Electronic Supplementary Information

Multiple magnetic relaxation processes, magnetocaloric effect and fluorescent properties of rhombus-shaped tetranuclear rare earth complexes

Hong-Ling Gao, Li Jiang, Shuang Liu, Hai-Yun Shen, Wen-Min Wang and Jian-Zhong Cui*[1]

Department of Chemistry, Tianjin University, Tianjin 300072, People's Republic of China

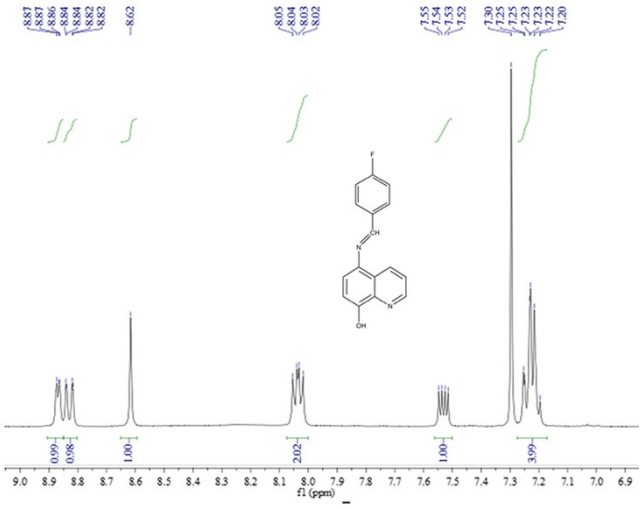
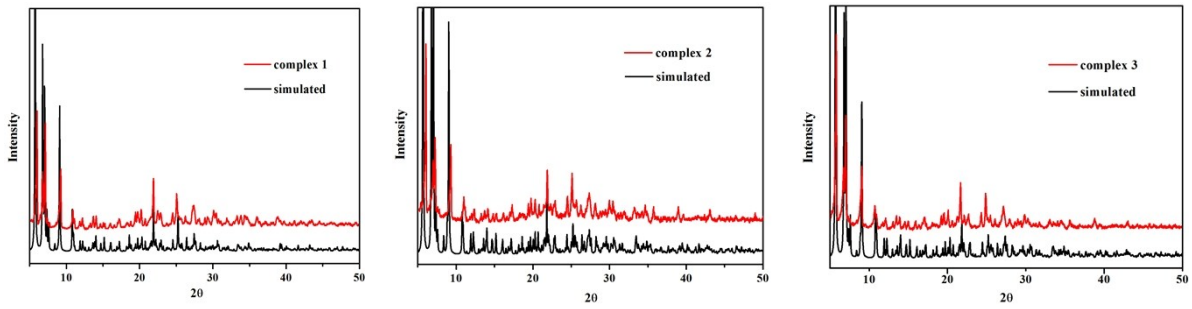


Fig. S1 The ^{1}H NMR spectrum of 5-(4-fluorobenzylidene)-8-hydroxylquinoline.



[1] Corresponding author. *E-mail:* cuijianzhong@tju.edu.cn (J.-Z. Cui).

