Two hexanuclear lanthanide clusters Ln_6^{III} featuring remarkable magnetocaloric effect and slow magnetic relaxation behavior

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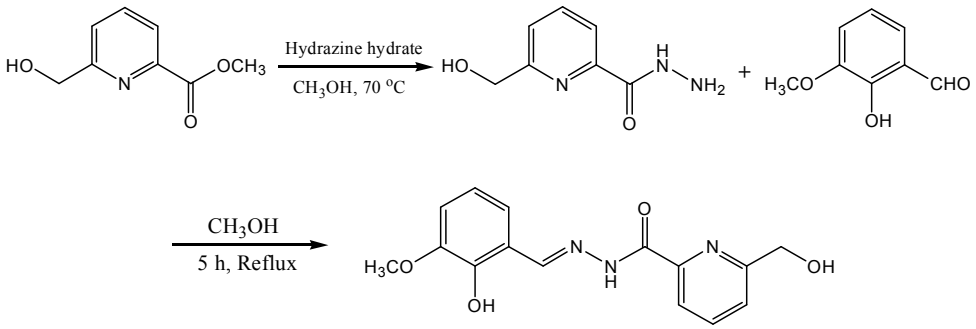

Scheme S1. The synthetic procedure of ligand H_3L.

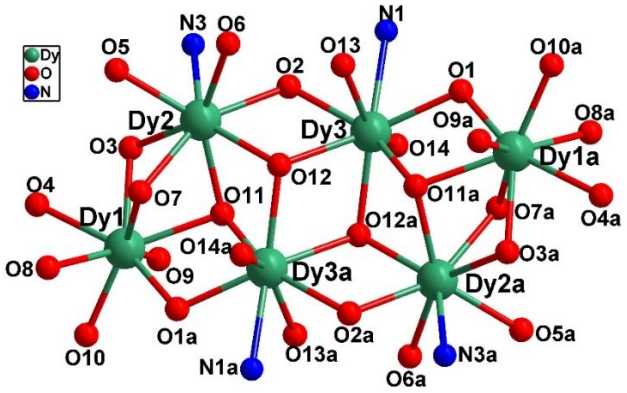

Fig. S1 Coordination environment of the Dy_6 core in **2**.

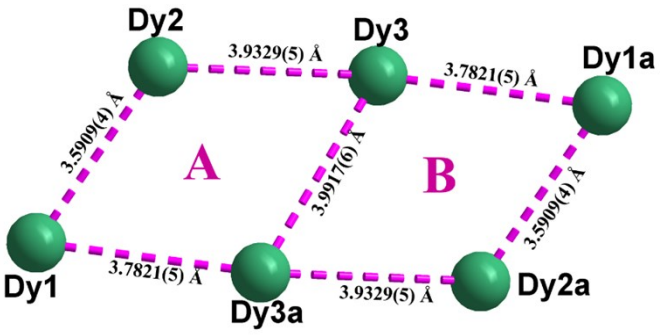

Fig. S2 The Dy_6 core of **2** highlighting the quadrangle units (dashed lines).

X-ray Crystallography

Crystallographic data collection of **1** and **2** were performed at 150.0 K on a Rigaku Saturn CCD diffractometer with graphite-monochromated Mo Kα radiation (λ =

0.71073 Å). The crystal structures were solved by direct methods and refined on F^2 using full-matrix least squares (SHELXL-2018). All non-hydrogen atoms were refined with anisotropic thermal parameters. Details for crystal data and refinement for **1** and **2** are summarized in Table S1, and the important bond distances (Å) and angles (°) are listed in Table S2 and Table S3. CCDC 2015150 for **1** and 2015151 for **2** contain the supplementary crystal data for this paper.

Table S1. Crystallographic data and structure refinements for compounds **1** and **2**.

Complexes	**1**·Gd	**2**·Dy
formula	$C_{70}H_{95}Gd_6N_{11}O_{34}$	$C_{70}H_{95}Dy_6N_{11}O_{34}$
fw	2578.08	2609.58
T/K	150.0	150.0
Cryst syst	Monoclinic	Triclinic
Space group	*P* $2_1/n$	*P*-1
a/Å	14.4727(6)	14.2565(6)
b/Å	19.6943(9)	14.3411(7)
c/Å	16.4655(7)	14.4407(7)
α/°	90	91.697(3)
β/°	90.532(2)	114.999(2)
γ/°	90	116.737(2)
Volume/Å^3	4693.0(4)	2299.99(19)
Z	2	1
ρ_{calc}mg/mm^3	1.824	1.884
μ/mm^{-1}	4.251	4.885
F(000)	2292	1158
θ/°	2.410 to 26.414	2.607 to 26.019
Reflections collected	58285	38431
Unique reflns	9621	9035
Goodness-of-fit on F^2	1.049	1.041
R_1, wR_2 ($I > 2\sigma(I)$)	0.0367, 0.0901	0.0404, 0.1034
R_1, wR_2 (all data)	0.0531, 0.0998	0.0570, 0.1134

