Electronic supplementary information

Large magnetocaloric effect and remarkable single-molecule-magnet behavior in triangle-assembled Ln^{III}_6 clusters

Wen-Min Wang,[a,b] Rong-Xin Yue,[a] Yu Gao,[a] Mei-Jiao Wang,[a] Sha-Sha Hao,[a] Ying Shi,[c] Xiao-Min Kang*[b] and Zhi-Lei Wu*[b]

Experimental Section

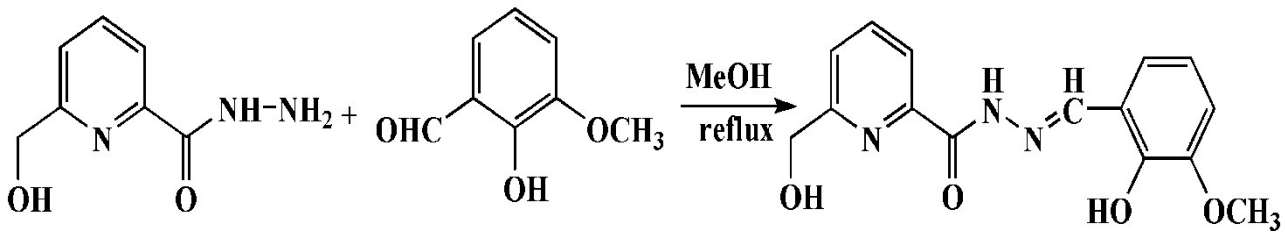
Synthesis of $Ln(acac)_3 \cdot 2H_2O$

The synthesis of $Ln(acac)_3 \cdot 2H_2O$ **(**Ln^{III} = Gd and Dy**)** is according the previous literature.[1] A solution of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln^{III} = Gd and Dy, 12 mmol) in distilled water (18 mL) was stirred for 30 min at room temperature, then 36 mmol acetylacetone (Hacac) was added to it, and the mixture was adjusted the pH to 7.0 by using NaOH solution (1 mol/L). Finally, the mixture was stirred for about 6.0 h. The mixture stood for about 3.0 hours, a precipitate formed was collected through filtration and washed with distilled water, vacuum drying for 2 day, obtaining the $Ln(acac)_3 \cdot 2H_2O$ **(**Ln^{III} = Gd and Dy**)** crude product.

Synthesis of H_3L

The synthesis of H_3L is according the reported reference (Scheme. S1).[2] A 30 mL methanolic solution of 3-methoxysalicylaldehyde (10 mmol) and 6-(hydroxymethyl) picolinohydrazide (10 mmol) was stirred at room temperature for about 30 min. After that, the reaction mixture was heated under reflux overnight, then cooled to room temperature. A precipitate formed was collected through filtration and washed with slight MeOH. Yield: 1.9 g (63%). Anal. Calcd. for $C_{15}H_{16}N_3O_4$: C, 59.60; H, 5.30; N, 13.91. Found: C, 59.64; H, 5.26; N, 13.87.

[a] *Department of Chemistry, Taiyuan Normal University, Jinzhong 030619, China.*
[b] *Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin 300071, PR China.*
[c] *Department of Biology, Taiyuan Normal University, Jinzhong 030619, China.*
** Corresponding Authors E-mail: 2120140825@mail.nankai.edu.cn (X-M. Kang), wuzhilei03@163.com (Z.-L. Wu).*



Scheme. S1. Detailed outline of the synthesis of the ligand (H_3L).