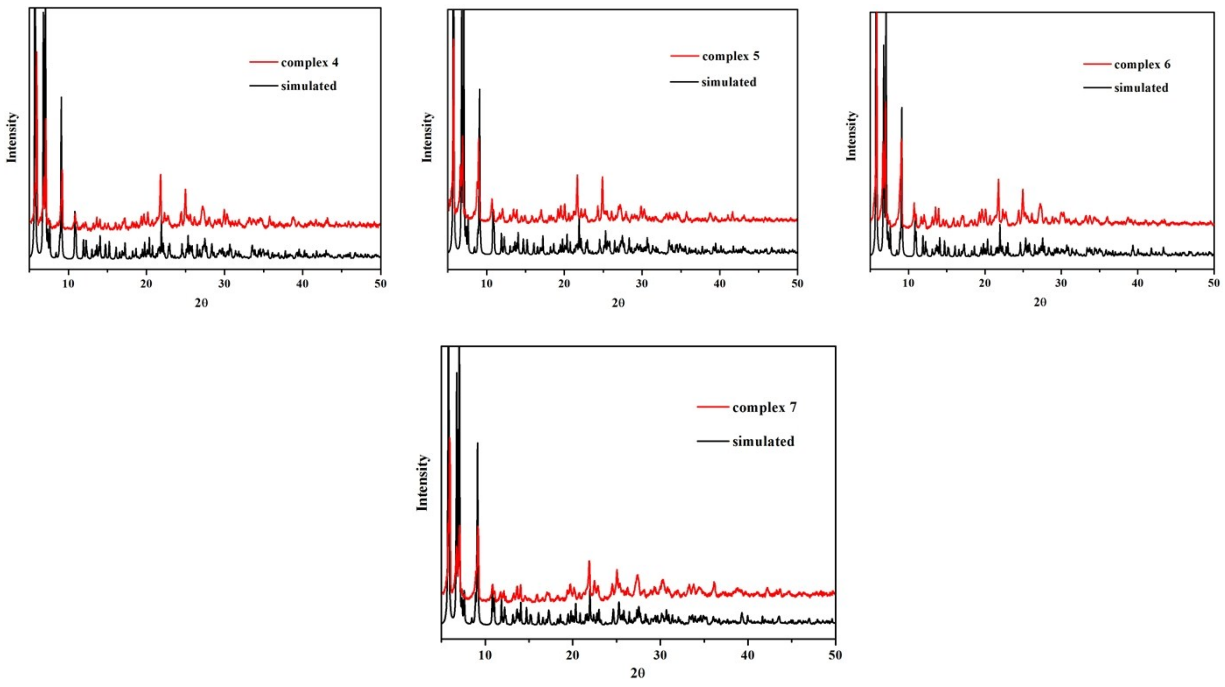


Fig. S2 The experimental and simulated PXRD patterns of complexes **1**−**7**.

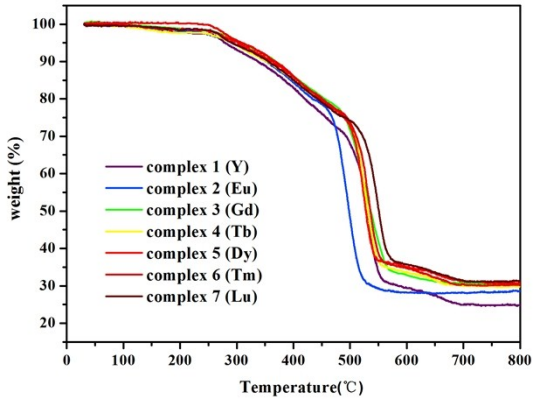


Fig. S3 TG curves of complexes **1**−**7**.

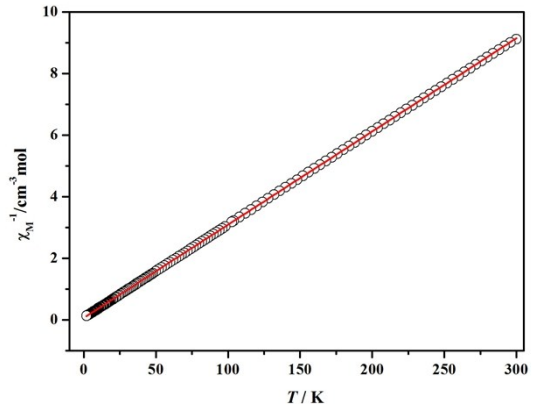


Fig. S4 The inverse magnetic susceptibility, $1/\chi_M$, at 2–300K with a *dc* field of 1000 Oe for complex **3**. The red solid line represents the least square fit for the Curie-Weiss law, giving a θ = -2.15 K.

