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Electronic Supporting Information

Molecular assembly from linear-shaped Ln_4 clusters to Ln_8 clusters via using different β-diketonate: disparate magnetocaloric effect and single-molecule magnet behaviours

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Table S1 Crystallographic Data and Structures Refinements for clusters **1-5**.

Clusters	1	2	3	4	5
formula	$C_{116}H_{106}Gd_4N_6O_{26}$	$C_{116}H_{106}Dy_4N_6O_{26}$	$C_{116}H_{106}Ho_4N_6O_{26}$	$C_{112}H_{134}N_{30}O_{52}Gd_8$	$C_{112}H_{134}N_{30}O_{52}Dy_8$
*M*r (g mol^{-1})	2629.14	2650.14	2659.86	3990.47	4032.47
T (K)	150.01	150.01	150.01	150.01	293(2)
cryst syst	*Triclinic*	*Triclinic*	*Triclinic*	*Monoclinic*	*Monoclinic*
Space group	*P*-1	*P*-1	*P*-1	$P2_1/c$	$P2_1/c$
a (Å)	14.0128(6)	14.0115(7)	14.0531(7)	14.5068(8)	14.4129(12)
b (Å)	17.0735(7)	17.0605(7)	17.0946(8)	17.0170(11)	16.7883(14)
c (Å)	23.9952(10)	23.9794(10)	24.0090(11)	44.979(3)	43.787(3)
α (°)	89.078(2)	89.0348(17)	88.946(2)	90	90
β (°)	89.403(2)	89.3377(19)	89.287(2)	94.068(2)	93.5526(18)
γ (°)	68.0660(18)	68.0886(18)	67.992(2)	90	90
V (Å^3)	5324.5(4)	5317.2(4)	5346.5(4)	11075.7(12)	10574.7(15)
Z	2	2	2	2	2
cryst size (mm^3)	0.26 x 0.21 x 0.14	0.26 x 0.21 x 0.14	0.32 x 0.21 x 0.11	0.26 x 0.21 x 0.14	0.26 x 0.21 x 0.14
D_c (g cm^{-3})	1.640	1.655	1.652	1.196	1.266
μ (mm^{-1})	2.534	2.854	3.003	2.419	2.851

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limiting indices	-17<=h<=17 -21<=k<=21 -30<=l<=30	-17<=h<=17 -21<=k<=21 -29<=l<=29	-17<=h<=17 -21<=k<=21 -29<=l<=29	-17<=h<=17, -21<=k<=21, -55<=l<=55	-17<=h<=17, -20<=k<=20, -52<=l<=50
reflns collected	91026	88457	85156	88240	71080
unique	21943	20932	21016	19276	19282
Params	1353	1353	1353	916	917
R_{int}	0.0653	0.0630	0.0716	0.0664	0.0419
GOF on F^2	1.028	1.038	1.019	1.056	1.028
R_1, wR_2 [$I>2\sigma(I)$]	0.0398, 0.0880	0.0399, 0.0903	0.0417, 0.0988	0.0528, 0.1436	0.0683, 0.1754
R_1, wR_2 (all data)	0.0648, 0.0984	0.0652, 0.1015	0.0701, 0.1122	0.0939, 0.1607	0.0808, 0.1825

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

Bond lengths			
Gd(2)-O(15)	2.293(4)	Gd(2)-O(17)	2.325(4)
Gd(2)-O(18)	2.331(4)	Gd(2)-N(4)	2.467(5)
Gd(2)-O(14)	2.309(4)	Gd(2)-O(14)#1	2.303(4)
Gd(2)-O(13)#1	2.380(4)	Gd(2)-O(23)	2.462(4)
Gd(4)-O(1)	2.373(4)	Gd(4)-O(2)	2.305(4)
Gd(4)-O(2)#2	2.310(4)	Gd(4)-O(9)	2.319(4)
Gd(4)-O(11)	2.488(4)	Gd(4)-O(10)	2.358(4)
Gd(4)-O(3)#2	2.288(4)	Gd(6)-O(15)#1	2.406(4)
Gd(6)-O(19)	2.327(4)	Gd(6)-O(20)	2.312(4)
Gd(6)-O(22)	2.327(4)	Gd(6)-O(13)	2.300(4)
Gd(6)-O(21)	2.328(4)	Gd(6)-O(24)	2.382(4)
Gd(6)-N(6)#1	2.570(5)	Gd(8)-O(1)	2.311(4)
Gd(8)-O(8)	2.354(4)	Gd(8)-O(12)	2.395(5)
Gd(8)-N(3)#2	2.567(5)	Gd(8)-O(3)#2	2.411(4)
Gd(8)-O(6)	2.294(5)	Gd(8)-O(7)	2.341(4)
Gd(8)-O(5)	2.349(5)		
Bond Angels			
O(15)-Gd(2)-O(17)	83.65(14)	O(15)-Gd(2)-O(18)	113.43(15)
O(15)-Gd(2)-O(14)#1	136.84(13)	O(15)-Gd(2)-O(14)	134.48(13)
O(15)-Gd(2)-O(13)#1	67.53(13)	O(15)-Gd(2)-O(23)	75.20(15)
O(17)-Gd(2)-O(18)	70.49(14)	O(17)-Gd(2)-O(13)#1	72.49(14)

O(17)-Gd(2)-O(23)	143.73(14)	O(18)-Gd(2)-O(13)#1	142.51(14)
O(18)-Gd(2)-O(23)	145.20(14)	O(14)#1-Gd(2)-O(17)	90.75(14)
O(14)-Gd(2)-O(17)	137.63(14)	O(14)#1-Gd(2)-O(18)	104.62(15)
O(14)-Gd(2)-O(18)	76.08(14)	O(14)#1-Gd(2)-O(14)	73.09(14)
O(14)-Gd(2)-O(13)#1	132.01(13)	O(14)#1-Gd(2)-O(13)#1	69.98(13)
O(14)#1-Gd(2)-O(23)	85.25(15)	O(14)-Gd(2)-O(23)	75.15(14)
O(13)#1-Gd(2)-O(23)	72.29(13)	O(1)-Gd(4)-O(11)	73.19(14)
O(2)-Gd(4)-O(1)	70.42(13)	O(2)#2-Gd(4)-O(1)	131.14(14)
O(2)-Gd(4)-O(2)#2	72.96(15)	O(2)#2-Gd(4)-O(9)	74.74(15)
O(2)-Gd(4)-O(9)	102.14(15)	O(2)-Gd(4)-O(11)	89.31(14)
O(2)#2-Gd(4)-O(11)	75.17(14)	O(2)-Gd(4)-O(10)	89.55(14)
O(2)#2-Gd(4)-O(10)	136.93(14)	O(9)-Gd(4)-O(1)	143.97(15)
O(9)-Gd(4)-O(11)	142.84(15)	O(9)-Gd(4)-O(10)	70.94(15)
O(10)-Gd(4)-O(1)	73.75(14)	O(10)-Gd(4)-O(11)	145.25(14)
O(3)#2-Gd(4)-O(1)	68.91(13)	O(3)#2-Gd(4)-O(2)#2	135.97(13)
O(3)#2-Gd(4)-O(2)	139.22(13)	O(3)#2-Gd(4)-O(9)	112.33(15)
O(3)#2-Gd(4)-O(11)	76.41(14)	O(3)#2-Gd(4)-O(10)	82.03(14)
O(19)-Gd(6)-O(15)#1	76.14(14)	O(19)-Gd(6)-O(22)	97.62(15)
O(19)-Gd(6)-O(21)	142.88(15)	O(19)-Gd(6)-O(24)	146.13(15)
O(20)-Gd(6)-O(15)#1	140.89(15)	O(20)-Gd(6)-O(19)	72.05(15)
O(20)-Gd(6)-O(22)	78.92(17)	O(20)-Gd(6)-O(21)	70.98(15)
O(20)-Gd(6)-O(24)	140.36(16)	O(22)-Gd(6)-O(15)#1	128.02(14)
O(22)-Gd(6)-O(21)	72.14(15)	O(22)-Gd(6)-O(24)	98.79(16)
O(13)-Gd(6)-O(15)#1	66.97(13)	O(13)-Gd(6)-O(19)	87.99(14)
O(13)-Gd(6)-O(20)	89.54(15)	O(13)-Gd(6)-O(22)	164.84(14)
O(13)-Gd(6)-O(21)	94.92(14)	O(13)-Gd(6)-O(24)	83.79(15)
O(21)-Gd(6)-O(15)#1	138.51(14)	O(21)-Gd(6)-O(24)	70.75(16)
O(24)-Gd(6)-O(15)#1	70.39(15)	O(1)-Gd(8)-O(8)	162.00(14)
O(1)-Gd(8)-O(12)	86.29(15)	O(1)-Gd(8)-O(3)#2	67.87(13)
O(1)-Gd(8)-O(7)	89.45(14)	O(1)-Gd(8)-O(5)	88.22(15)
O(8)-Gd(8)-O(12)	86.79(16)	O(8)-Gd(8)-O(3)#2	125.08(14)
O(12)-Gd(8)-O(3)#2	71.47(15)	O(6)-Gd(8)-O(1)	97.62(16)
O(6)-Gd(8)-O(8)	143.78(16)	O(6)-Gd(8)-O(12)	143.78(16)
O(6)-Gd(8)-O(3)#2	143.07(16)	O(6)-Gd(8)-O(7)	72.08(17)
O(6)-Gd(8)-O(5)	71.67(16)	O(7)-Gd(8)-O(8)	72.60(15)
O(7)-Gd(8)-O(12)	71.97(17)	O(7)-Gd(8)-O(3)#2	137.77(15)
O(7)-Gd(8)-O(5)	143.01(17)	O(5)-Gd(8)-O(8)	106.85(16)

O(5)-Gd(8)-O(12)	144.55(16)	O(5)-Gd(8)-O(3)#2	74.03(15)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z+1; #2 -x+2, -y, -z+2.

