Electronic Supplementary Information

Structures, magnetic refrigeration and single molecule-magnet behavior of five rhombus-shaped tetranuclear Ln(III)-based clusters

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Experimental Section

Synthesis of 5-amino-8-hydroxylquinoline. The synthesis of 5-amino-8-hydroxyquinoline was optimized compared to the method reported previously in the literature.[1] A mixture of 5-nitryl-8-hydroxylquinoline (50 mmol) and 5 % Pd/C (0.75 g), which was used as catalyst, in a 1.3 % ratio in absolute isopropanol was heated to 65 °C, and then 12 mL of 85 % hydrazine hydrate was dropped into the mixture over 1 h. It was heated to 90 °C and refluxed for 6 h. Finally, the solvent was removed, and dichloromethane was used to wash the grass green solid product (yield: 50.8%). Elemental analysis (%): Calcd for $C_9H_8ON_2$ (F_w = 160.42): C 67.32, H 5.00, N 17.50. Found: C 67.28, H 4.97, N 17.82. IR (KBr, cm^{-1}): 3345 (s), 1689 (s), 1625 (s), 1489 (s), 1346 (s), 914 (s), 746 (m).

Synthesis of 5-(2-thenylidene)-8-hydroxylquinoline (HL). The synthesis of 5-(2-thenylidene)-8-hydroxylquinoline (HL1) is similar to that of HL, the only di□erence being the use of 2-thenaldehyde (10 mmol) instead of 4-methyl benzaldehyde (10 mmol), the detailed outline of the synthesis of the ligand (HL1) is shown as Scheme. S1. Elemental analysis (%) Calcd for $C_{14}H_9N_2OS$ (F_w = 253): C, 77.86; H, 5.34; N,

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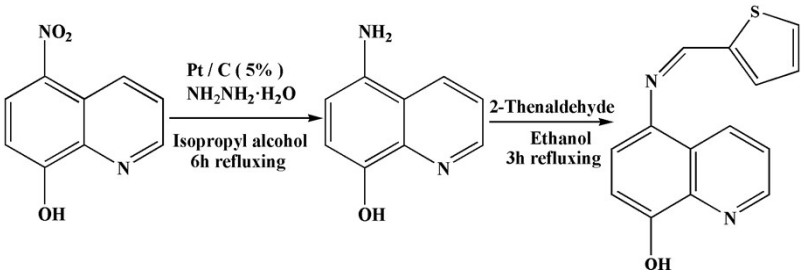
10.69. Found: C, 77.65; H, 5.62; N, 10.40. IR (cm^{-1}): 3518 (s), 1612 (w), 1502 (s), 1468 (w), 1413 (s), 1280 (m), 1243 (m), 1193 (m), 1048 (w), 788 (m), 700 (m), 566 (w), 498 (w).



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

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

Bond lengths			
Eu(1)-O(5)	2.339(6)	Eu(1)-O(4)	2.355(6)
Eu(1)-O(8)	2.376(5)	Eu(1)–O(1)	2.399(6)
Eu(1)-O(8)#1	2.401(5)	Eu(1)-O(2)#1	2.422(6)
Eu(1)-O(3)#1	2.449(6)	Eu(2)-O(6)	2.335(6)
Eu(2)-O(8)	2.350(5)	Eu(2)-O(7)	2.355(6)
Eu(2)-O(2)	2.413(6)	Eu(2)–O(3)	2.418(6)
Eu(2)-N(3)	2.549(7)	Eu(2)-O(1)	2.441(5)
Eu(2)-N(5)	2.573(7)	Eu(1)-N(1)	2.586(7)
Bond angle			
O(5)-Eu(1)- O(4)	72.6(2)	O(5)-Eu(1)-O(8)	139.3(2)
O(4)-Eu(1)-O(8)	77.8(2)	O(4)-Eu(1)-O(1)	86.7(2)
O(5)-Eu(1)-O(1)	81.0(2)	O(8)-Eu(1)-O(1)	69.79(18)

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

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

Bond lengths			
Gd(1)-O(5)	2.335(4)	Gd(2)-O(6)	2.327(5)
Gd(1)-O(4)	2.335(5)	Gd(2)-O(7)	2.343(5)
Gd(1)-O(8)#1	2.339(4)	Gd(2)-O(8)#1	2.363(4)
Gd(1)-O(3)#1	2.408(4)	Gd(2)-O(2)	2.382(4)
Gd(1)-O(1)	2.418(5)	Gd(2)-O(8)	2.392(4)
Gd(1)-O(2)	2.419(4)	Gd(2)-O(3)	2.420(5)

Gd(1)-N(5)#1	2.528(6)	Gd(2)-O(1)#1	2.441(4)
Gd(1)-N(1)	2.558(5)	Gd(2)-N(3)	2.571(5)

Bond angles

Gd(1)-O(1)-Gd(2)#1	95.16(15)	Gd(1)#1-O(8)-Gd(2)#1	111.78(18)
Gd(2)-O(2)-Gd(1)	108.36(17)	Gd(1)#1-O(8)-Gd(2)	98.59(14)
Gd(1)#1-O(3)-Gd(2)	95.98(15)	Gd(2)#1-O(8)-Gd(2)	108.15(16)

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

Tables S3 Selected bond lengths (Å) and angles (°) for cluster **3**[a].