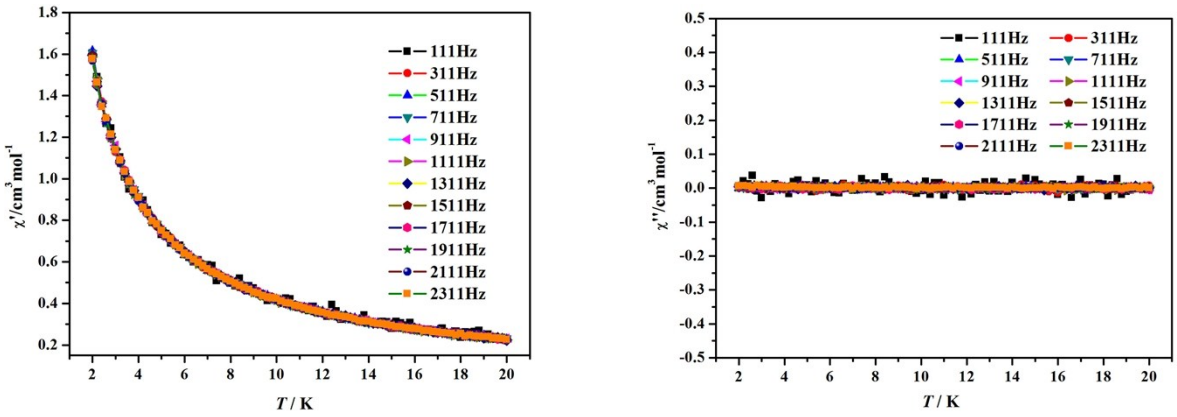


Fig. S5 Temperature dependence of the *ac* susceptibility for complex **4** as a function of the temperature below 20 K under an oscillating *ac* field of 3 Oe.

Table S1 Selected bond lengths and angles for complexes **1**−**7**.

Complex **1**			
Y(1)–O(8)	2.291(3)	Y(2)–O(7)	2.289(3)
Y(1)–O(4)	2.294(3)	Y(2)–O(8)	2.306(3)
Y(1)–O(5)	2.303(3)	Y(2)–O(6)	2.307(3)
Y(1)–O(3)#1	2.366(3)	Y(2)–O(2)	2.319(3)
Y(1)–O(1)	2.373(3)	Y(2)–O(3)	2.388(3)
Y(1)–O(8) #1	2.377(3)	Y(2)–O(1)	2.394(3)
Y(1)–O(2) #1	2.426(3)	Y(2)–N(3)	2.488(3)