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

bond lengths			
Gd(1)-O(14)	2.510(5)	Gd(2)-O(5)	2.323(5)
Gd(1)-N(1)#1	2.539(5)	Gd(2)-O(7)	2.320(5)
Gd(1)-O(11)#1	2.433(4)	Gd(2)-O(3)	2.344(4)
Gd(1)-O(11)	2.401(4)	Gd(2)-O(8)	2.463(4)
Gd(1)-O(2)#1	2.377(4)	Gd(3)-O(11)	2.393(4)
Gd(1)-O(1)#1	2.322(4)	Gd(3)-O(2)	2.311(4)
Gd(1)-O(12)	2.325(4)	Gd(3)-O(12)	2.361(4)
Gd(1)-O(13)	2.409(5)	Gd(3)-O(10)	2.360(4)
Gd(2)-O(6)	2.297(5)	Gd(3)-N(3)	2.474(5)
Gd(2)-O(1)#1	2.253(4)	Gd(3)-O(9)	2.312(4)
Gd(2)-O(4)	2.521(5)	Gd(3)-O(3)	2.334(4)
Gd(2)-O(12)	2.400(4)	Gd(3)-O(8)	2.391(5)
bond angles			
O(14)-Gd(1)-N(1)#1	72.94(15)	O(12)-Gd(2)-O(8)	68.47(15)
O(11)-Gd(1)-O(14)	76.33(14)	O(5)-Gd(2)-O(4)	95.32(16)
O(11)#1-Gd(1)-O(14)	122.99(14)	O(5)-Gd(2)-O(12)	72.01(17)
O(11)-Gd(1)-N(1)#1	149.05(15)	O(5)-Gd(2)-O(3)	83.07(15)
O(11)#1-Gd(1)-N(1)#1	124.30(15)	O(5)-Gd(2)-O(8)	139.08(16)
O(11)-Gd(1)-O(11)#1	70.93(16)	O(7)-Gd(2)-O(4)	73.40(16)
O(11)-Gd(1)-O(13)	133.35(15)	O(7)-Gd(2)-O(12)	136.66(16)
O(2)#1-Gd(1)-O(14)	77.31(14)	O(7)-Gd(2)-O(5)	149.12(17)
O(2)#1-Gd(1)-N(1)#1	63.63(16)	O(7)-Gd(2)-O(3)	115.42(16)
O(2)#1-Gd(1)-O(11)#1	69.00(14)	O(7)-Gd(2)-O(8)	71.77(16)
O(2)#1-Gd(1)-O(11)	106.08(14)	O(3)-Gd(2)-O(4)	64.57(15)
O(2)#1-Gd(1)-O(13)	82.31(15)	O(3)-Gd(2)-O(12)	67.93(15)
O(1)#1-Gd(1)-O(14)	92.01(16)	O(3)-Gd(2)-O(8)	72.80(15)
O(1)#1-Gd(1)-N(1)#1	64.52(16)	O(8)-Gd(2)-O(4)	103.07(15)
O(1)#1-Gd(1)-O(11)#1	144.90(15)	O(11)-Gd(3)-N(3)	135.31(16)
O(1)#1-Gd(1)-O(11)	120.74(15)	O(2)-Gd(3)-O(11)	70.78(14)
O(1)#1-Gd(1)-O(2)#1	127.94(15)	O(2)-Gd(3)-O(12)	89.35(15)
O(1)#1-Gd(1)-O(12)	70.39(15)	O(2)-Gd(3)-O(10)	78.93(16)
O(1)#1-Gd(1)-O(13)	81.55(16)	O(2)-Gd(3)-N(3)	64.53(16)
O(12)-Gd(1)-O(14)	122.05(15)	O(2)-Gd(3)-O(9)	129.57(17)
O(12)-Gd(1)-N(1)#1	133.04(16)	O(2)-Gd(3)-O(3)	117.50(15)
O(12)-Gd(1)-O(11)	68.39(15)	O(2)-Gd(3)-O(8)	151.57(15)
O(12)-Gd(1)-O(11)#1	86.84(14)	O(12)-Gd(3)-O(11)	67.94(14)
O(12)-Gd(1)-O(2)#1	155.41(15)	O(12)-Gd(3)-N(3)	110.37(17)
O(12)-Gd(1)-O(13)	85.13(16)	O(12)-Gd(3)-O(8)	70.30(15)
O(13)-Gd(1)-O(14)	148.24(15)	O(10)-Gd(3)-O(11)	77.40(15)
O(13)-Gd(1)-N(1)#1	76.25(16)	O(10)-Gd(3)-O(12)	145.35(16)