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

Bond lengths			
Dy(1)-O(7)	2.374(3)	Dy(1)-O(8)	2.304(3)
Dy(1)-O(8)#1	2.314(3)	Dy(1)-O(1)	2.323(4)
Dy(1)-O(2)	2.353(4)	Dy(1)-O(9)#1	2.294(3)
Dy(1)-O(12)	2.485(4)	Dy(3)-O(19)#2	2.377(3)
Dy(3)-O(21)	2.297(3)	Dy(3)-O(14)	2.331(4)
Dy(3)-O(20)#2	2.309(4)	Dy(3)-O(20)	2.308(3)
Dy(3)-O(13)	2.334(4)	Dy(3)-O(24)	2.465(4)
Dy(3)-N(4)	2.460(5)	Dy(6)-O(19)	2.302(3)
Dy(6)-O(21)#2	2.407(3)	Dy(6)-O(15)	2.318(4)
Dy(6)-O(16)	2.312(4)	Dy(6)-O(17)	2.333(4)
Dy(6)-O(18)	2.330(4)	Dy(6)-N(6)#2	2.569(5)
Dy(6)-O(23)	2.385(4)	Dy(8)-O(7)	2.316(3)
Dy(8)-O(5)	2.355(4)	Dy(8)-O(6)	2.343(4)
Dy(8)-O(9)#1	2.406(4)	Dy(8)-O(11)	2.395(4)
Dy(8)-O(3)	2.345(4)	Dy(8)-O(4)	2.298(4)
Dy(8)-N(3)#1	2.575(5)		
Bond Angels			
O(7)-Dy(1)-O(12)	73.24(13)	O(8)-Dy(1)-O(7)	70.32(12)
O(8)#1-Dy(1)-O(7)	131.10(12)	O(8)-Dy(1)-O(8)#1	73.20(14)
O(8)#1-Dy(1)-O(1)	74.75(13)	O(8)-Dy(1)-O(1)	101.91(13)
O(8)#1-Dy(1)-O(2)	137.08(13)	O(8)-Dy(1)-O(2)	89.44(13)
O(8)-Dy(1)-O(12)	89.65(13)	O(8)#1-Dy(1)-O(12)	75.13(12)
O(1)-Dy(1)-O(7)	143.92(14)	O(1)-Dy(1)-O(2)	70.88(14)
O(1)-Dy(1)-O(12)	142.83(14)	O(2)-Dy(1)-O(7)	73.81(13)
O(2)-Dy(1)-O(12)	145.26(13)	O(9)#1-Dy(1)-O(7)	69.04(12)
O(9)#1-Dy(1)-O(8)#1	135.84(13)	O(9)#1-Dy(1)-O(8)	139.28(12)
O(9)#1-Dy(1)-O(1)	112.35(14)	O(9)#1-Dy(1)-O(2)	81.93(13)
O(9)#1-Dy(1)-O(12)	76.36(13)	O(19)#2-Dy(3)-O(24)	72.23(13)
O(21)-Dy(3)-O(19)#2	67.70(12)	O(21)-Dy(3)-O(14)	113.17(14)
O(21)-Dy(3)-O(20)	134.39(13)	O(21)-Dy(3)-O(20)#2	136.94(12)
O(21)-Dy(3)-O(13)	83.60(14)	O(21)-Dy(3)-O(24)	75.20(14)

O(14)-Dy(3)-O(19)#2	142.80(14)	O(14)-Dy(3)-O(13)	70.69(13)
O(14)-Dy(3)-O(24)	144.96(14)	O(20)#2-Dy(3)-O(19)#2	69.90(12)
O(20)-Dy(3)-O(19)#2	132.09(13)	O(20)-Dy(3)-O(14)	75.85(13)
O(20)#2-Dy(3)-O(14)	104.88(14)	O(20)-Dy(3)-O(20)#2	73.25(13)
O(20)-Dy(3)-O(13)	137.62(13)	O(20)#2-Dy(3)-O(13)	90.83(14)
O(20)-Dy(3)-O(24)	75.29(13)	O(20)#2-Dy(3)-O(24)	85.28(14)
O(13)-Dy(3)-O(19)#2	72.57(13)	O(13)-Dy(3)-O(24)	143.71(12)
O(19)-Dy(6)-O(21)#2	67.12(12)	O(19)-Dy(6)-O(15)	87.87(14)
O(19)-Dy(6)-O(16)	89.74(14)	O(19)-Dy(6)-O(17)	164.95(13)
O(19)-Dy(6)-O(18)	95.00(13)	O(19)-Dy(6)-O(23)	83.98(14)
O(15)-Dy(6)-O(21)#2	76.20(13)	O(15)-Dy(6)-O(17)	97.63(14)
O(15)-Dy(6)-O(18)	143.06(14)	O(15)-Dy(6)-O(23)	146.12(14)
O(16)-Dy(6)-O(21)#2	141.32(14)	O(16)-Dy(6)-O(15)	72.23(14)
O(16)-Dy(6)-O(17)	78.73(15)	O(16)-Dy(6)-O(18)	70.97(15)
O(16)-Dy(6)-O(23)	140.28(15)	O(17)-Dy(6)-O(21)#2	127.77(13)
O(17)-Dy(6)-O(23)	98.66(15)	O(18)-Dy(6)-O(21)#2	138.35(13)
O(18)-Dy(6)-O(17)	72.21(14)	O(18)-Dy(6)-O(23)	70.60(14)
O(23)-Dy(6)-O(21)#2	70.32(14)	O(7)-Dy(8)-O(5)	161.82(14)
O(7)-Dy(8)-O(6)	89.35(13)	O(7)-Dy(8)-O(9)#1	68.13(12)
O(7)-Dy(8)-O(11)	86.37(13)	O(7)-Dy(8)-O(3)	88.72(14)
O(5)-Dy(8)-O(9)#1	125.04(13)	O(5)-Dy(8)-O(11)	86.70(14)
O(6)-Dy(8)-O(5)	72.51(14)	O(6)-Dy(8)-O(9)#1	137.97(14)
O(6)-Dy(8)-O(11)	71.88(15)	O(6)-Dy(8)-O(3)	142.73(15)
O(11)-Dy(8)-O(9)#1	71.70(14)	O(3)-Dy(8)-O(5)	106.41(15)
O(3)-Dy(8)-O(9)#1	74.34(14)	O(3)-Dy(8)-O(11)	145.01(15)
O(4)-Dy(8)-O(7)	97.16(14)	O(4)-Dy(8)-O(5)	78.82(15)
O(4)-Dy(8)-O(6)	72.01(15)	O(4)-Dy(8)-O(9)#1	142.85(14)
O(4)-Dy(8)-O(11)	143.66(15)	O(4)-Dy(8)-O(3)	71.32(15)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z+1; #2 -x+1, -y, -z+2.

