Single molecule magnet behavior and magnetic refrigeration of four tetranuclear lanthanide (Ln = Gd^{III}, Tb^{III}, Dy^{III}) clusters

Hong Yu,[a] Jia-Miao Cao,[a] Jun-Rui Zhang,[a] Rui-Cong Li,[a] Yan Cheng,[a] Chen Yang,[a] Yin-Ling Hou,[b,*] Ming Fang,[a,c,*]

a Department of Chemistry, Hebei Normal University of Science & Technology, Qinhuangdao 066004, Hebei province, P. R.China. E-mail:fangmingchem@163.com
b School of Life and Health Science, Kaili University, Kaili, 556011, China, hyl0506@126.com
c Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China

Electronic supplementary information

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

Gd(1)-O(1)	2.380(3)	Gd(1)-O(2)	2.409(4)
Gd(1)-O(3)	2.438(4)	Gd(1)-O(4)	2.361(4)
Gd(1)-O(5)	2.330(4)	Gd(1)-O(8)	2.399(3)
Gd(1)-O(8)#1	2.443(4)	Gd(1)-N(2)	2.579(5)
Gd(2)-O(1)	2.423(3)	Gd(2)-O(2)#1	2.408(4)
Gd(2)-O(3)#1	2.401(4)	Gd(2)-O(6)	2.350(4)
Gd(2)-O(7)	2.323(4)	Gd(2)-O(8)	2.336(3)
Gd(2)-N(4)#1	2.589(5)	Gd(2)-N(6)#1	2.561(5)
Gd(1)-Gd(1)#1	3.9311(5)	Gd(1)-Gd(2)	3.9249(4)
Gd(1)-Gd(2)#1	3.6060(4)		
O(1)-Gd(1)-O(2)	145.78(12)	O(1)-Gd(1)-O(3)	143.57(13)
O(1)-Gd(1)-O(8)#1	100.84(12)	O(1)-Gd(1)-O(8)	68.99(12)
O(1)-Gd(1)-N(2)	65.67(13)	O(2)-Gd(1)-O(3)	66.43(12)
O(2)-Gd(1)-O(8)#1	71.28(12)	O(2)-Gd(1)-N(2)	137.85(13)
O(3)-Gd(1)-O(8)#1	69.49(12)	O(3)-Gd(1)-N(2)	77.90(13)
O(4)-Gd(1)-O(1)	81.94(13)	O(4)-Gd(1)-O(2)	125.37(13)
O(4)-Gd(1)-O(3)	85.56(13)	O(4)-Gd(1)-O(8)	141.10(13)
O(4)-Gd(1)-O(8)#1	141.63(12)	O(4)-Gd(1)-N(2)	70.61(14)
O(5)-Gd(1)-O(1)	90.22(14)	O(5)-Gd(1)-O(2)	81.23(13)
O(5)-Gd(1)-O(3)	118.03(14)	O(5)-Gd(1)-O(4)	71.88(13)
O(5)-Gd(1)-O(8)#1	145.54(12)	O(5)-Gd(1)-O(8)	82.64(13)
O(5)-Gd(1)-N(2)	137.59(14)	O(8)-Gd(1)-O(2)	77.05(12)

O(8)-Gd(1)-O(3)	132.98(12)	O(8)-Gd(1)-O(8)#1	71.45(13)
O(8)-Gd(1)-N(2)	116.31(13)	O(8)#1-Gd(1)-N(2)	75.82(13)
O(1)-Gd(2)-N(4)#1	82.37(13)	O(1)-Gd(2)-N(6)#1	156.61(13)
O(2)#1-Gd(2)-O(1)	77.60(13)	O(2)#1-Gd(2)-N(4)#1	65.22(13)
O(2)#1-Gd(2)-N(6)#1	105.85(14)	O(3)#1-Gd(2)-O(1)	133.32(12)
O(3)#1-Gd(2)-O(2)#1	67.02(13)	O(3)#1-Gd(2)-N(4)#1	107.59(14)
O(3)#1-Gd(2)-N(6)#1	66.32(13)	O(6)-Gd(2)-O(1)	117.44(13)
O(6)-Gd(2)-O(2)#1	142.48(13)	O(6)-Gd(2)-O(3)#1	79.77(14)
O(6)-Gd(2)-N(4)#1	145.83(14)	O(6)-Gd(2)-N(6)#1	74.25(15)
O(7)-Gd(2)-O(1)	82.79(13)	O(7)-Gd(2)-O(2)#1	144.49(13)
O(7)-Gd(2)-O(3)#1	142.61(13)	O(7)-Gd(2)-O(6)	73.01(13)
O(7)-Gd(2)-O(8)	126.33(13)	O(7)-Gd(2)-N(4)#1	83.15(15)
O(7)-Gd(2)-N(6)#1	81.74(15)	O(8)-Gd(2)-O(1)	69.29(12)
O(8)-Gd(2)-O(2)#1	73.14(12)	O(8)-Gd(2)-O(3)#1	71.91(12)
O(8)-Gd(2)-O(6)	80.54(13)	O(8)-Gd(2)-N(4)#1	133.63(13)
O(8)-Gd(2)-N(6)#1	134.08(13)	N(6)#1-Gd(2)-N(4)#1	78.46(15)