Bond lengths

Tb(1)–O(5)	2.317(3)	Tb(1)–O(4)	2.335(3)
Tb(1)–O(8)	2.351(3)	Tb(1)–O(1)	2.375(3)
Tb(1)–O(8)#1	2.367(3)	Tb(1)–O(2)#1	2.401(3)
Tb(1)–N(1)	2.563(4)	Tb(1)–O(3)#1	2.426(3)
Tb(2)–O(6)	2.314(3)	Tb(2)–O(7)	2.330(3)
Tb(2)–O(8)	2.329(3)	Tb(2)–O(3)	2.394(3)
Tb(2)–O(2)	2.385(3)	Tb(2)–O(1)	2.412(3)
Tb(2)–N(3)	2.528(4)	Tb(2)–N(5)	2.549(4)

Bond angles

Tb(1)–O(1)–Tb(2)	108.20(11)	Tb(2)–O(2)–Tb(1)#1	96.21(10)
Tb(2)–O(3)–Tb(1)#1	95.31(11)	Tb(2)–O(8)–Tb(1)	111.90(11)
Tb(2)–O(8)–Tb(1)#1	98.50(10)	Tb(1)–O(8)–Tb(1)#1	108.58(11)

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

Tables S4 Selected bond lengths (Å) and angles (°) for cluster **4**[a].

Bond lengths

Dy(1)-O(4)	2.301(2)	Dy(1)-O(5)	2.315(2)
Dy(1)-O(8)	2.330(2)	Dy(1)-O(2)	2.367(2)
Dy(1)-O(1)	2.383(2)	Dy(1)-O(3)	2.401(2)
Dy(1)-N(3)	2.513(3)	Dy(1)-N(1)	2.546(3)
Dy(2)-O(1)#1	2.416(2)	Dy(2)-N(5)	2.548(3)
Dy(2)-O(7)	2.300(2)	Dy(2)-O(6)	2.324(2)

Dy(2)-O(8)	2.341(2)	Dy(2)-O(8)#1	2.346(2)
Dy(2)-O(3)	2.365(2)	Dy(2)-O(2)#1	2.393(2)
Bond angles			
Dy(1)-O(1)-Dy(2)#1	95.01(8)	Dy(1)-O(2)-Dy(2)#1	96.03(8)
Dy(2)-O(3)-Dy(1)	108.23(9)	Dy(1)-O(8)-Dy(2)	111.49(9)
Dy(1)-O(8)-Dy(2)#1	98.34(8)	Dy(2)-O(8)-Dy(2)#1	108.81(9)

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

Tables S5 Selected bond lengths (Å) and angles (°) for cluster **5**[a].

Bond lengths			
Er(1)-O(4)	2.282(3)	Er(2)-O(7)	2.303(3)
Er(1)-O(8)	2.288(3)	Er(2)-O(8)	2.308(3)
Er(1)-O(5)	2.297(3)	Er(2)-O(8)#1	2.330(3)
Er(1)-O(1)	2.351(3)	Er(2)-O(3)	2.332(3)
Er(1)-O(2)	2.352(3)	Er(2)-O(2)#1	2.360(3)
Er(1)-O(3)	2.371(3)	Er(2)-O(1)#1	2.392(3)
Er(1)-N(3)	2.492(4)	Er(2)-N(5)	2.518(3)
Er(2)-O(6)	2.285(3)	Er(1)-N(1)	2.517(4)
Bond angles			
Er(1)-O(1)-Er(2)#1	95.02(10)	Er(1)-O(8)-Er(2)	112.14(10)
Er(1)-O(2)-Er(2)#1	95.84(9)	Er(1)-O(8)-Er(2)#1	98.47(10)
Er(2)-O(3)-Er(1)	108.31(11)	Er(2)-O(8)-Er(2)#1	108.63(10)

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

Table S6 The Dy^{III} geometry analysis by SHAPE 2.0 for cluster **4**.

Cluster 4	D_{4d}**SAPR**	D_{2d}**TDD**	C_{2v}**JBTPR**	C_{2v}**BTPR**	D_{2d}**JSD**
Dy_1^{3+}	1.075	2.213	2.886	2.119	5.064
Dy_2^{3+}	0.818	2.515	2.043	1.478	4.650

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

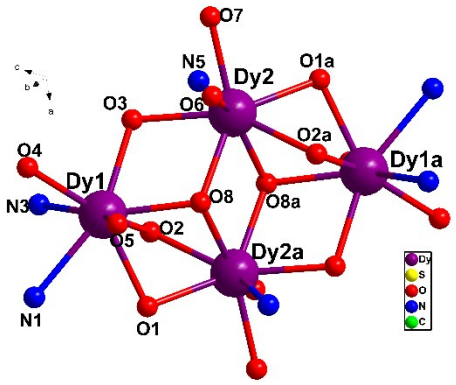


Fig. S1 The coordinate atom labels of central Dy(III) ions in cluster **4**.