Table S1 Selected bond lengths (Å) and angles (°) for cluster **1** [a]

Bond lengths			
Gd(2)-O(4)	2.359(5)	Gd(2)-O(14)	2.767(6)
Gd(2)-O(11)	2.316(5)	Gd(2)-O(10)#1	2.461(5)
Gd(2)-O(10)	2.599(6)	Gd(2)-O(15)	2.382(6)
Gd(2)-N(3)	2.566(7)	Gd(2)-O(3)	2.409(5)
Gd(2)-N(5)	2.579(7)	Gd(1)-O(2)	2.421(5)
Gd(1)-O(5)	2.376(6)	Gd(1)-O(14)#1	2.324(5)
Gd(1)-O(11)#1	2.376(5)	Gd(1)-O(10)	2.468(5)
Gd(1)-O(6)	2.363(6)	Gd(1)-O(3)	2.369(6)
Gd(1)-N(1)	2.497(7)	Gd(3)-O(2)#1	2.399(6)
Gd(3)-O(4)	2.278(5)	Gd(3)-O(14)	2.397(6)
Gd(3)-O(11)	2.562(5)	Gd(3)-O(7)	2.378(6)
Gd(3)-O(1)#1	2.602(6)	Gd(3)-O(8)	2.376(6)
Gd(3)-O(13)	2.627(7)	Gd(3)-N(4)	2.579(8)
Bond angles			
O(4)-Gd(2)-O(14)	67.19(18)	O(4)-Gd(2)-O(10)	137.73(19)
O(4)-Gd(2)-O(10)#1	133.87(18)	O(4)-Gd(2)-O(15)	87.8(2)
O(4)-Gd(2)-O(3)	127.22(18)	O(11)-Gd(2)-O(4)	74.57(19)
O(11)-Gd(2)-O(14)	58.81(18)	O(11)-Gd(2)-O(10)#1	74.20(18)
O(11)-Gd(2)-O(10)	77.74(18)	O(11)-Gd(2)-O(15)	134.2(2)
O(11)-Gd(2)-O(3)	146.44(19)	O(10)-Gd(2)-O(14)	121.96(16)
O(10)#1-Gd(2)-O(14)	67.78(17)	O(10)#1-Gd(2)-O(10)	64.5(2)
O(15)-Gd(2)-O(14)	75.42(19)	O(15)-Gd(2)-O(10)#1	90.4(2)
O(15)-Gd(2)-O(10)	134.0(2)	O(15)-Gd(2)-O(3)	76.8(2)
O(3)-Gd(2)-O(14)	147.99(18)	O(3)-Gd(2)-O(10)#1	96.90(18)
O(3)-Gd(2)-O(10)	69.40(17)	O(2)-Gd(1)-O(10)	138.76(18)
O(5)-Gd(1)-O(2)	73.5(2)	O(5)-Gd(1)-O(11)#1	131.06(19)
O(5)-Gd(1)-O(10)	132.8(2)	O(14)#1-Gd(1)-O(2)	80.00(19)
O(14)#1-Gd(1)-O(5)	81.4(2)	O(14)#1-Gd(1)-O(11)#1	65.00(19)
O(14)#1-Gd(1)-O(10)	75.20(19)	O(14)#1-Gd(1)-O(6)	116.4(2)
O(14)#1-Gd(1)-O(3)	144.35(19)	O(11)#1-Gd(1)-O(2)	66.72(18)
O(11)#1-Gd(1)-O(10)	73.04(18)	O(6)-Gd(1)-O(2)	138.12(19)
O(6)-Gd(1)-O(10)	82.89(18)	O(6)-Gd(1)-O(3)	73.8(2)
O(3)-Gd(1)-O(2)	116.4(2)	O(3)-Gd(1)-O(5)	132.38(19)