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

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

Tb(1)-O(1)	2.370(7)	Tb(1)-O(2)	2.397(7)
Tb(1)-O(3)#1	2.404(6)	Tb(1)-O(4)	2.329(8)
Tb(1)-O(5)	2.318(7)	Tb(1)-O(8)	2.322(6)
Tb(1)-N(1)	2.548(8)	Tb(1)-N(3)	2.552(8)
Tb(2)-O(1)	2.388(6)	Tb(2)-O(2)	2.398(7)
Tb(2)-O(3)	2.385(6)	Tb(2)-O(6)	2.300(10)
Tb(2)-O(7)	2.342(9)	Tb(2)-O(8)#1	2.346(6)
Tb(2)-O(8)	2.423(7)	Tb(2)-N(5)	2.546(9)
Tb(1)-Tb(2)	3.6052(8)	Tb(1)-Tb(2)#1	3.8645(7)
Tb(2)-Tb(2)#1	3.8755(10)		
O(1)-Tb(1)-O(2)	66.1(3)	O(1)-Tb(1)-O(3)#1	78.3(2)
O(1)-Tb(1)-N(1)	66.3(2)	O(1)-Tb(1)-N(3)	103.2(3)
O(2)-Tb(1)-O(3)#1	133.2(2)	O(2)-Tb(1)-N(1)	110.1(3)
O(2)-Tb(1)-N(3)	66.4(2)	O(3)#1-Tb(1)-N(1)	79.8(2)
O(3)#1-Tb(1)-N(3)	155.2(2)	O(4)-Tb(1)-O(1)	144.6(2)
O(4)-Tb(1)-O(2)	142.1(2)	O(4)-Tb(1)-O(3)#1	83.6(2)
O(4)-Tb(1)-N(1)	80.7(3)	O(4)-Tb(1)-N(3)	81.4(3)
O(5)-Tb(1)-O(1)	141.8(3)	O(5)-Tb(1)-O(2)	79.1(3)
O(5)-Tb(1)-O(3)#1	119.2(3)	O(5)-Tb(1)-O(4)	73.5(3)
O(5)-Tb(1)-O(8)	82.2(3)	O(5)-Tb(1)-N(1)	145.2(3)
O(5)-Tb(1)-N(3)	75.0(3)	O(8)-Tb(1)-O(1)	72.1(2)
O(8)-Tb(1)-O(2)	70.5(2)	O(8)-Tb(1)-O(3)#1	70.3(2)