Table S4 Selected bond lengths (Å) and angles (°) for cluster **3** [a]

Bond lengths			
Ho(1)-O(9)	2.348(4)	Ho(1)-O(3)	2.307(4)
Ho(1)-O(2)#1	2.389(4)	Ho(1)-O(10)	2.339(4)
Ho(1)-O(1)#1	2.322(4)	Ho(1)-O(1)	2.315(3)
Ho(1)-N(1)	2.475(5)	Ho(1)-O(12)	2.484(4)

Ho(3)-O(14)#2	2.376(4)	Ho(3)-O(13)	2.318(3)
Ho(3)-O(13)#2	2.312(4)	Ho(3)-O(15)	2.330(4)
Ho(3)-O(16)	2.374(4)	Ho(3)-O(23)	2.502(4)
Ho(3)-O(21)	2.303(4)	Ho(3)-N(4)	2.485(5)
Ho(2)-O(3)	2.418(4)	Ho(2)-O(2)#1	2.315(4)
Ho(2)-O(5)	2.339(4)	Ho(2)-O(7)	2.336(4)
Ho(2)-O(6)	2.323(4)	Ho(2)-O(8)	2.341(4)
Ho(2)-O(11)	2.404(4)	Ho(2)-N(3)	2.586(5)
Ho(4)-O(14)#2	2.324(4)	Ho(4)-O(17)	2.355(4)
Ho(4)-O(24)	2.408(4)	Ho(4)-O(21)	2.417(4)
Ho(4)-O(18)	2.348(4)	Ho(4)-O(19)	2.361(4)
Ho(4)-O(20)	2.306(4)	Ho(4)-N(6)	2.594(5)
Bond Angels			
O(9)-Ho(1)-O(2)#1	142.36(14)	O(9)-Ho(1)-O(12)	145.28(14)
O(3)-Ho(1)-O(9)	113.51(14)	O(3)-Ho(1)-O(2)#1	67.86(13)
O(3)-Ho(1)-O(10)	84.08(14)	O(3)-Ho(1)-O(1)	133.52(14)
O(3)-Ho(1)-O(1)#1	136.55(13)	O(3)-Ho(1)-O(12)	74.79(14)
O(2)#1-Ho(1)-O(12)	72.36(13)	O(10)-Ho(1)-O(9)	70.05(14)
O(10)-Ho(1)-O(2)#1	72.81(13)	O(10)-Ho(1)-O(12)	144.03(13)
O(1)#1-Ho(1)-O(9)	105.16(14)	O(1)-Ho(1)-O(9)	76.29(14)
O(1)-Ho(1)-O(2)#1	132.09(13)	O(1)#1-Ho(1)-O(2)#1	69.53(12)
O(1)#1-Ho(1)-O(10)	91.36(14)	O(1)-Ho(1)-O(10)	137.90(14)
O(1)-Ho(1)-O(1)#1	73.58(14)	O(1)#1-Ho(1)-O(12)	84.79(14)
O(1)-Ho(1)-O(12)	74.90(13)	O(14)#2-Ho(3)-O(23)	73.42(14)
O(13)-Ho(3)-O(14)#2	130.85(13)	O(13)#2-Ho(3)-O(14)#2	70.13(12)
O(13)#2-Ho(3)-O(13)	73.25(15)	O(13)-Ho(3)-O(15)	75.07(14)
O(13)#2-Ho(3)-O(15)	102.19(14)	O(13)#2-Ho(3)-O(16)	89.98(14)
O(13)-Ho(3)-O(16)	137.49(14)	O(13)#2-Ho(3)-O(23)	89.59(14)
O(13)-Ho(3)-O(23)	74.70(13)	O(15)-Ho(3)-O(14)#2	143.96(14)
O(15)-Ho(3)-O(16)	70.71(14)	O(15)-Ho(3)-O(23)	142.62(14)
O(16)-Ho(3)-O(14)#2	74.06(14)	O(16)-Ho(3)-O(23)	145.52(14)
O(21)-Ho(3)-O(14)#2	68.99(13)	O(21)-Ho(3)-O(13)	135.28(14)
O(21)-Ho(3)-O(13)#2	138.98(13)	O(21)-Ho(3)-O(15)	112.70(14)
O(21)-Ho(3)-O(16)	82.15(14)	O(21)-Ho(3)-O(23)	75.81(13)
O(2)#1-Ho(2)-O(3)	67.25(13)	O(2)#1-Ho(2)-O(5)	87.91(14)
O(2)#1-Ho(2)-O(7)	164.88(14)	O(2)#1-Ho(2)-O(6)	89.89(14)
O(2)#1-Ho(2)-O(8)	94.88(14)	O(2)#1-Ho(2)-O(11)	83.57(14)

O(5)-Ho(2)-O(3)	76.05(14)	O(5)-Ho(2)-O(8)	142.85(14)
O(5)-Ho(2)-O(11)	146.14(15)	O(7)-Ho(2)-O(3)	127.60(14)
O(7)-Ho(2)-O(5)	98.21(15)	O(7)-Ho(2)-O(8)	71.91(14)
O(7)-Ho(2)-O(11)	98.40(15)	O(6)-Ho(2)-O(3)	141.07(14)
O(6)-Ho(2)-O(5)	71.87(15)	O(6)-Ho(2)-O(7)	79.03(15)
O(6)-Ho(2)-O(8)	71.10(14)	O(6)-Ho(2)-O(11)	140.50(16)
O(8)-Ho(2)-O(3)	138.65(14)	O(8)-Ho(2)-O(11)	70.73(15)
O(11)-Ho(2)-O(3)	70.42(14)	O(14)#2-Ho(4)-O(17)	161.84(14)
O(14)#2-Ho(4)-O(24)	86.18(14)	O(14)#2-Ho(4)-O(21)	67.94(13)
O(14)#2-Ho(4)-O(18)	89.58(14)	O(14)#2-Ho(4)-O(19)	88.46(15)
O(17)-Ho(4)-O(24)	86.16(15)	O(17)-Ho(4)-O(21)	124.62(14)
O(17)-Ho(4)-O(19)	107.10(15)	O(24)-Ho(4)-O(21)	71.66(14)
O(18)-Ho(4)-O(17)	72.37(15)	O(18)-Ho(4)-O(24)	71.77(15)
O(18)-Ho(4)-O(21)	137.93(14)	O(18)-Ho(4)-O(19)	142.97(15)
O(19)-Ho(4)-O(24)	144.84(15)	O(19)-Ho(4)-O(21)	74.12(14)
O(20)-Ho(4)-O(14)#2	98.09(14)	O(20)-Ho(4)-O(17)	78.84(15)
O(20)-Ho(4)-O(24)	144.02(16)	O(20)-Ho(4)-O(21)	142.83(14)
O(20)-Ho(4)-O(18)	72.56(15)	O(20)-Ho(4)-O(19)	71.14(15)

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z+1; #2 -x+1, -y, -z.

Table S5 The important bond lengths and angles for cluster **4**.

Bond lengths			
Gd(1)-O(2)	2.384(5)	Gd(1)-O(17)#1	2.324(4)
Gd(1)-O(18)#1	2.332(5)	Gd(1)-O(18)	2.313(4)
Gd(1)-O(23)	2.449(5)	Gd(1)-O(1)	2.284(5)
Gd(1)-O(19)	2.361(5)	Gd(3)-O(14)	2.264(6)
Gd(3)-O(6)	2.321(5)	Gd(3)-O(13)	2.441(5)
Gd(3)-O(3)	2.316(5)	Gd(3)-O(9)	2.337(5)
Gd(3)-O(5)	2.340(5)	Gd(2)-O(2)	2.282(5)
Gd(3)-O(10)	2.318(5)	Gd(2)-O(17)#1	2.324(5)
Gd(2)-O(3)	2.313(5)	Gd(4)-O(22)	2.411(6)
Gd(2)-O(15)	2.345(6)	Gd(4)-O(7)	2.432(5)
Gd(2)-O(9)	2.360(5)	Gd(4)-O(21)	2.466(6)
Gd(2)-O(19)	2.446(5)	Gd(4)-O(13)	2.375(5)
Gd(4)-O(6)	2.318(5)	Gd(4)-O(11)	2.369(5)
Gd(4)-O(10)	2.333(5)		
Bond angles			
O(2)-Gd(1)-O(23)	140.35(16)	O(17)#1-Gd(1)-O(2)	71.76(16)
O(17)#1-Gd(1)-O(18)#1	69.35(16)	O(17)#1-Gd(1)-O(23)	79.54(17)