O(3)-Gd(1)-O(11)#1	91.47(19)	O(3)-Gd(1)-O(10)	72.32(18)
O(2)#1-Gd(3)-O(11)	64.14(17)	O(2)#1-Gd(3)-O(1)#1	63.26(18)
O(2)#1-Gd(3)-O(13)	67.9(2)	O(4)-Gd(3)-O(2)#1	135.16(19)
O(4)-Gd(3)-O(14)	75.28(19)	O(4)-Gd(3)-O(11)	71.34(18)
O(4)-Gd(3)-O(7)	80.3(2)	O(4)-Gd(3)-O(1)#1	151.3(2)
O(4)-Gd(3)-O(8)	84.6(2)	O(4)-Gd(3)-O(13)	132.9(2)
O(14)-Gd(3)-O(2)#1	79.00(18)	O(14)-Gd(3)-O(11)	61.13(18)
O(14)-Gd(3)-O(1)#1	133.37(19)	O(14)-Gd(3)-O(13)	70.7(2)
O(11)-Gd(3)-O(1)#1	117.57(18)	O(11)-Gd(3)-O(13)	116.22(19)
O(7)-Gd(3)-O(2)#1	97.6(2)	O(7)-Gd(3)-O(14)	140.1(2)
O(7)-Gd(3)-O(11)	81.47(19)	O(7)-Gd(3)-O(1)#1	74.6(2)
O(7)-Gd(3)-O(13)	144.9(2)	O(1)#1-Gd(3)-O(13)	70.3(2)
O(8)-Gd(3)-O(2)#1	138.14(19)	O(8)-Gd(3)-O(14)	133.8(2)
O(8)-Gd(3)-O(11)	147.5(2)	O(8)-Gd(3)-O(7)	73.1(2)
O(8)-Gd(3)-O(1)#1	75.01(19)	O(8)-Gd(3)-O(13)	96.1(2)

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

Table S2 Selected bond lengths (Å) and angles (°) for cluster **2** [a]

Bond lengths			
Dy(1)-O(3)#1	2.417(6)	Dy(1)-O(10)	2.612(6)
Dy(1)-O(10)#1	2.461(6)	Dy(1)-O(11)	2.322(6)
Dy(1)-O(4)#1	2.358(6)	Dy(1)-O(14)	2.769(6)
Dy(1)-N(4)	2.582(8)	Dy(1)-O(15)	2.363(7)
Dy(1)-N(3)#1	2.569(7)	Dy(2)-O(3)	2.359(6)
Dy(2)-O(10)#1	2.463(6)	Dy(2)-O(11)	2.378(6)
Dy(2)-O(5)	2.372(6)	Dy(2)-O(2)	2.419(6)
Dy(2)-O(6)	2.377(6)	Dy(2)-O(14)	2.318(6)
Dy(2)-N(1)	2.503(7)	Dy(3)-O(11)	2.559(6)
Dy(3)-O(4)#1	2.275(6)	Dy(3)-O(2)	2.407(6)
Dy(3)-O(14)	2.402(6)	Dy(3)-O(7)	2.379(7)
Dy(3)-O(1)	2.622(7)	Dy(3)-O(8)	2.362(7)
Dy(3)-O(13)	2.633(8)	Dy(3)-N(5)	2.558(10)
Bond angles			
O(3)#1-Dy(1)-O(10)	69.1(2)	O(3)#1-Dy(1)-O(14)	148.2(2)
O(10)#1-Dy(1)-O(10)	64.8(2)	O(10)-Dy(1)-O(14)	121.91(17)
O(10)#1-Dy(1)-O(14)	67.41(19)	O(11)-Dy(1)-O(3)#1	146.2(2)
O(11)-Dy(1)-O(10)#1	74.2(2)	O(11)-Dy(1)-O(10)	77.8(2)
O(11)-Dy(1)-O(4)#1	74.5(2)	O(11)-Dy(1)-O(14)	58.8(2)
O(11)-Dy(1)-O(15)	134.2(2)	O(4)#1-Dy(1)-O(3)#1	127.4(2)
O(4)#1-Dy(1)-O(10)#1	133.6(2)	O(4)#1-Dy(1)-O(10)	137.8(2)
O(4)#1-Dy(1)-O(14)	67.2(2)	O(4)#1-Dy(1)-O(15)	87.1(3)
O(15)-Dy(1)-O(3)#1	77.3(2)	O(15)-Dy(1)-O(10)	134.6(2)
O(15)-Dy(1)-O(10)#1	90.9(2)	O(15)-Dy(1)-O(14)	75.5(2)