O(8)-Tb(1)-O(4)	129.2(3)	O(8)-Tb(1)-N(1)	132.6(2)
O(8)-Tb(1)-N(3)	134.1(2)	N(1)-Tb(1)-N(3)	78.4(3)
O(1)-Tb(2)-O(2)	65.8(2)	O(1)-Tb(2)-O(8)	70.1(2)
O(1)-Tb(2)-N(5)	135.0(3)	O(2)-Tb(2)-O(8)	68.8(2)
O(2)-Tb(2)-N(5)	76.5(2)	O(3)-Tb(2)-O(1)	147.2(2)
O(3)-Tb(2)-O(2)	142.9(2)	O(3)-Tb(2)-O(8)	102.3(2)
O(3)-Tb(2)-N(5)	66.5(2)	O(6)-Tb(2)-O(1)	82.9(3)
O(6)-Tb(2)-O(2)	120.4(3)	O(6)-Tb(2)-O(3)	88.2(3)
O(6)-Tb(2)-O(7)	72.6(4)	O(6)-Tb(2)-O(8)	144.8(3)
O(6)-Tb(2)-O(8)#1	81.3(3)	O(6)-Tb(2)-N(5)	139.6(3)
O(7)-Tb(2)-O(1)	127.8(3)	O(7)-Tb(2)-O(2)	87.8(3)
O(7)-Tb(2)-O(3)	78.3(2)	O(7)-Tb(2)-O(8)#1	139.4(3)
O(7)-Tb(2)-O(8)	142.2(3)	O(7)-Tb(2)-N(5)	71.6(3)
O(8)#1-Tb(2)-O(1)	77.3(2)	O(8)#1-Tb(2)-O(2)	132.6(2)
O(8)#1-Tb(2)-O(3)	70.2(2)	O(8)#1-Tb(2)-O(8)	71.3(3)
O(8)#1-Tb(2)-N(5)	115.6(2)	O(8)-Tb(2)-N(5)	74.1(3)

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

Table S3 Selected bond lengths (Å) and angles (°) for complex **3**[a]

Dy(1)-O(1)	2.353(7)	Dy(1)-O(2)	2.426(8)
Dy(1)-O(3)	2.401(7)	Dy(1)-O(4)	2.333(7)
Dy(1)-O(5)	2.294(7)	Dy(1)-O(8)	2.406(7)
Dy(1)-O(8)#1	2.344(7)	Dy(1)-N(1)	2.527(7)
Dy(2)-O(1)#1	2.399(8)	Dy(2)-O(2)	2.356(7)
Dy(2)-O(3)	2.379(7)	Dy(2)-O(6)	2.271(7)
Dy(2)-O(7)	2.341(7)	Dy(2)-O(8)	2.313(7)
Dy(2)-N(3)	2.600(10)	Dy(2)-N(5)	2.530(9)
Dy(1)-Dy(1)#1	3.8221(11)	Dy(1)-Dy(2)#1	3.8780(8)
Dy(1)-Dy(2)	3.5784(8)		
Dy(3)-O(9)	2.365(7)	Dy(3)-O(10)	2.391(7)
Dy(3)-O(11)	2.430(7)	Dy(3)-O(12)	2.343(7)
Dy(3)-O(13)	2.316(8)	Dy(3)-O(16)#2	2.382(7)
Dy(3)-O(16)	2.367(7)	Dy(3)-N(7)	2.551(8)
Dy(4)-O(9)#2	2.404(8)	Dy(4)-O(10)	2.360(7)
Dy(4)-O(11)	2.398(7)	Dy(4)-O(14)	2.331(7)
Dy(4)-O(15)	2.280(8)	Dy(4)-O(16)#2	2.314(7)
Dy(4)-N(9)	2.549(8)	Dy(4)-N(11)	2.557(9)
Dy(3)-Dy(3)#2	3.8674(11)	Dy(3)-Dy(4)#2	3.8799(8)
Dy(3)-Dy(4)	3.5797(9)		
O(1)-Dy(1)-O(2)	146.1(2)	O(1)-Dy(1)-O(3)	144.6(2)
O(1)-Dy(1)-O(8)	103.6(3)	O(1)-Dy(1)-N(1)	67.2(2)