O(17)#1-Gd(1)-O(19)	70.27(18)	O(18)-Gd(1)-O(2)	142.74(16)
O(18)#1-Gd(1)-O(2)	115.30(17)	O(18)-Gd(1)-O(17)#1	140.49(17)
O(18)-Gd(1)-O(18)#1	75.71(18)	O(18)#1-Gd(1)-O(23)	77.51(17)
O(18)-Gd(1)-O(23)	75.38(16)	O(18)#1-Gd(1)-O(19)	136.22(17)
O(18)-Gd(1)-O(19)	132.20(17)	O(1)-Gd(1)-O(2)	68.83(17)
O(1)-Gd(1)-O(17)#1	119.58(18)	O(1)-Gd(1)-O(18)#1	88.58(18)
O(1)-Gd(1)-O(18)	76.36(17)	O(1)-Gd(1)-O(23)	150.80(17)
O(1)-Gd(1)-O(19)	126.40(18)	O(19)-Gd(1)-O(2)	65.75(18)
O(19)-Gd(1)-O(23)	79.26(17)	O(6)-Gd(3)-O(5)	67.00(17)
O(6)-Gd(3)-O(13)	64.63(18)	O(6)-Gd(3)-O(9)	133.35(17)
O(3)-Gd(3)-O(6)	135.82(18)	O(3)-Gd(3)-O(5)	75.91(18)
O(3)-Gd(3)-O(10)	138.76(17)	O(3)-Gd(3)-O(13)	141.11(18)
O(3)-Gd(3)-O(9)	69.47(17)	O(5)-Gd(3)-O(13)	131.24(18)
O(10)-Gd(3)-O(6)	72.62(17)	O(10)-Gd(3)-O(5)	99.46(19)
O(10)-Gd(3)-O(13)	71.78(18)	O(10)-Gd(3)-O(9)	69.90(17)
O(14)-Gd(3)-O(6)	131.20(19)	O(14)-Gd(3)-O(3)	79.34(19)
O(14)-Gd(3)-O(5)	154.40(19)	O(14)-Gd(3)-O(10)	103.4(2)
O(14)-Gd(3)-O(13)	68.05(19)	O(14)-Gd(3)-O(9)	84.47(19)
O(9)-Gd(3)-O(5)	92.84(17)	O(9)-Gd(3)-O(13)	125.14(18)
O(2)-Gd(2)-O(17)#1	73.62(17)	O(2)-Gd(2)-O(3)	134.71(17)
O(2)-Gd(2)-O(15)	93.20(19)	O(2)-Gd(2)-O(9)	154.35(16)
O(2)-Gd(2)-O(19)	65.92(16)	O(17)#1-Gd(2)-O(15)	76.72(18)
O(17)#1-Gd(2)-O(9)	89.41(17)	O(17)#1-Gd(2)-O(19)	68.80(17)
O(3)-Gd(2)-O(17)#1	144.81(17)	O(3)-Gd(2)-O(15)	80.65(18)
O(3)-Gd(2)-O(9)	69.10(17)	O(3)-Gd(2)-O(19)	135.59(17)
O(15)-Gd(2)-O(9)	101.60(18)	O(15)-Gd(2)-O(19)	143.38(17)
O(9)-Gd(2)-O(19)	90.27(16)	O(6)-Gd(4)-O(7)	110.22(18)
O(6)-Gd(4)-O(22)	141.7(2)	O(6)-Gd(4)-O(13)	65.74(19)
O(6)-Gd(4)-O(21)	73.89(19)	O(6)-Gd(4)-O(11)	134.34(19)
O(10)-Gd(4)-O(22)	86.73(18)	O(10)-Gd(4)-O(7)	147.92(19)
O(10)-Gd(4)-O(21)	85.53(19)	O(10)-Gd(4)-O(13)	72.72(18)
O(10)-Gd(4)-O(11)	133.40(18)	O(22)-Gd(4)-O(7)	71.86(19)
O(22)-Gd(4)-O(21)	137.4(2)	O(7)-Gd(4)-O(21)	126.38(19)
O(13)-Gd(4)-O(22)	77.7(2)	O(13)-Gd(4)-O(7)	79.40(18)
O(13)-Gd(4)-O(21)	138.21(19)	O(11)-Gd(4)-O(22)	83.2(2)
O(11)-Gd(4)-O(7)	68.74(19)	O(11)-Gd(4)-O(21)	72.46(19)
O(11)-Gd(4)-O(13)	146.65(19)		

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

Table S6. The important bond lengths and angles for cluster **5**.

Bond lengths			
Dy(2)-O(3)	2.419(7)	Dy(2)-O(11)	2.298(6)
Dy(2)-O(10)	2.294(6)	Dy(2)-O(1)#1	2.312(8)
Dy(2)-O(15)	2.307(7)	Dy(2)-O(17)	2.353(6)

Dy(1)-O(2)#1	2.329(8)	Dy(1)-O(3)	2.350(7)
Dy(1)-O(2)	2.312(7)	Dy(1)-O(10)	2.391(7)
Dy(1)-O(21)	2.438(7)	Dy(1)-O(1)#1	2.318(6)
Dy(1)-O(9)	2.286(7)	Dy(3)-O(18)	2.313(7)
Dy(3)-O(11)	2.314(6)	Dy(3)-O(14)	2.243(9)
Dy(3)-O(6)	2.313(8)	Dy(3)-O(5)	2.325(8)
Dy(3)-O(17)	2.322(6)	Dy(3)-O(13)	2.423(7)
Dy(4)-O(18)	2.326(6)	Dy(4)-O(6)	2.306(7)
Dy(4)-O(19)	2.383(8)	Dy(4)-O(23)	2.468(9)
Dy(4)-O(7)	2.424(8)	Dy(4)-O(22)	2.413(8)
Dy(4)-O(13)	2.354(9)		

Bond angles

O(10)-Dy(2)-O(3)	65.7(2)	O(10)-Dy(2)-O(11)	134.9(2)
O(10)-Dy(2)-O(1)#1	74.0(3)	O(10)-Dy(2)-O(15)	91.9(2)
O(10)-Dy(2)-O(17)	154.1(2)	O(11)-Dy(2)-O(3)	136.9(3)
O(11)-Dy(2)-O(1)#1	143.5(2)	O(11)-Dy(2)-O(15)	80.1(3)
O(11)-Dy(2)-O(17)	69.3(2)	O(1)#1-Dy(2)-O(3)	68.8(3)
O(1)#1-Dy(2)-O(17)	89.1(2)	O(15)-Dy(2)-O(3)	142.7(3)
O(15)-Dy(2)-O(1)#1	76.6(3)	O(15)-Dy(2)-O(17)	103.3(2)
O(17)-Dy(2)-O(3)	90.1(2)	O(2)-Dy(1)-O(2)#1	75.2(3)
O(2)-Dy(1)-O(3)	133.1(2)	O(2)#1-Dy(1)-O(3)	136.3(2)
O(2)-Dy(1)-O(10)	142.3(2)	O(2)#1-Dy(1)-O(10)	115.6(2)
O(2)-Dy(1)-O(21)	75.0(2)	O(2)#1-Dy(1)-O(21)	77.8(3)
O(2)-Dy(1)-O(1)#1	140.3(3)	O(3)-Dy(1)-O(10)	65.3(2)
O(3)-Dy(1)-O(21)	79.8(3)	O(10)-Dy(1)-O(21)	141.1(2)
O(1)#1-Dy(1)-O(2)#1	69.6(3)	O(1)#1-Dy(1)-O(3)	70.0(3)
O(1)#1-Dy(1)-O(10)	72.1(2)	O(1)#1-Dy(1)-O(21)	80.3(2)
O(9)-Dy(1)-O(2)	76.7(2)	O(9)-Dy(1)-O(2)#1	88.8(3)
O(9)-Dy(1)-O(3)	125.5(3)	O(9)-Dy(1)-O(10)	68.0(2)
O(9)-Dy(1)-O(21)	151.0(3)	O(9)-Dy(1)-O(1)#1	119.2(3)
O(18)-Dy(3)-O(11)	138.6(2)	O(18)-Dy(3)-O(5)	99.4(3)
O(18)-Dy(3)-O(17)	70.0(2)	O(18)-Dy(3)-O(13)	71.2(3)
O(11)-Dy(3)-O(5)	75.2(3)	O(11)-Dy(3)-O(17)	69.6(2)
O(11)-Dy(3)-O(13)	141.8(3)	O(14)-Dy(3)-O(18)	105.3(3)
O(14)-Dy(3)-O(11)	79.4(3)	O(14)-Dy(3)-O(6)	130.2(3)
O(14)-Dy(3)-O(5)	153.2(3)	O(14)-Dy(3)-O(17)	84.6(3)
O(14)-Dy(3)-O(13)	67.5(3)	O(6)-Dy(3)-O(18)	71.9(3)
O(6)-Dy(3)-O(11)	136.1(3)	O(6)-Dy(3)-O(5)	67.6(3)
O(6)-Dy(3)-O(17)	134.0(3)	O(6)-Dy(3)-O(13)	64.8(3)
O(5)-Dy(3)-O(13)	132.1(3)	O(17)-Dy(3)-O(5)	94.3(3)
O(17)-Dy(3)-O(13)	123.0(3)	O(18)-Dy(4)-O(19)	133.0(3)
O(18)-Dy(4)-O(23)	84.7(3)	O(18)-Dy(4)-O(7)	148.4(3)
O(18)-Dy(4)-O(22)	86.9(3)	O(18)-Dy(4)-O(13)	72.2(3)
O(6)-Dy(4)-O(18)	71.8(2)	O(6)-Dy(4)-O(19)	133.1(3)

O(6)-Dy(4)-O(23)	73.2(3)	O(6)-Dy(4)-O(7)	111.2(3)
O(6)-Dy(4)-O(22)	141.1(3)	O(6)-Dy(4)-O(13)	66.1(3)
O(19)-Dy(4)-O(23)	71.6(3)	O(19)-Dy(4)-O(7)	69.3(3)
O(19)-Dy(4)-O(22)	85.2(3)	O(7)-Dy(4)-O(23)	126.8(3)
O(22)-Dy(4)-O(23)	138.2(3)	O(22)-Dy(4)-O(7)	71.5(3)
O(13)-Dy(4)-O(19)	148.4(3)	O(13)-Dy(4)-O(23)	137.6(3)
O(13)-Dy(4)-O(7)	80.4(3)	O(13)-Dy(4)-O(22)	76.7(3)

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

Table S7 The Gd^{III} geometry analysis by SHAPE 2.0 for clusters **1** and **4**.