O(3)-Dy(2)-O(10)#1	72.6(2)	O(3)-Dy(2)-O(11)	91.7(2)
O(3)-Dy(2)-O(5)	73.8(2)	O(3)-Dy(2)-O(2)	116.4(2)
O(3)-Dy(2)-O(6)	132.2(2)	O(11)-Dy(2)-O(10)#1	73.22(19)
O(11)-Dy(2)-O(2)	66.7(2)	O(5)-Dy(2)-O(10)#1	83.0(2)
O(5)-Dy(2)-O(11)	155.0(2)	O(5)-Dy(2)-O(2)	137.9(2)
O(5)-Dy(2)-O(6)	71.6(2)	O(2)-Dy(2)-O(10)#1	138.9(2)
O(6)-Dy(2)-O(10)#1	132.8(2)	O(6)-Dy(2)-O(11)	130.9(2)
O(6)-Dy(2)-O(2)	73.2(2)	O(14)-Dy(2)-O(3)	144.5(2)
O(14)-Dy(2)-O(10)#1	75.0(2)	O(14)-Dy(2)-O(11)	65.1(2)
O(14)-Dy(2)-O(5)	116.2(2)	O(14)-Dy(2)-O(2)	80.2(2)
O(14)-Dy(2)-O(6)	81.4(2)	O(11)-Dy(3)-O(1)	117.3(2)
O(11)-Dy(3)-O(13)	116.2(2)	O(4)#1-Dy(3)-O(11)	71.4(2)
O(4)#1-Dy(3)-O(2)	135.2(2)	O(4)#1-Dy(3)-O(14)	75.3(2)
O(4)#1-Dy(3)-O(7)	80.6(2)	O(4)#1-Dy(3)-O(1)	151.8(2)
O(4)#1-Dy(3)-O(8)	84.4(2)	O(4)#1-Dy(3)-O(13)	132.5(2)
O(2)-Dy(3)-O(11)	64.11(19)	O(2)-Dy(3)-O(1)	62.9(2)
O(2)-Dy(3)-O(13)	68.0(2)	O(14)-Dy(3)-O(11)	61.2(2)
O(14)-Dy(3)-O(2)	78.8(2)	O(14)-Dy(3)-O(1)	132.9(2)
O(14)-Dy(3)-O(13)	70.5(2)	O(7)-Dy(3)-O(11)	81.4(2)
O(7)-Dy(3)-O(2)	97.6(2)	O(7)-Dy(3)-O(14)	140.2(2)
O(7)-Dy(3)-O(1)	74.8(2)	O(7)-Dy(3)-O(13)	145.0(2)
O(1)-Dy(3)-O(13)	70.3(2)	O(8)-Dy(3)-O(11)	147.3(2)
O(8)-Dy(3)-O(2)	138.3(2)	O(8)-Dy(3)-O(14)	133.9(2)
O(8)-Dy(3)-O(7)	73.0(2)	O(8)-Dy(3)-O(1)	75.5(2)
O(8)-Dy(3)-O(13)	96.3(2)		

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

Table S3 The Gd^{III} geometry analysis by SHAPE 2.0 for cluster **1**.

Cluster 3	D_{4d}**SAPR**	D_{2d}**TDD**	C_{2v}**JBTPR**	C_{2v}**BTPR**	D_{2d}**JSD**
eight-coordinated $Gd1^{III}$	1.487	3.197	3.173	2.769	5.001
	C_{4v}**JCSAPR**	C_{4v}**CSAPR**	D_{3h}**JTCTPR**	D_{3h}**TCTPR**	C_s**MFF**
nine-coordinated $Gd2^{III}$	2.336	2.179	2.342	2.515	2.340
nine-coordinated $Gd3^{III}$	2.039	1.460	2.308	1.335	1.384

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.