O(2)-Dy(1)-N(1)	79.2(2)	O(3)-Dy(1)-O(2)	66.2(2)
O(3)-Dy(1)-O(8)	69.7(2)	O(3)-Dy(1)-N(1)	136.3(2)
O(4)-Dy(1)-O(1)	80.6(3)	O(4)-Dy(1)-O(2)	84.7(3)
O(4)-Dy(1)-O(3)	127.7(2)	O(4)-Dy(1)-O(8)#1	141.2(2)
O(4)-Dy(1)-O(8)	139.8(2)	O(4)-Dy(1)-N(1)	71.3(3)
O(5)-Dy(1)-O(1)	89.5(2)	O(5)-Dy(1)-O(2)	115.1(2)
O(5)-Dy(1)-O(3)	81.1(2)	O(5)-Dy(1)-O(4)	73.2(2)
O(5)-Dy(1)-O(8)	145.6(2)	O(5)-Dy(1)-O(8)#1	82.9(2)
O(5)-Dy(1)-N(1)	140.0(2)	O(8)#1-Dy(1)-O(1)	68.9(2)
O(8)#1-Dy(1)-O(2)	133.7(2)	O(8)-Dy(1)-O(2)	69.7(3)
O(8)#1-Dy(1)-O(3)	76.1(2)	O(8)#1-Dy(1)-O(8)	72.9(3)
O(8)-Dy(1)-N(1)	73.8(2)	O(8)#1-Dy(1)-N(1)	115.0(3)
O(1)#1-Dy(2)-N(3)	158.8(3)	O(1)#1-Dy(2)-N(5)	83.5(3)
O(2)-Dy(2)-O(1)#1	133.2(3)	O(2)-Dy(2)-O(3)	67.7(2)
O(2)-Dy(2)-N(3)	65.4(3)	O(2)-Dy(2)-N(5)	106.6(3)
O(3)-Dy(2)-O(1)#1	76.2(2)	O(3)-Dy(2)-N(3)	109.2(3)
O(3)-Dy(2)-N(5)	66.0(3)	O(6)-Dy(2)-O(1)#1	83.2(3)
O(6)-Dy(2)-O(2)	142.8(3)	O(6)-Dy(2)-O(3)	143.0(2)
O(6)-Dy(2)-O(7)	74.1(2)	O(6)-Dy(2)-O(8)	128.0(3)
O(6)-Dy(2)-N(3)	80.9(3)	O(6)-Dy(2)-N(5)	81.5(3)
O(7)-Dy(2)-O(1)#1	115.8(3)	O(7)-Dy(2)-O(2)	81.0(2)
O(7)-Dy(2)-O(3)	142.8(2)	O(7)-Dy(2)-N(3)	72.9(3)
O(7)-Dy(2)-N(5)	146.1(3)	O(8)-Dy(2)-O(1)#1	68.6(2)
O(8)-Dy(2)-O(2)	72.5(3)	O(8)-Dy(2)-O(3)	71.7(2)
O(8)-Dy(2)-O(7)	80.2(2)	O(8)-Dy(2)-N(3)	132.6(3)
O(8)-Dy(2)-N(5)	133.7(3)	N(5)-Dy(2)-N(3)	80.4(3)
O(9)-Dy(3)-O(10)	145.7(2)	O(9)-Dy(3)-O(11)	145.1(2)
O(9)-Dy(3)-O(16)	69.3(2)	O(9)-Dy(3)-O(16)#2	103.5(3)
O(9)-Dy(3)-N(7)	66.6(3)	O(10)-Dy(3)-O(11)	66.3(2)
O(10)-Dy(3)-N(7)	136.8(3)	O(11)-Dy(3)-N(7)	78.7(3)
O(12)-Dy(3)-O(9)	87.1(3)	O(12)-Dy(3)-O(10)	81.8(3)
O(12)-Dy(3)-O(11)	119.0(3)	O(12)-Dy(3)-O(16)	81.2(3)
O(12)-Dy(3)-O(16)#2	143.8(2)	O(12)-Dy(3)-N(7)	139.5(3)
O(13)-Dy(3)-O(9)	82.5(3)	O(13)-Dy(3)-O(10)	124.0(3)
O(13)-Dy(3)-O(11)	83.8(3)	O(13)-Dy(3)-O(12)	72.8(3)
O(13)-Dy(3)-O(16)#2	142.2(2)	O(13)-Dy(3)-O(16)	142.5(3)
O(13)-Dy(3)-N(7)	73.6(3)	O(16)#2-Dy(3)-O(10)	69.9(2)
O(16)-Dy(3)-O(10)	76.9(2)	O(16)#2-Dy(3)-O(11)	70.0(2)
O(16)-Dy(3)-O(11)	133.2(2)	O(16)-Dy(3)-O(16)#2	70.9(3)
O(16)-Dy(3)-N(7)	114.2(3)	O(16)#2-Dy(3)-N(7)	74.8(2)
O(9)#2-Dy(4)-N(9)	82.4(3)	O(9)#2-Dy(4)-N(11)	156.9(2)
O(10)-Dy(4)-O(9)#2	78.8(2)	O(10)-Dy(4)-O(11)	67.3(2)
O(10)-Dy(4)-N(9)	65.9(3)	O(10)-Dy(4)-N(11)	106.5(2)
O(11)-Dy(4)-O(9)#2	134.6(2)	O(11)-Dy(4)-N(9)	108.4(3)