Cluster 1	D_{4d}**SAPR**	D_{2d}**TDD**	C_{2v}**JBTPR**	C_{2v}**BTPR**	D_{2d}**JSD**
$Gd1^{III}$	2.647	1.463	2.494	1.556	3.767
$Gd2^{III}$	3.488	2.465	2.499	1.697	3.666
Cluster 4	D_{4d}**SAPR**	D_{2d}**TDD**	C_{2v}**JBTPR**	C_{2v}**BTPR**	D_{2d}**JSD**
$Gd1^{III}$	3.267	2.561	3.406	2.289	5.244
$Gd2^{III}$	2.647	1.463	2.494	1.556	3.767
$Gd3^{III}$	5.297	3.057	3.921	2.770	4.441
	C_{4v}**JCSAPR**	C_{4v}**CSAPR**	D_{3h}**JTCTPR**	D_{3h}**TCTPR**	C_s**MFF**
$Gd4^{III}$	1.277	0.546	2.636	1.043	1.016

SAPR-8 = Square antiprism; **TDD-8 =** Triangular dodecahedron; **JBTPR-8 =** Biaugmented trigonal prism J50; **BTPR-8 =** Biaugmented trigonal prism; **JSD-8 =** Snub diphenoid J84.
JCSAPR-9 = Capped square antiprism J10; **CSAPR-9** = Spherical capped square antiprism; **JTCTPR-9** = Tricapped trigonal prism J51; **TCTPR-9** = Spherical tricapped trigonal prism; **MFF-9** = Muffin.

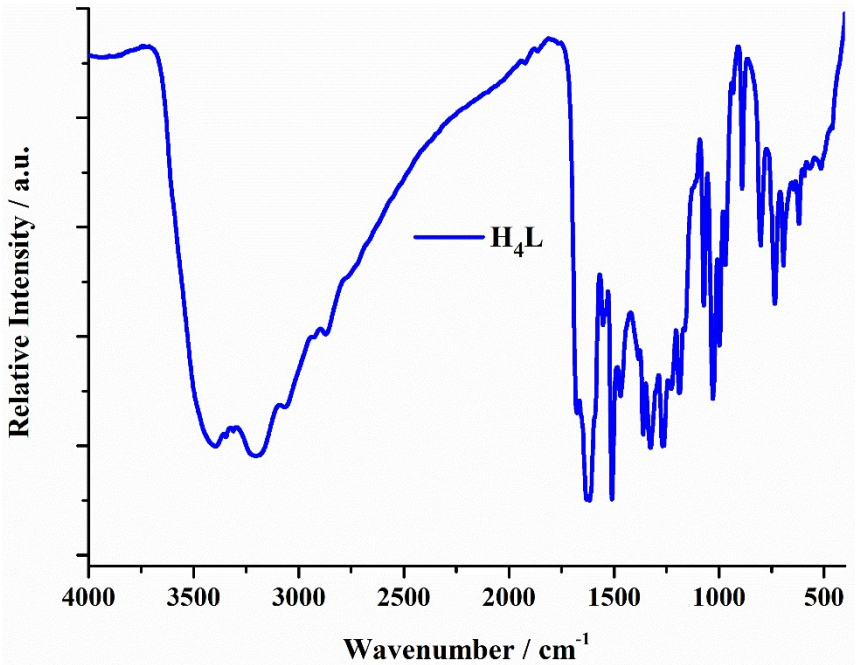


Fig. S1 The IR spectra of H_3L ligand.

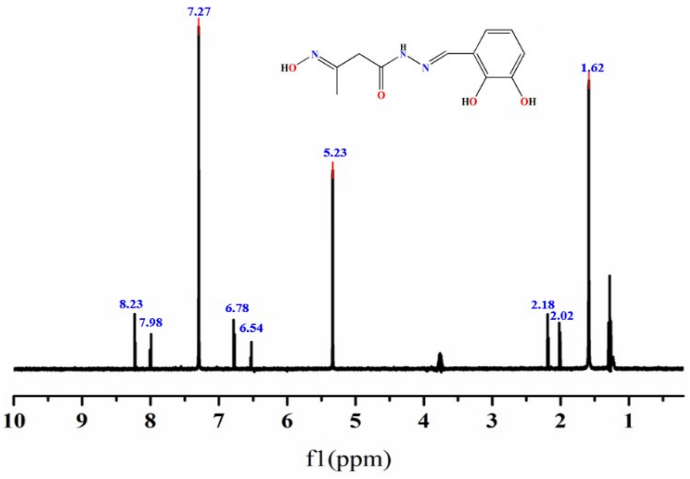


Fig. S2 The ^{1}H NMR spectra of H_3L.

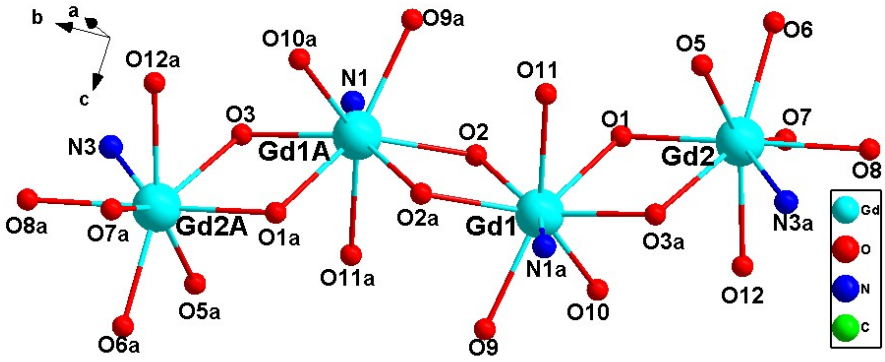


Fig. S3 The coordinate atom labels of central Gd(III) ions in cluster **1**.

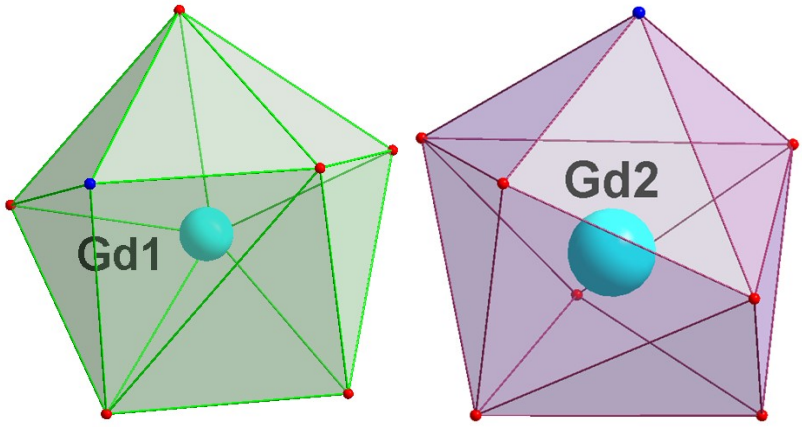


Fig. S4 The geometry polyhedron around the Gd^{3+} ions in cluster **1** (red, O; blue, N; and turquoise, Gd).

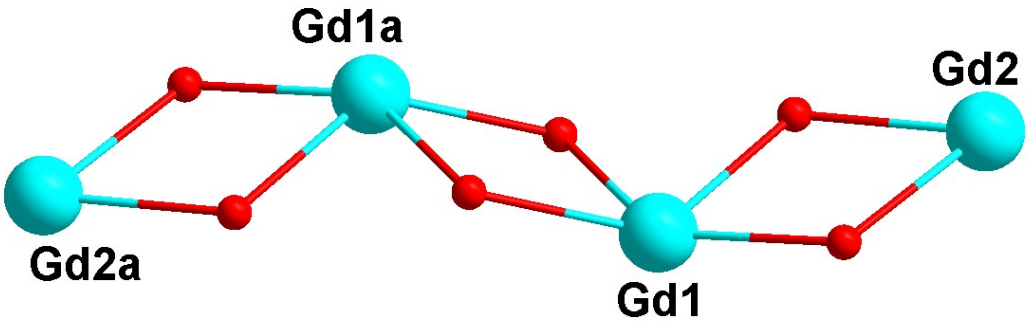


Fig. S5 The four central Gd atoms are bridged by six μ_2-O atoms forming the Gd_4 core (red, O; and turquoise, Gd).