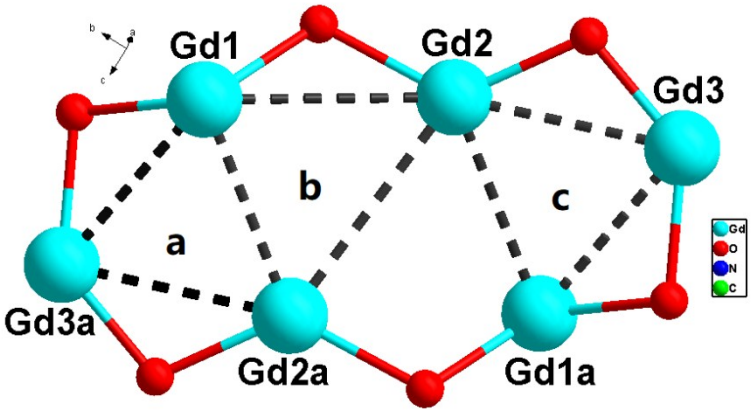


Fig. S1 The Gd_6 core of **1** highlighting the triangular units (dashed lines).

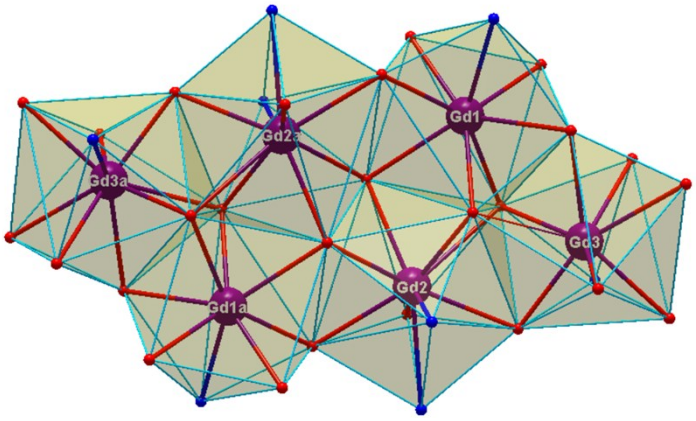


Fig. S2 The geometric polyhedra of Gd^{III} ions observed in cluster **1**.