Y(1)–N(1)	2.522(3)	Y(2)–N(5)	2.544(4)
O(8)–Y(1)–O(1)	70.16(9)	O(8)#1–Y(1)–N(1)	74.80(10)
O(5)–Y(1)–O(3)#1	82.06(10)	O(4)–Y(1)–O(2)#1	76.28(10)
O(6)–Y(2)–O(1)	109.40(10)	O(7)–Y(2)–O(8)	129.11(10)
O(2)–Y(2)–N(5)	108.59(11)	O(3)–Y(2)–N(3)	111.96(11)
Complex **2**			
Eu(1)–O(8)	2.335(5)	Eu(2)–O(7)	2.328(6)
Eu(1)–O(4)	2.342(6)	Eu(2)–O(6)	2.357(6)
Eu(1)–O(5)	2.349(6)	Eu(2)–O(8)	2.359(5)
Eu(1)–O(3)#1	2.419(5)	Eu(2)–O(2)	2.376(5)
Eu(1)–O(1)	2.430(6)	Eu(2)–O(3)	2.436(5)
Eu(1)–O(8)#1	2.447(5)	Eu(2)–O(1)	2.448(5)
Eu(1)–O(2)#1	2.473(5)	Eu(2)–N(3)	2.534(7)
Eu(1)–N(1)	2.552(6)	Eu(2)–N(5)	2.593(7)
O(8)–Eu(1)–O(1)	70.00(17)	O(8)#1–Eu(1)–N(1)	74.20(19)
O(5)–Eu(1)–O(3)#1	82.66(19)	O(4)–Eu(1)–O(2)#1	76.46(19)
O(6)–Eu(2)–O(1)	110.08(19)	O(7)–Eu(2)–O(8)	129.7(2)
O(2)–Eu(2)–N(5)	107.9(2)	O(3)–Eu(2)–N(3)	111.7(2)
Complex **3**			
Gd(1)–O(8)	2.325(6)	Gd(2)–O(7)	2.330(6)
Gd(1)–O(4)	2.327(6)	Gd(2)–O(6)	2.346(6)
Gd(1)–O(5)	2.344(6)	Gd(2)–O(8)	2.351(6)
Gd(1)–O(3)#1	2.404(6)	Gd(2)–O(2)	2.367(6)
Gd(1)–O(1)	2.409(6)	Gd(2)–O(3)	2.419(6)
Gd(1)–O(8)#1	2.427(6)	Gd(2)–O(1)	2.450(6)
Gd(1)–O(2)#1	2.451(6)	Gd(2)–N(3)	2.523(8)
Gd(1)–N(1)	2.551(7)	Gd(2)–N(5)	2.590(8)
O(8)–Gd(1)–O(1)	70.5(2)	O(8)#1–Gd(1)–N(1)	74.4(2)
O(5)–Gd(1)–O(3)#1	82.7(2)	O(4)–Gd(1)–O(2)#1	76.4(2)
O(6)–Gd(2)–O(1)	109.5(2)	O(7)–Gd(2)–O(8)	129.8(2)
O(2)–Gd(2)–N(5)	107.9(2)	O(3)–Gd(2)–N(3)	111.5(2)
Complex **4**			
Tb(1)–O(5)	2.3131(19)	Tb(2)–O(7)	2.310(2)
Tb(1)–O(8)#1	2.3164(18)	Tb(2)–O(6)	2.327(2)
Tb(1)–O(4)	2.331(2)	Tb(2)–O(8)#1	2.3386(19)
Tb(1)–O(1)	2.3901(19)	Tb(2)–O(2)	2.3394(19)
Tb(1)–O(3)#1	2.392(2)	Tb(2)–O(3)	2.420(2)
Tb(1)–O(8)	2.4036(18)	Tb(2)–O(1)	2.4284(18)
Tb(1)–O(2)#1	2.452(2)	Tb(2)–N(3)	2.520(2)
Tb(1)–N(1)	2.542(2)	Tb(2)–N(5)	2.547(3)

