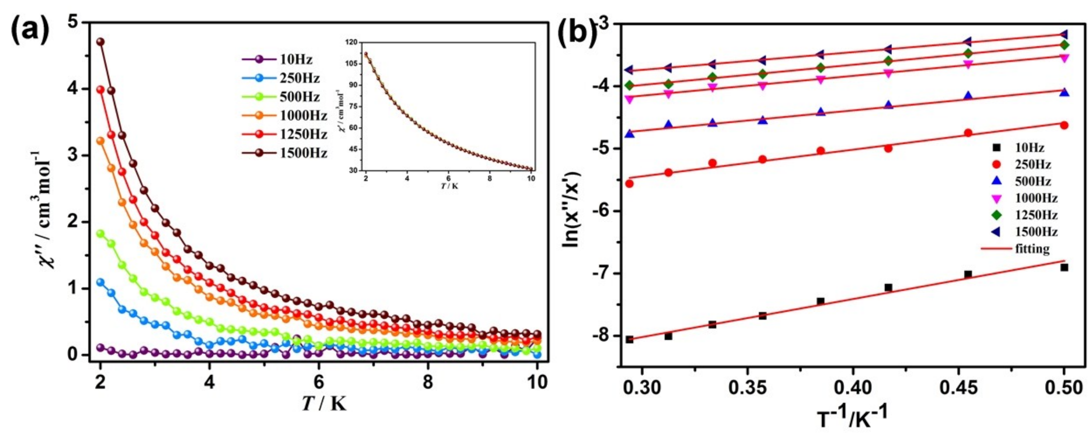

Figure S5. (a) Temperature dependence of the in-phase (inset) and out-of phase ac susceptibilities at the indicated frequencies with H_{dc} = 0 Oe for **2;** (b) Plots of ln(χ''/χ') vs. 1/T for **2**. The solid lines represent the fitting results over the temperature range of 2.0 – 3.4 K.

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