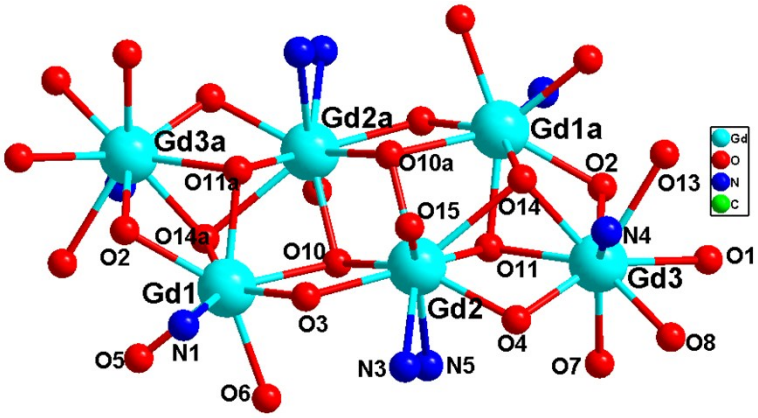


Fig. S3 Coordination atoms labels of the Gd_6 core in **1.**

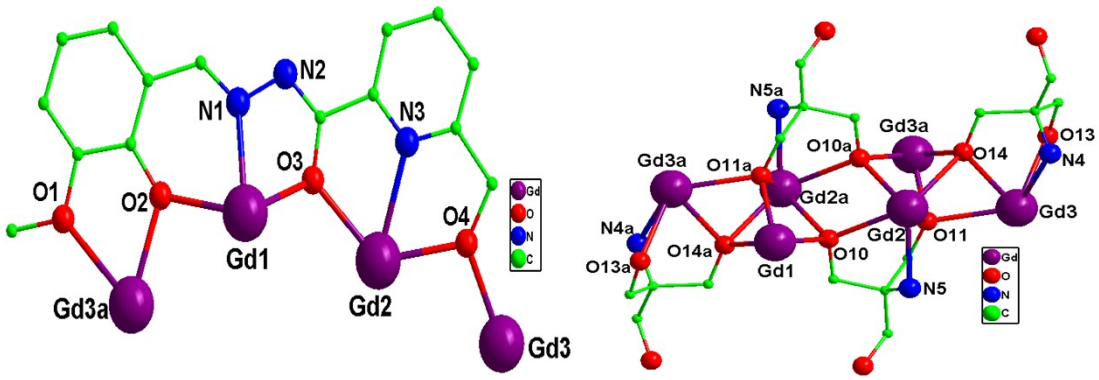


Fig. S4 Binding modes of the ligand H_3L (left) and THAM (right) in cluster **1**.

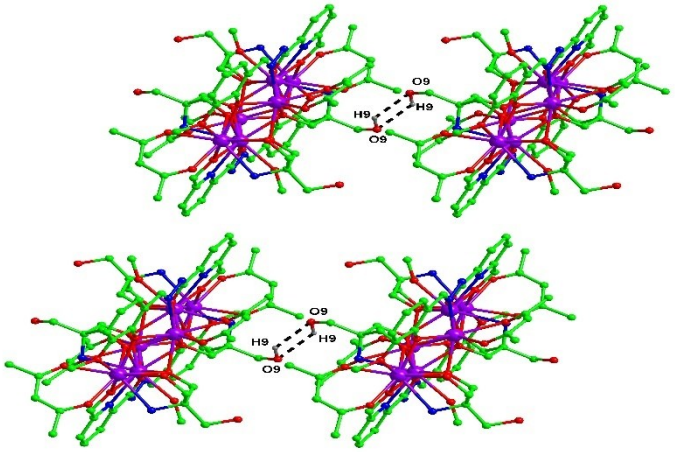


Fig. S5 The hydrogen bond connected mode and crystal packing in cluster **1**.

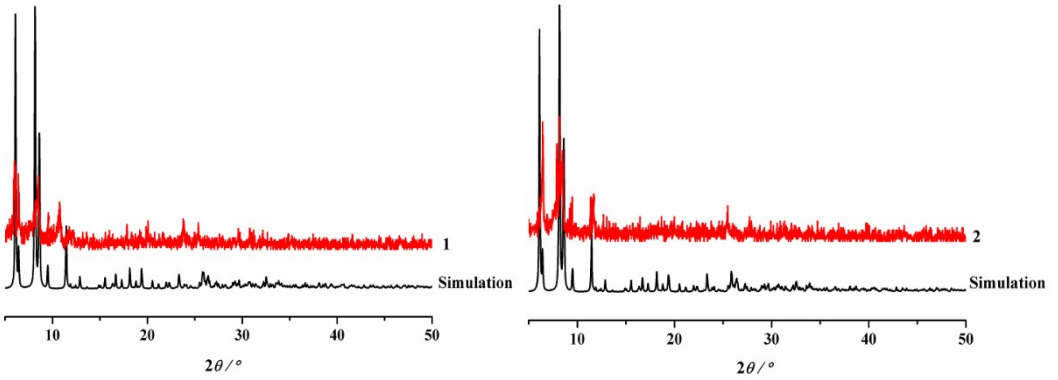


Fig. S6 PXRD patterns for clusters **1** and **2**.

References

1 S. Katagiri, Y. Tsukahara, Y. Hasegawa and Y. Wada, *Bull. Chem. Soc. Jpn*., 2007, **80**, 1492.

2 (a) V. Chandrasekhar, S. Hossain, S. Das, S. Biswas and J. P. Sutter, *Inorg. Chem*., 2013, **52**, 6346; (b)W. M. Wang, X. Z. Li, L. Zhang, J. L. Chen, J. H. Wang, Z. L. Wu and J. Z. Cui, *New J. Chem.,* 2019, **43**, 7419.