O(1)–Tb(1)–O(8)	104.02(6)	O(8)#1–Tb(1)–N(1)	114.72(7)
O(5)–Tb(1)–O(3)#1	116.48(7)	O(4)–Tb(1)–O(2)#1	119.06(7)
O(6)–Tb(2)–O(1)	109.72(7)	O(7)–Tb(2)–O(8)	129.80(7)
O(2)–Tb(2)–N(5)	108.04(8)	O(3)–Tb(2)–N(3)	112.05(7)
Complex **5**			
Dy(1)–O(4)	2.299(3)	Dy(2)–O(7)	2.301(4)
Dy(1)–O(8)	2.310(3)	Dy(2)–O(6)	2.321(4)
Dy(1)–O(5)	2.316(4)	Dy(2)–O(2)	2.323(3)
Dy(1)–O(8)#1	2.381(3)	Dy(2)–O(8)	2.333(3)
Dy(1)–O(1)	2.385(3)	Dy(2)–O(3)	2.407(4)
Dy(1)–O(3)#1	2.387(4)	Dy(2)–O(1)	2.414(3)
Dy(1)–O(2)#1	2.443(4)	Dy(2)–N(3)	2.509(5)
Dy(1)–N(1)	2.525(4)	Dy(2)–N(5)	2.551(5)
O(8)–Dy(1)–O(1)	70.34(12)	O(8)#1–Dy(1)–N(1)	74.67(13)
O(5)–Dy(1)–O(3)#1	81.90(12)	O(4)–Dy(1)–O(2)#1	76.41(12)
O(6)–Dy(2)–O(1)	109.04(12)	O(7)–Dy(2)–O(8)	129.19(13)
O(2)–Dy(2)–N(5)	109.02(14)	O(3)–Dy(2)–N(3)	112.20(14)
Complex **6**			
Tm(1)–O(8)	2.276(3)	Tm(2)–O(7)	2.268(4)
Tm(1)–O(4)	2.277(4)	Tm(2)–O(8)	2.290(3)
Tm(1)–O(5)	2.285(4)	Tm(2)–O(6)	2.291(4)
Tm(1)–O(8)#1	2.345(3)	Tm(2)–O(2)	2.295(4)
Tm(1)–O(1)	2.351(4)	Tm(2)–O(3)	2.376(4)
Tm(1)–O(3)#1	2.354(4)	Tm(2)–O(1)	2.380(3)
Tm(1)–O(2)#1	2.416(4)	Tm(2)–N(3)	2.479(5)
Tm(1)–N(1)	2.492(4)	Tm(2)–N(5)	2.516(5)
O(8)–Tm(1)–O(1)	70.44(12)	O(8)#1–Tm(1)–N(1)	75.35(13)
O(5)–Tm(1)–O(3)#1	82.05(13)	O(4)–Tm(1)–O(2)#1	76.71(13)
O(6)–Tm(2)–O(1)	109.03(13)	O(7)–Tm(2)–O(8)	129.10(13)
O(2)–Tm(2)–N(5)	109.30(14)	O(3)–Tm(2)–N(3)	112.55(14)
Complex **7**			
Lu(1)–O(8)	2.260(4)	Lu(2)–O(7)	2.252(5)
Lu(1)–O(4)	2.263(5)	Lu(2)–O(8)	2.268(5)
Lu(1)–O(5)	2.276(5)	Lu(2)–O(6)	2.275(5)
Lu(1)–O(1)	2.323(4)	Lu(2)–O(2)	2.278(5)
Lu(1)–O(8)#1	2.325(4)	Lu(2)–O(3)	2.350(5)
Lu(1)–O(3)#1	2.330(5)	Lu(2)–O(1)	2.356(4)
Lu(1)–O(2)#1	2.388(5)	Lu(2)–N(3)	2.460(6)
Lu(1)–N(1)	2.476(6)	Lu(2)–N(5)	2.495(6)

O(8)–Lu(1)–O(1)	70.30(16)	O(8)#1–Lu(1)–N(1)	75.37(17)
O(5)–Lu(1)–O(3)#1	81.72(17)	O(4)–Lu(1)–O(2)#1	76.11(17)
O(6)–Lu(2)–O(1)	108.63(17)	O(7)–Lu(2)–O(8)	128.42(17)
O(2)–Lu(2)–N(5)	109.55(19)	O(3)–Lu(2)–N(3)	112.42(19)

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

Table S2 The parameters obtained from Cole-Cole plots using the Debye model.

Slow Relaxation (SR)			
T / K	χ_1	χ_2	α_1
2	0.58	14.05	0.53
3	0.60	11.26	0.49
4	0.64	8.58	0.45
5	0.65	6.75	0.39
6	0.62	5.58	0.35
7	0.58	4.68	0.31
8	0.496	4.03	0.29
9	0.25	3.65	0.35
10	6.14×10^{-5}	3.32	0.40
11	9.81×10^{-15}	2.99	0.43
12	2.60×10^{-12}	2.92	0.55

Fast Relaxation (FR)			
T / K	χ_1	χ_2	α_2
11	2.38	4.26	0.21
12	2.22	3.87	0.16
13	2.11	3.51	0.092
14	1.81	3.29	0.16
15	1.77	3.08	0.11
16	1.72	2.89	0.069