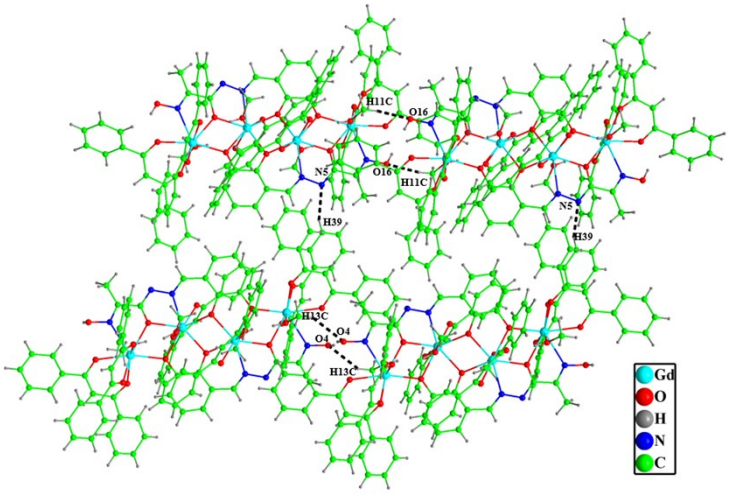


Fig. S6 The H bonds of cluster **1**.

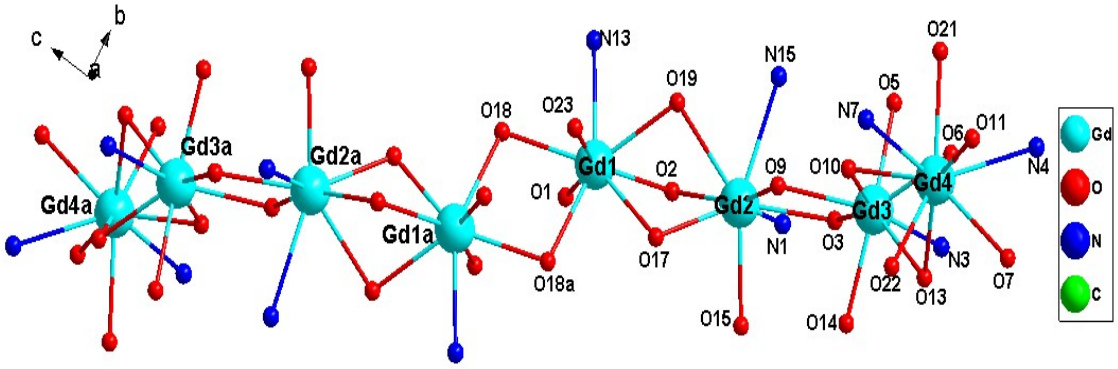
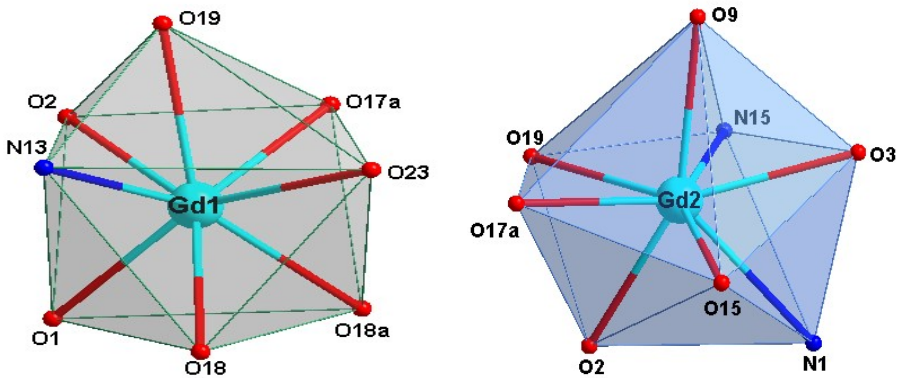


Fig. S7 The coordinate atom labels of central Gd(III) ions in cluster **4**.



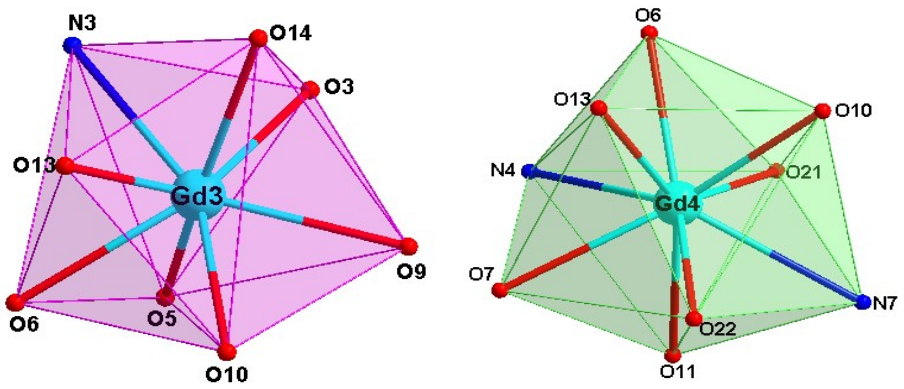


Fig. S8 The geometry polyhedron around the Gd^{3+} ions in cluster **4**.

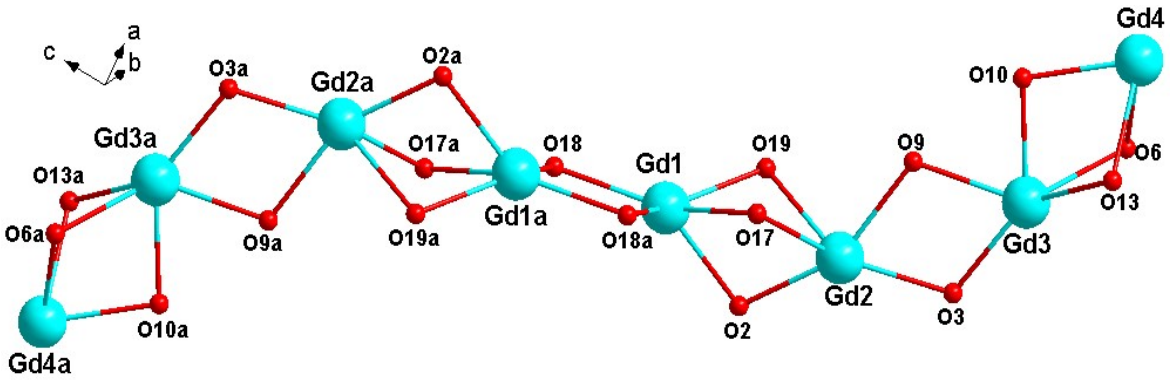


Fig. S9 The eight central Gd atoms are bridged by eighteen μ_2-O atoms forming the Gd_8 core in **4** (red, O; and turquoise, Gd).

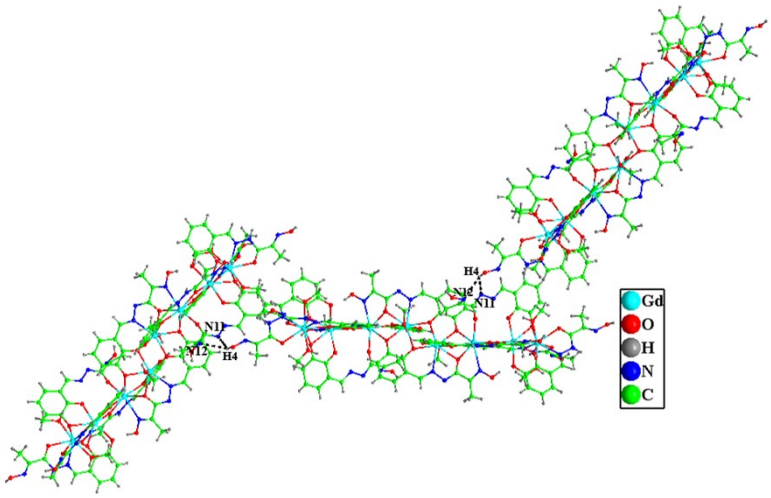


Fig. S10 The H bonds of cluster **4**.

