Electronic supplementary information

'Windmill'-shaped Ln^{III}_4 (Ln^{III} = Gd and Dy) clusters: magnetocaloric effect and single-molecule-magnet behavior

Wen-Min Wang,[a,b] Mei-Jiao Wang,[a] Sha-Sha Hao,[a] Qin-Yu Shen,[a] Mei-Ling Wang,[a] Qiao-Ling Liu,[a] Xiao-Fen Guan,[*a] Xiu-Tang Zhang,[*c] Zhi-Lei Wu[*b]

Experimental Section

Materials and Methods

Solvents and other chemicals used in this paper were reagent grade without further purification. Dimethylpyridine-2,6-dicarboxylate, sodium borohydride, acetyl acetone, hydrazine hydrate (80%), sodium sulfate, 4-(diethylamino)salicylaldehyde and lanthanide salts ($Gd(NO_3)_3 \cdot 6H_2O$ and $Dy(NO_3)_3 \cdot 6H_2O$) were procured from chemical reagent company. The β-diketone salts ($Gd(acac)_3 \cdot 2H_2O$ and $Dy(acac)_3 \cdot 2H_2O$) and the Schiff base ligand H_2L were synthesized according to the method in the literature.[1,2] Elemental analyses (EA) for C, H and N were performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were measured on a Bruker TENOR 27 spectrophotometer using a KBr pellet in the range of $4000-400$ cm^{-1}. PXRD data were examined on a Rigaku Ultima IV instrument with Cu Kα radiation (λ = 1.54056 Å), with a scan speed of $10°$ min^{-1} in the range of $2\theta = 5-50°$. The magnetic measurements were carried out with a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. Polycrystalline samples of clusters **1** and **2** were collected by solvent evaporation and dried them in the air, which using for magnetic measurements were frozen in eicosane to avoid torquing of the crystallites. Dc susceptibility was measured in the temperature domain $2.0-300$ K under an applied field of 1000 Oe. Ac susceptibility was measured with an oscillating ac field of 3.0 Oe using frequencies between 111 to 2311 Hz. The diamagnetic corrections for the complexes were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.[3]

[a] Department of Chemistry, Taiyuan Normal University, Jinzhong 030619, China. Corresponding Authors E-mail: wuzhilei03@163.com (Z.-L. Wu), lucia0812@163.com (Y. Shi), xiutangzhang@163.com(X-T. Zhang).
[b] Department of Chemistry, Tianjin University, Tianjin, 300072, China.
[c] Department of Chemistry, College of Science, North University of China, Taiyuan 030051, China.

Synthesis of H₃L

According to the previous method reported by references (Scheme. S1),[2] the ligand N′-(4-diethylamino-2-hydroxybenzylidene)-6-(hydroxymethyl)picolinohydrazide (H_2L) has been obtained. A methanolic solution (20.0 mL) of 3-methoxysalicylaldehyde (10 mmol) was added dropwise to a stirred suspension of 6-(hydroxymethyl) picolinohydrazide (10 mmol) in methanol (5.0 mL) at room temperature. 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: 1.7 g (51%). Anal. Calcd. for $C_{18}H_{19}N_4O_3$: C, 63.72; H, 5.60; N, 16.52. Found: C, 63.66; H, 5.65; N, 16.46.
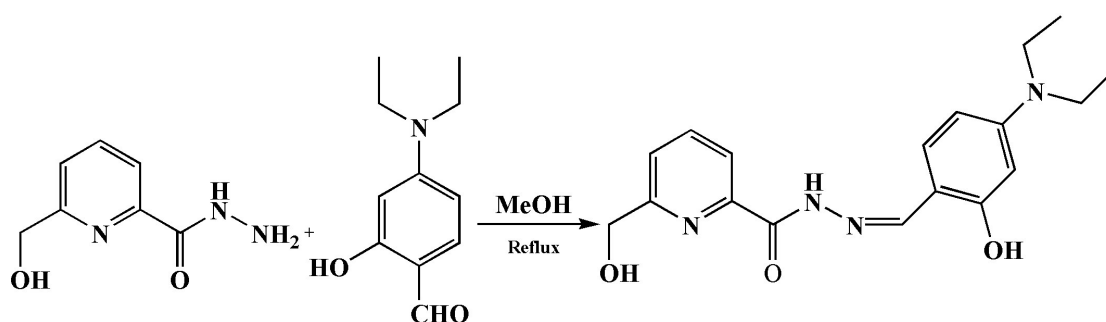
Scheme. S1. Detailed outline of the synthesis of the ligand (H_3L).