O(11)-Dy(4)-N(11)	65.8(3)	O(14)-Dy(4)-O(9)#2	114.7(3)
O(14)-Dy(4)-O(10)	141.7(3)	O(14)-Dy(4)-O(11)	80.0(3)
O(14)-Dy(4)-N(9)	147.4(3)	O(14)-Dy(4)-N(11)	75.4(3)
O(15)-Dy(4)-O(9)#2	83.8(3)	O(15)-Dy(4)-O(10)	144.2(2)
O(15)-Dy(4)-O(11)	140.6(3)	O(15)-Dy(4)-O(14)	74.1(3)
O(15)-Dy(4)-O(16)#2	130.1(3)	O(15)-Dy(4)-N(9)	81.0(3)
O(15)-Dy(4)-N(11)	79.2(3)	O(16)#2-Dy(4)-O(9)#2	69.5(2)
O(16)#2-Dy(4)-O(10)	71.7(2)	O(16)#2-Dy(4)-O(11)	71.7(2)
O(16)#2-Dy(4)-O(14)	79.8(3)	O(16)#2-Dy(4)-N(9)	132.7(3)
O(16)#2-Dy(4)-N(11)	133.6(2)	N(9)-Dy(4)-N(11)	79.6(3)

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

Table S4 Selected bond lengths (Å) and angles (°) for complex **4**[a]

Gd(1)-O(3)	2.378(4)	Gd(1)-O(1)	2.392(4)
Gd(1)-O(2)	2.435(4)	Gd(1)-O(8)	2.446(4)
Gd(1)-O(8)#1	2.399(4)	Gd(1)-O(7)	2.360(4)
Gd(1)-O(6)	2.322(4)	Gd(1)-N(6)	2.585(5)
Gd(2)-O(3)#1	2.421(4)	Gd(2)-O(1)	2.403(4)
Gd(2)-O(2)	2.401(4)	Gd(2)-O(8)	2.321(4)
Gd(2)-O(5)	2.310(4)	Gd(2)-N(2)	2.564(5)
Gd(2)-N(4)	2.559(5)	Gd(2)-O(4)	2.382(4)
O(3)-Gd(1)-O(1)	145.24(13)	O(3)-Gd(1)-O(2)	144.70(13)
O(3)-Gd(1)-O(8)	99.76(14)	O(3)-Gd(1)-O(8)#1	69.45(13)
O(3)-Gd(1)-N(6)	65.64(14)	O(1)-Gd(1)-O(2)	65.71(13)
O(1)-Gd(1)-O(8)	71.19(14)	O(1)-Gd(1)-O(8)#1	75.96(14)
O(1)-Gd(1)-N(6)	137.90(14)	O(2)-Gd(1)-O(8)	71.05(13)
O(2)-Gd(1)-N(6)	79.07(14)	O(8)#1-Gd(1)-O(2)	132.46(13)
O(8)#1-Gd(1)-O(8)	70.72(17)	O(8)#1-Gd(1)-N(6)	117.24(15)
O(8)-Gd(1)-N(6)	76.21(15)	O(7)-Gd(1)-O(3)	82.60(14)
O(7)-Gd(1)-O(1)	125.62(14)	O(7)-Gd(1)-O(2)	85.16(14)
O(7)-Gd(1)-O(8)#1	141.73(14)	O(7)-Gd(1)-O(8)	141.95(14)
O(7)-Gd(1)-N(6)	70.28(15)	O(6)-Gd(1)-O(3)	91.06(14)
O(6)-Gd(1)-O(1)	81.08(13)	O(6)-Gd(1)-O(2)	116.25(14)
O(6)-Gd(1)-O(8)#1	82.65(15)	O(6)-Gd(1)-O(8)	145.19(14)
O(6)-Gd(1)-O(7)	71.96(14)	O(6)-Gd(1)-N(6)	137.56(14)
O(3)#1-Gd(2)-N(2)	80.78(14)	O(3)#1-Gd(2)-N(4)	155.83(14)
O(1)-Gd(2)-O(3)#1	77.17(13)	O(1)-Gd(2)-N(2)	64.94(14)
O(1)-Gd(2)-N(4)	108.70(15)	O(2)-Gd(2)-O(3)#1	134.20(13)
O(2)-Gd(2)-O(1)	66.07(13)	O(2)-Gd(2)-N(2)	105.67(15)
O(2)-Gd(2)-N(4)	66.49(15)	O(8)-Gd(2)-O(3)#1	69.98(14)