O(13)-Gd(1)-O(11)#1	69.88(15)	O(10)-Gd(3)-N(3)	93.90(17)
O(6)-Gd(2)-O(4)	78.67(17)	O(10)-Gd(3)-O(8)	106.37(16)
O(6)-Gd(2)-O(12)	135.07(17)	O(9)-Gd(3)-O(11)	137.33(16)
O(6)-Gd(2)-O(5)	73.28(18)	O(9)-Gd(3)-O(12)	135.77(17)
O(6)-Gd(2)-O(7)	76.31(18)	O(9)-Gd(3)-O(10)	72.40(17)
O(6)-Gd(2)-O(3)	133.91(16)	O(9)-Gd(3)-N(3)	76.87(18)
O(6)-Gd(2)-O(8)	145.84(17)	O(9)-Gd(3)-O(3)	73.93(16)
O(1)#1-Gd(2)-O(6)	88.55(17)	O(9)-Gd(3)-O(8)	77.54(18)
O(1)#1-Gd(2)-O(4)	156.76(16)	O(3)-Gd(3)-O(11)	135.72(14)
O(1)#1-Gd(2)-O(12)	70.19(15)	O(3)-Gd(3)-O(12)	68.75(15)
O(1)#1-Gd(2)-O(5)	99.51(17)	O(3)-Gd(3)-O(10)	145.21(15)
O(1)#1-Gd(2)-O(7)	84.82(17)	O(3)-Gd(3)-N(3)	69.98(16)
O(1)#1-Gd(2)-O(3)	134.85(15)	O(3)-Gd(3)-O(8)	74.30(15)
O(1)#1-Gd(2)-O(8)	76.91(16)	O(8)-Gd(3)-O(11)	82.97(15)
O(12)-Gd(2)-O(4)	131.96(15)	O(8)-Gd(3)-N(3)	140.49(16)

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

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

bond lengths			
Dy(1)-O(10)	2.331(4)	Dy(2)-O(7)	2.405(5)
Dy(1)-O(1)#1	2.271(5)	Dy(2)-O(11)	2.397(4)
Dy(1)-O(3)	2.375(4)	Dy(2)-N(3)	2.476(6)
Dy(1)-O(9)	2.314(5)	Dy(2)-O(12)	2.403(5)
Dy(1)-O(4)	2.520(5)	Dy(3)-O(1)	2.333(4)
Dy(1)-O(8)	2.325(5)	Dy(3)-O(2)	2.393(4)
Dy(1)-O(7)	2.466(4)	Dy(3)-O(13)	2.443(4)
Dy(1)-O(11)	2.390(4)	Dy(3)-O(14)	2.283(5)
Dy(2)-O(6)	2.381(4)	Dy(3)-N(1)	2.525(5)
Dy(2)-O(2)	2.338(5)	Dy(3)-O(11)#1	2.349(5)
Dy(2)-O(3)	2.342(4)	Dy(3)-O(12)	2.471(5)
Dy(2)-O(5)	2.333(5)	Dy(3)-O(12)#1	2.425(4)
bond angles			
O(10)-Dy(1)-O(3)	140.79(16)	O(3)-Dy(2)-O(12)	137.12(14)
O(10)-Dy(1)-O(4)	83.21(16)	O(5)-Dy(2)-O(6)	72.23(16)
O(10)-Dy(1)-O(7)	143.17(17)	O(5)-Dy(2)-O(2)	131.04(16)
O(10)-Dy(1)-O(11)	131.32(16)	O(5)-Dy(2)-O(3)	74.79(15)
O(1)#1-Dy(1)-O(10)	83.22(17)	O(5)-Dy(2)-O(7)	75.12(16)
O(1)#1-Dy(1)-O(3)	134.25(15)	O(5)-Dy(2)-O(11)	135.62(15)
O(1)#1-Dy(1)-O(9)	107.39(18)	O(5)-Dy(2)-N(3)	77.54(18)
O(1)#1-Dy(1)-O(4)	158.63(16)	O(5)-Dy(2)-O(12)	135.02(17)
O(1)#1-Dy(1)-O(8)	85.81(17)	O(7)-Dy(2)-N(3)	138.39(18)
O(1)#1-Dy(1)-O(7)	76.05(16)	O(11)-Dy(2)-O(7)	70.21(15)
O(1)#1-Dy(1)-O(11)	70.98(16)	O(11)-Dy(2)-N(3)	112.04(17)