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

Bond lengths			
Gd(1)-O(2)	2.330(5)	Gd(1)-O(2)#2	2.356(5)
Gd(1)-O(3)#2	2.282(6)	Gd(1)-N(3)#2	2.512(8)
Gd(1)-N(1)	2.530(8)	Gd(1)-O(1)	2.434(6)
Gd(1)-O(4)	2.303(5)	Gd(1)-O(4)#1	2.280(6)
Bond angles			
O(2)-Gd(1)-O(2)#2	134.9(3)	O(2)-Gd(1)-O(1)	127.5(2)
O(2)#2-Gd(1)-O(1)	86.4(2)	O(3)#2-Gd(1)-O(2)#2	135.8(2)
O(3)#2-Gd(1)-O(2)	82.2(2)	O(3)#2-Gd(1)-O(1)	84.6(2)
O(3)#2-Gd(1)-O(4)	154.9(2)	O(4)-Gd(1)-O(2)#2	66.2(2)
O(4)#1-Gd(1)-O(2)	67.0(2)	O(4)-Gd(1)-O(2)	85.7(2)
O(4)#1-Gd(1)-O(2)#2	84.2(2)	O(4)#1-Gd(1)-O(3)#2	93.7(2)
O(4)#1-Gd(1)-O(1)	164.7(2)	O(4)-Gd(1)-O(1)	85.4(2)
O(4)#1-Gd(1)-O(4)	101.7(3)		

[a] Symmetry transformations used to generate equivalent atoms: #1 y+1/4, -x+3/4, -z+3/4; #2 -y+3/4, x-1/4, -z+3/4.

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

Bond lengths

Dy(1)-O(3)	2.320(10)	Dy(1)-O(2)#2	2.360(10)
Dy(1)-O(2)	2.366(9)	Dy(1)-O(1)#2	2.452(10)
Dy(1)-O(4)#1	2.343(10)	Dy(1)-O(4)	2.277(9)
Dy(1)-N(3)	2.564(13)	Dy(1)-N(1)#2	2.517(8)

Bond angles

O(3)-Dy(1)-Dy(1)#1	169.3(3)	O(3)-Dy(1)-Dy(1)#2	96.2(3)
O(3)-Dy(1)-O(2)	134.4(4)	O(3)-Dy(1)-O(2)#2	84.3(4)
O(3)-Dy(1)-O(1)#2	85.8(3)	O(3)-Dy(1)-O(4)#1	157.1(4)
O(2)#2-Dy(1)-O(2)	136.1(4)	O(2)#2-Dy(1)-O(1)#2	128.2(4)
O(2)-Dy(1)-O(1)#2	82.0(4)	O(4)-Dy(1)-O(3)	93.9(4)
O(4)#1-Dy(1)-O(2)	66.1(4)	O(4)#1-Dy(1)-O(2)#2	82.2(3)
O(4)-Dy(1)-O(2)#2	67.3(4)	O(4)-Dy(1)-O(2)	87.1(3)
O(4)#1-Dy(1)-O(1)#2	88.0(4)	O(4)-Dy(1)-O(1)#2	164.3(4)
O(4)-Dy(1)-O(4)#1	97.9(5)		

^{a} Symmetry transformations used to generate equivalent atoms: #1 y+1/4, -x+3/4, -z+3/4; #2 -y+3/4x-1/4-z+3/4.

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

Cluster 1	D_{4d}SAPR	D_{2d}TDD	C_{2v}JBTPR	C_{2v}BTPR	D_{2d}JSD
Gd1^{III}	4.368	1.008	3.137	3.065	3.013
Gd2^{III}	4.257	0.986	2.956	2.457	2.967

SAPR-8 = Square antiprism; **TDD-8** = Triangular dodecahedron; **JBTPR-8** = Biaugmented trigonal prism J50; **BTPR-8** = Biaugmented trigonal prism; **JSD-8** = Snub diphenoid J84.
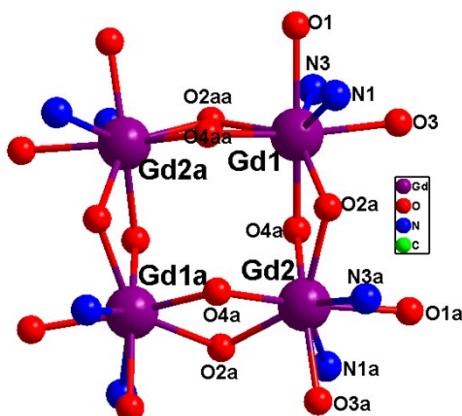