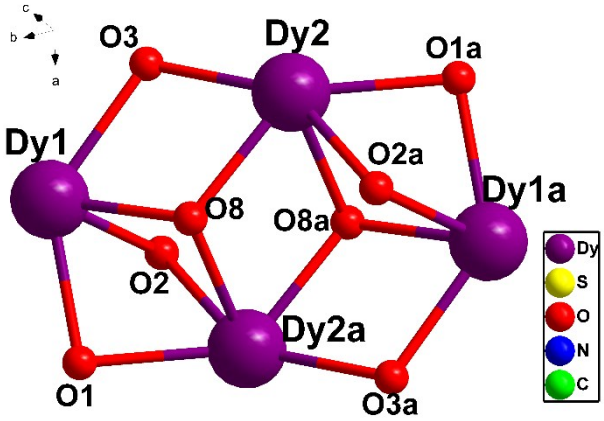


Fig. S2 The four central Dy atoms are bridged by six μ_2-O and two μ_3-O atoms forming the Dy_4 core.

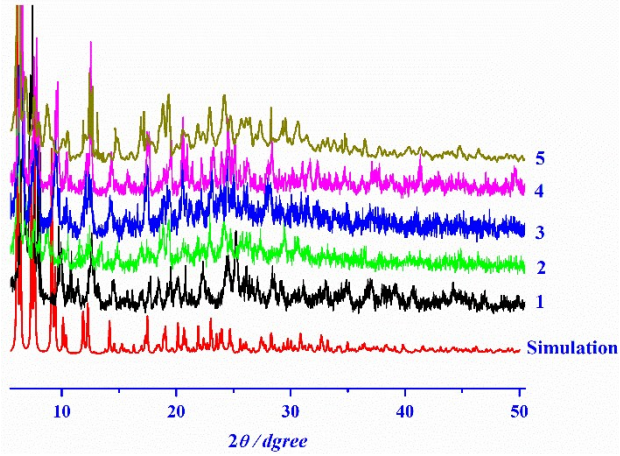


Fig. S3 The PXRD patterns for **1-5** and the corresponding simulated one.

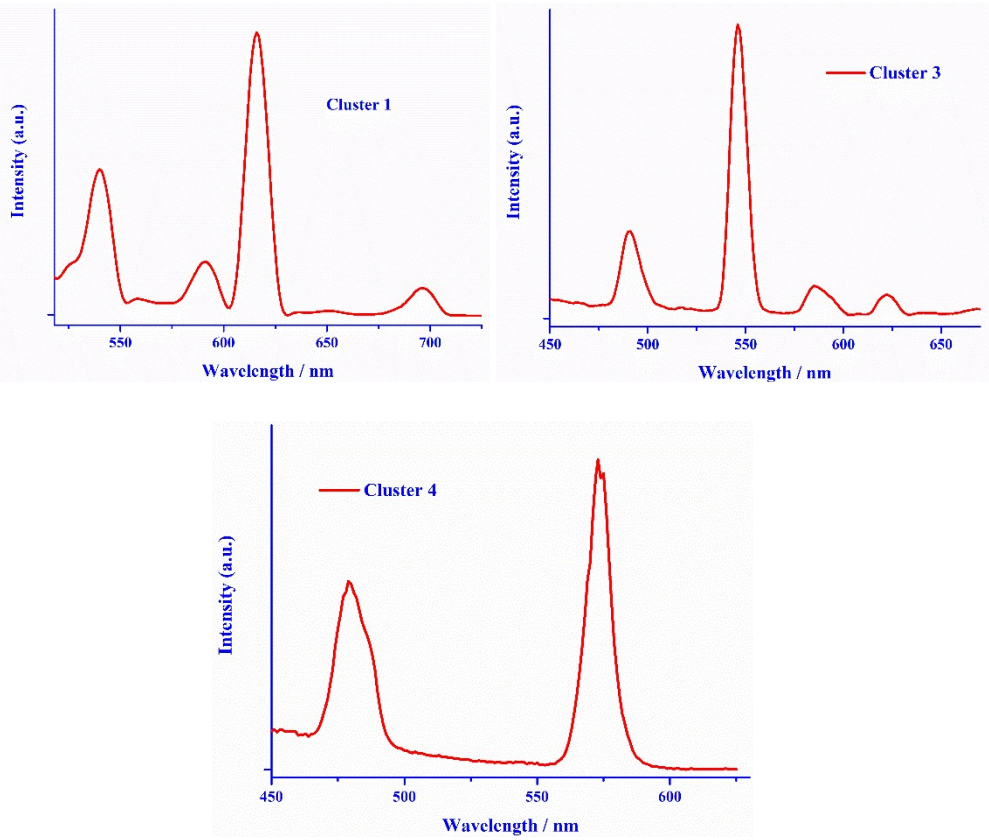


Fig. S4 The solid-state luminescence spectrums of clusters **1, 3**, and **4** at room temperature.