O(3)-Dy(1)-O(4)	63.69(14)	O(11)-Dy(2)-O(12)	69.15(14)
O(3)-Dy(1)-O(7)	70.57(15)	O(12)-Dy(2)-O(7)	85.85(17)
O(3)-Dy(1)-O(11)	68.49(15)	O(12)-Dy(2)-N(3)	135.04(18)
O(9)-Dy(1)-O(10)	72.90(17)	O(1)-Dy(3)-O(2)	128.18(15)
O(9)-Dy(1)-O(3)	82.89(16)	O(1)-Dy(3)-O(13)	79.77(16)
O(9)-Dy(1)-O(4)	84.17(19)	O(1)-Dy(3)-N(1)	65.18(17)
O(9)-Dy(1)-O(8)	144.71(18)	O(1)-Dy(3)-O(11)#1	70.66(16)
O(9)-Dy(1)-O(7)	142.37(16)	O(1)-Dy(3)-O(12)	142.52(16)
O(9)-Dy(1)-O(11)	76.46(17)	O(1)-Dy(3)-O(12)#1	122.30(16)
O(8)-Dy(1)-O(10)	76.55(17)	O(2)-Dy(3)-O(13)	80.20(16)
O(8)-Dy(1)-O(3)	111.56(16)	O(2)-Dy(3)-N(1)	63.44(16)
O(8)-Dy(1)-O(4)	75.02(18)	O(2)-Dy(3)-O(12)#1	105.37(15)
O(8)-Dy(1)-O(7)	71.93(17)	O(2)-Dy(3)-O(12)	68.87(16)
O(8)-Dy(1)-O(11)	138.45(17)	O(13)-Dy(3)-N(1)	73.73(18)
O(7)-Dy(1)-O(4)	106.04(16)	O(13)-Dy(3)-O(12)	70.28(15)
O(11)-Dy(1)-O(4)	130.07(16)	O(14)-Dy(3)-O(1)	91.87(19)
O(11)-Dy(1)-O(7)	69.31(15)	O(14)-Dy(3)-O(2)	81.43(18)
O(6)-Dy(2)-O(7)	113.33(17)	O(14)-Dy(3)-O(13)	148.42(19)
O(6)-Dy(2)-O(11)	147.77(16)	O(14)-Dy(3)-N(1)	75.13(19)
O(6)-Dy(2)-N(3)	86.83(18)	O(14)-Dy(3)-O(11)#1	120.49(18)
O(6)-Dy(2)-O(12)	79.01(15)	O(14)-Dy(3)-O(12)	125.34(18)
O(2)-Dy(2)-O(6)	76.08(16)	O(14)-Dy(3)-O(12)#1	74.71(18)
O(2)-Dy(2)-O(3)	116.17(16)	O(11)#1-Dy(3)-O(2)	152.97(16)
O(2)-Dy(2)-O(7)	153.17(16)	O(11)#1-Dy(3)-O(13)	85.59(16)
O(2)-Dy(2)-O(11)	88.58(15)	O(11)#1-Dy(3)-N(1)	133.66(16)
O(2)-Dy(2)-N(3)	64.25(17)	O(11)#1-Dy(3)-O(12)#1	69.56(15)
O(2)-Dy(2)-O(12)	70.94(16)	O(11)#1-Dy(3)-O(12)	84.75(16)
O(3)-Dy(2)-O(6)	143.35(16)	O(12)#1-Dy(3)-O(13)	135.16(17)
O(3)-Dy(2)-O(7)	72.18(16)	O(12)#1-Dy(3)-N(1)	149.11(18)
O(3)-Dy(2)-O(11)	68.88(15)	O(12)-Dy(3)-N(1)	123.71(16)
O(3)-Dy(2)-N(3)	70.74(17)	O(12)#1-Dy(3)-O(12)	70.77(17)

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

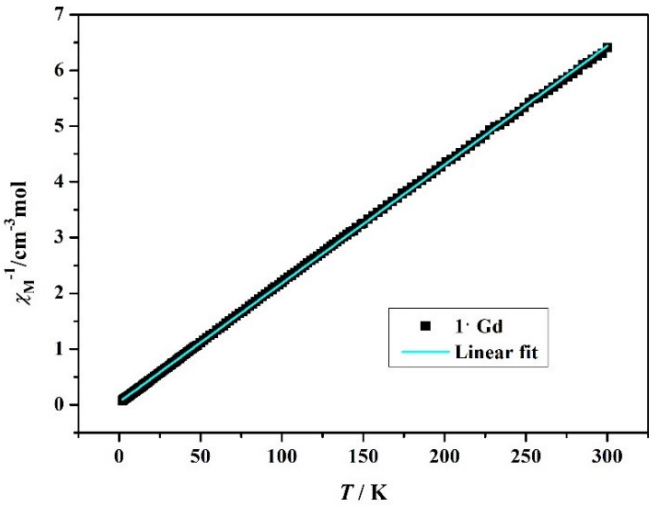

Fig. S3 Plot of χ_M^{-1} *vs. T* at for **1**. The solid line represents the Curie-Weiss fit.