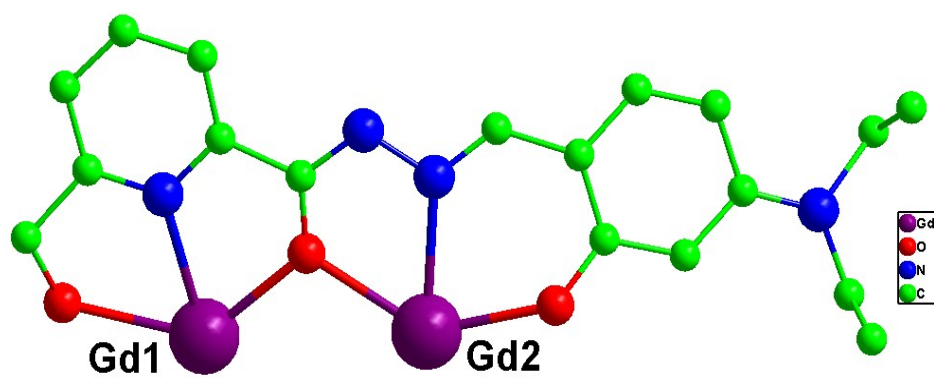**Fig. S1** Coordination atoms labels of the Gd$_4$ core in **1**.
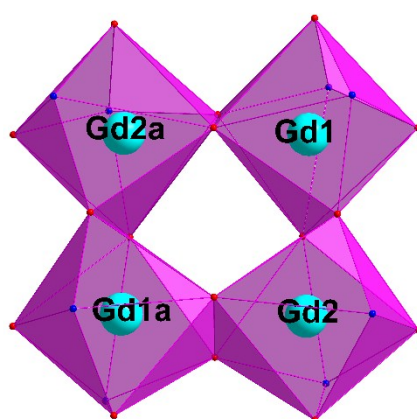
Fig. S2 Binding modes of the ligand H_2L in cluster **1**.

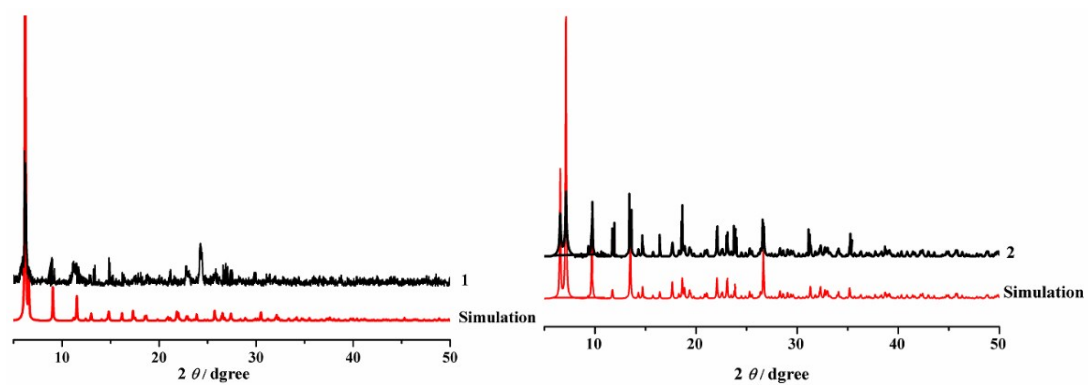**Fig. S3** The geometric polyhedra of Gd^{III} ions observed in cluster **1**.

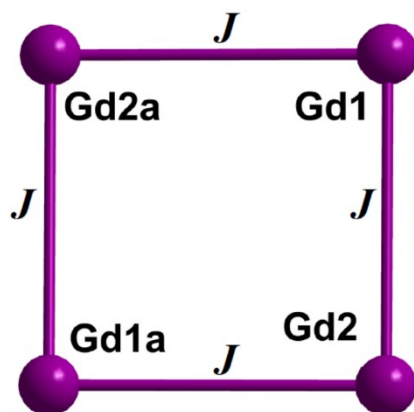**Fig. S4** PXRD patterns for clusters **1** and **2**.

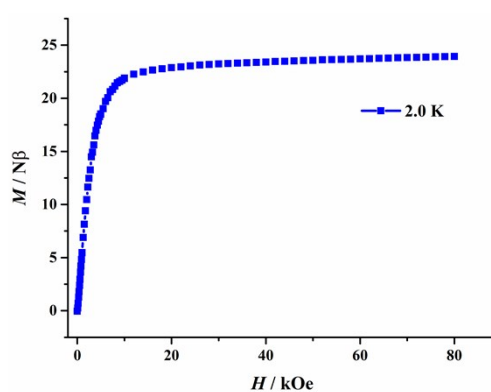**Fig. S5** The magetic coupling model of Gd(III) ions in cluster **1**.

Fig. S6 Magnetization data vs H for cluster **2** in the field range 0–80 kOe at 2.0 K.
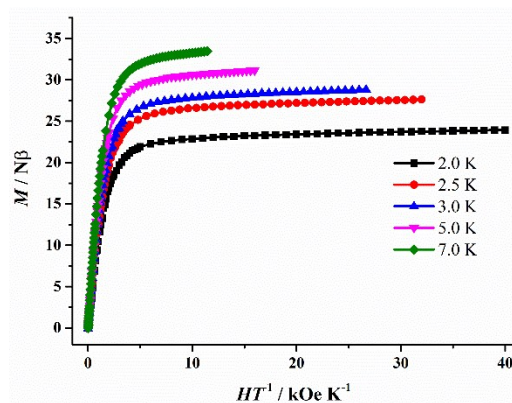

Fig. S7 Magnetization data vs HT^{-1} for cluster **2** in the field range 0–80 kOe.

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) S. Biswas, S. Das, S. Hossain, A. K. Bar, J. P. Sutter and V. Chandrasekhar, *Eur. J. Inorg. Chem.,* 2016, **28**, 4683.