O(8)-Gd(2)-O(1)	73.17(14)	O(8)-Gd(2)-O(2)	73.81(14)
O(8)-Gd(2)-N(2)	133.10(16)	O(8)-Gd(2)-N(4)	134.12(15)
O(8)-Gd(2)-O(4)	78.21(15)	O(5)-Gd(2)-O(3)#1	82.51(14)
O(5)-Gd(2)-O(1)	146.34(14)	O(5)-Gd(2)-O(2)	142.33(14)
O(5)-Gd(2)-O(8)	124.08(15)	O(5)-Gd(2)-N(2)	85.63(15)
O(5)-Gd(2)-N(4)	80.55(16)	O(5)-Gd(2)-O(4)	73.35(14)
N(4)-Gd(2)-N(2)	80.85(16)	O(4)-Gd(2)-O(3)#1	118.00(14)
O(4)-Gd(2)-O(1)	140.16(14)	O(4)-Gd(2)-O(2)	79.79(14)
O(4)-Gd(2)-N(2)	148.67(15)	O(4)-Gd(2)-N(4)	73.11(15)

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

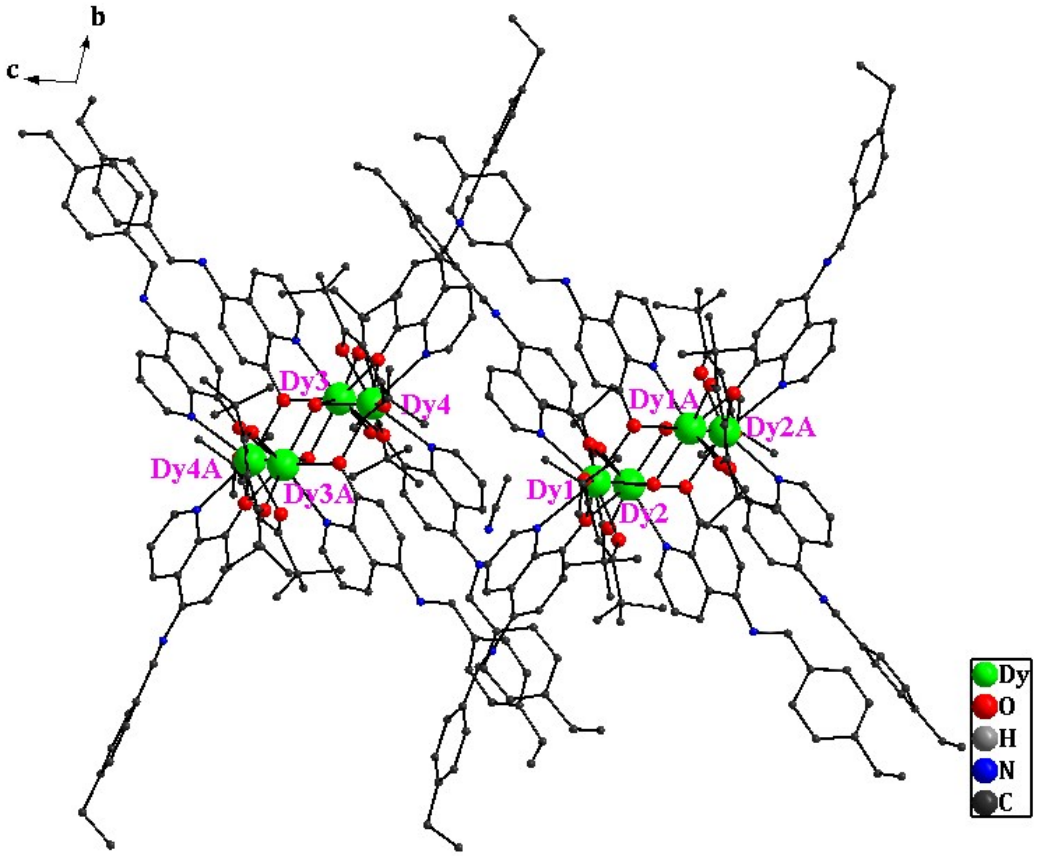

Figure S1. The two distinct tetranuclear units in the centrosymmetric unit in **3**.