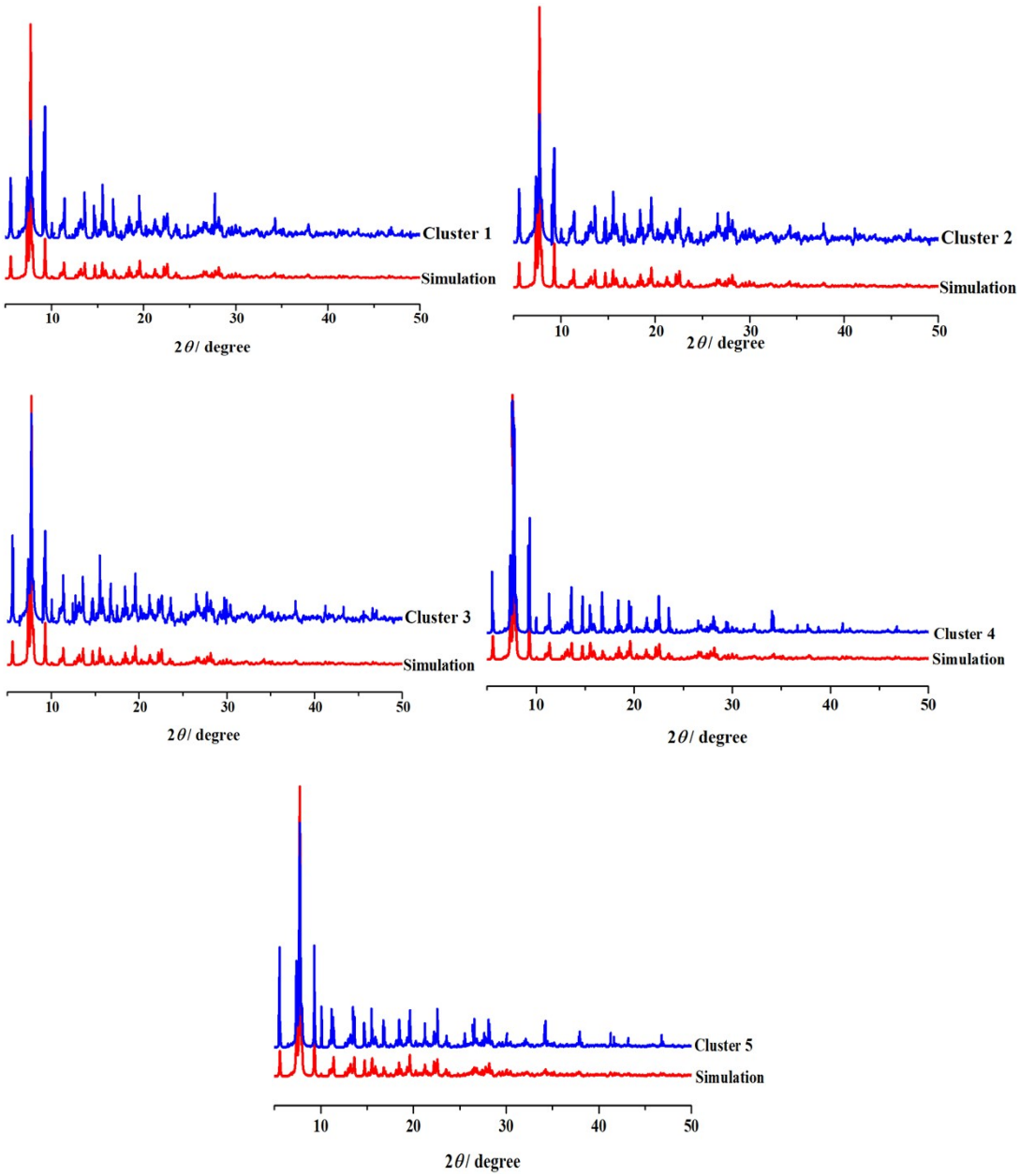


Fig. S11 PXRD patterns for clusters **1-5**.

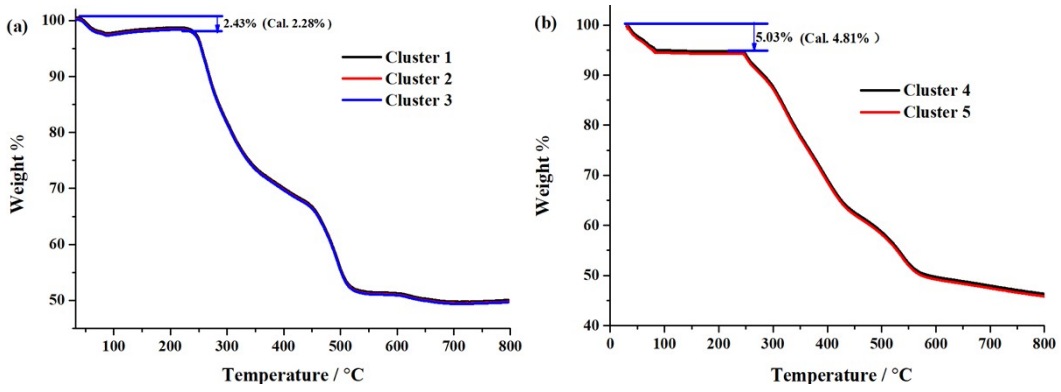


Fig. S12 The TGA curves of clusters **1-5**.

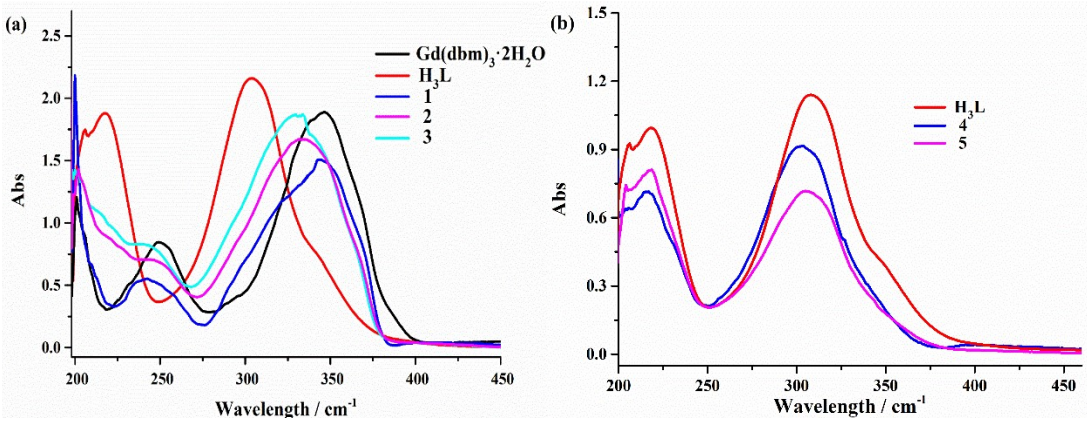


Fig. S13 (a) The UV-vis spectra of clusters **1-3,** $Gd(dbm)_3 \cdot 2H_2O$ and the H_3L ligand were performed at room temperature in ethanol solution; (b) The UV-vis spectra of clusters **4**, **5** and the H_3L ligand were performed at room temperature in ethanol solution.

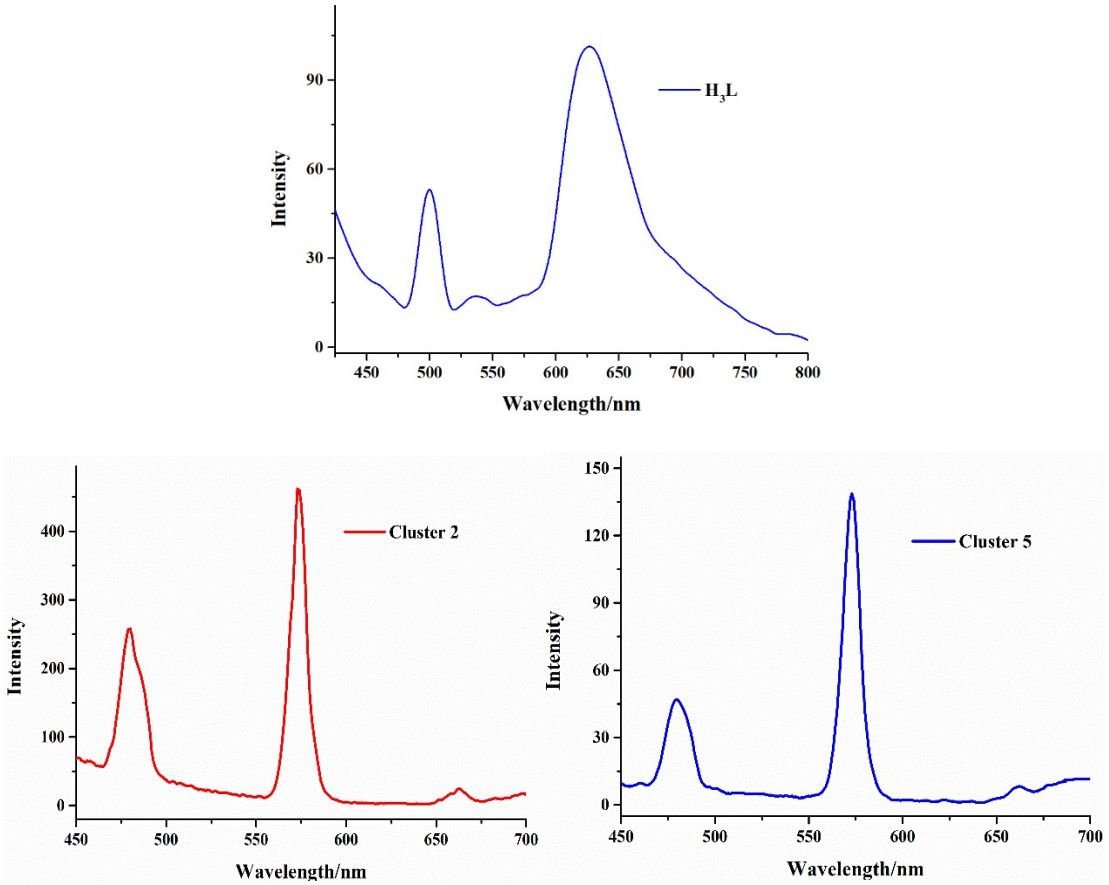


Fig. S14 The solid-state fluorescent spectra of **2** and **5** at room temperature.

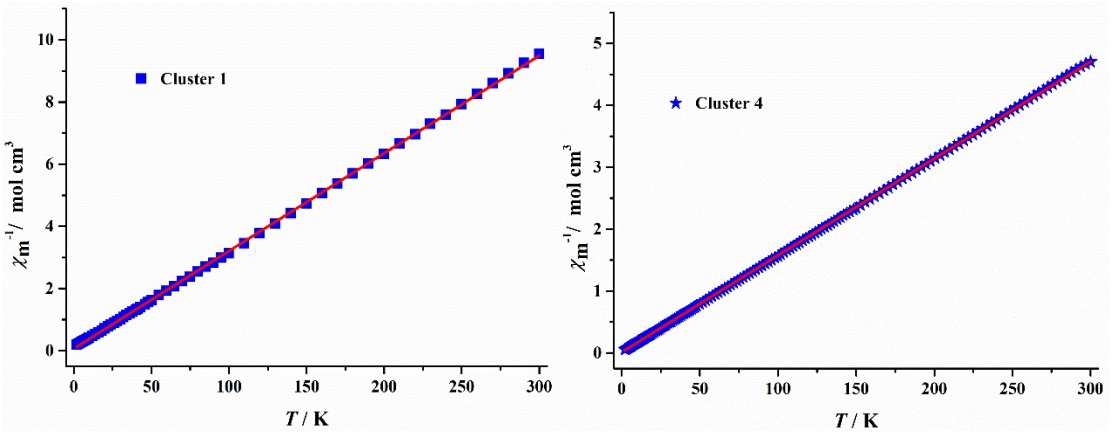


Fig. S15 Plots of χ_M^{-1} vs T for clusters **1** (left) and **4** (right). The solid lines were generated from the best fit by the Curie-Weiss expression.

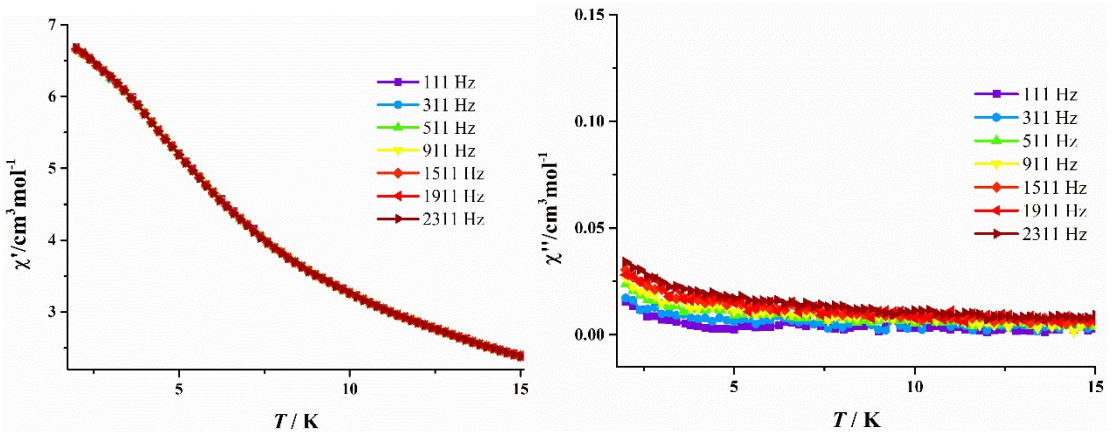


Fig. S16 Temperature dependence of the in-phase (left) and out-of-phase (right) components of the ac magnetic susceptibility for **3** in zero dc field with an oscillation of 3.0 Oe.

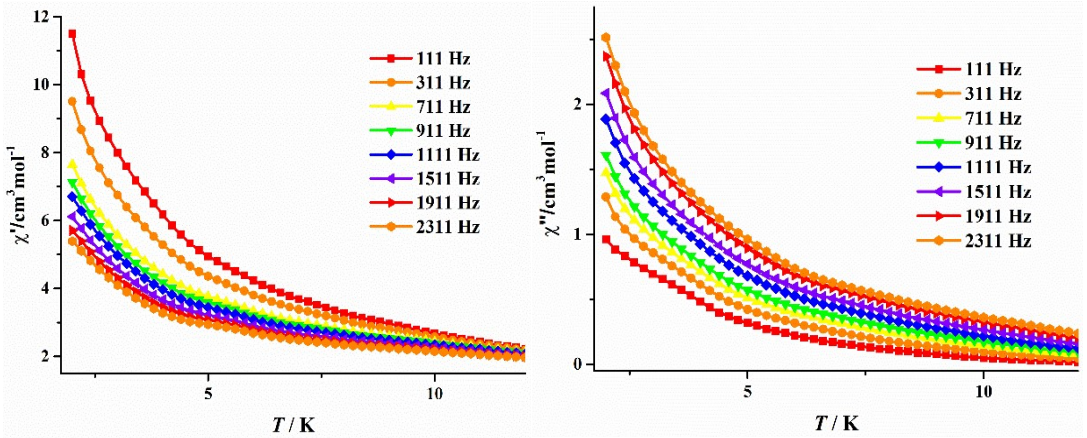


Fig. S17 Temperature dependence of the in-phase (left) and out-of-phase (right) components of the ac magnetic susceptibility for **5** in zero dc field with an oscillation of 3.0 Oe.

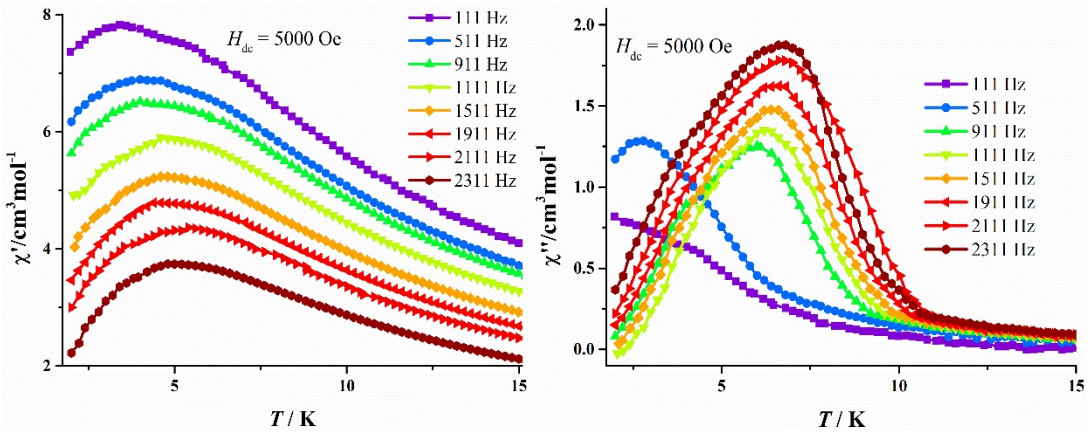


Fig. S18 Temperature dependence of the in-phase (left) and out-of-phase (right) components of the ac magnetic susceptibility for **5** under H_{dc} = 5000 Oe field with an oscillation of 3.0 Oe.

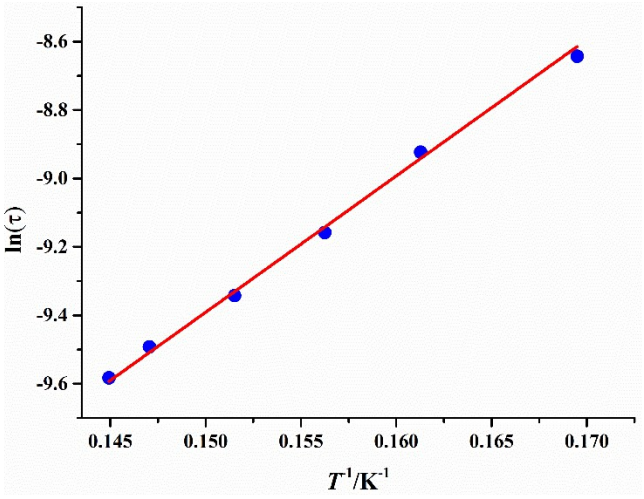


Fig. S19 lnτ versus T^{-1} plot for **5** under H_{dc} = 5000 Oe field. The red solid lines represent the least-squares fits of the experimental data to the Arrhenius law.