Supporting Information

Tuning spin dynamics of binuclear Dy complexes using the different nitroxide biradical derivatives

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Table S1. Selected bond lengths [Å] and angles [°] for **1** and **2**.

1 GdZn		**2 DyZn**	
Gd(1)-O(7)	2.377(3)	Dy(1)-O(7)	2.352(4)
Gd(1)-O(7)#1	2.385(3)	Dy(1)-O(7)#1	2.360(4)
Gd(1)-O(6)	2.359(3)	Dy(1)-O(6)	2.325(4)
Gd(1)-O(5)	2.365(3)	Dy(1)-O(5)	2.333(4)
Gd(1)-O(4)	2.357(4)	Dy(1)-O(4)	2.334(5)
Gd(1)-O(3)	2.425(3)	Dy(1)-O(3)	2.380(4)
Gd(1)-O(2)	2.349(4)	Dy(1)-O(2)	2.323(4)
Gd(1)-O(1)	2.388(4)	Dy(1)-O(1)	2.360(5)
Zn(1)-O(9)	2.060(4)	Zn(1)-O(9)	2.054(4)
Zn(1)-O(10)	1.982(4)	Zn(1)-O(10)	1.981(5)
Zn(1)-O(11)	2.006(4)	Zn(1)-O(11)	2.003(5)
Zn(1)-O(12)	2.087(4)	Zn(1)-O(12)	2.088(5)
Zn(1)-N(5)	2.046(4)	Zn(1)-N(5)	2.036(6)
O(8)-N(2)	1.284(6)	O(8)-N(2)	1.277(8)
O(13)-N(4)	1.266(6)	O(13)-N(4)	1.258(8)

Gd(1)#1-O(7)-Gd(1)	110.6(1)	Dy(1)-O(7)-Dy(1)#1	110.5(2)
O(7)#1-Gd(1)-O(7)	69.5(1)	O(7)-Dy(1)-O(7)#1	69.5(2)
O(2)-Gd(1)-O(1)	72.1(1)	O(2)-Dy(1)-O(1)	72.8(2)
O(4)-Gd(1)-O(3)	70.9(1)	O(4)-Dy(1)-O(3)	71.5(2)
O(6)-Gd(1)-O(5)	73.3(1)	O(6)-Dy(1)-O(5)	73.6(2)
C(34)-N(5)-Zn(1)	121.7(4)	C(34)-N(5)-Zn(1)	121.2(4)
O(10)-Zn(1)-O(9)	89.5(2)	O(10)-Zn(1)-O(9)	89.6(2)
O(11)-Zn(1)-O(12)	87.9(2)	O(11)-Zn(1)-O(12)	87.6(2)

Table S2. Selected bond lengths [Å] and angles [°] for **3.**

3 DyZn			
Dy(1)-O(7)	2.349(4)	Dy(1)-O(4)	2.335(5)
Dy(1)-O(7)#1	2.373(4)	Dy(1)-O(3)	2.326(5)
Dy(1)-O(6)	2.353(5)	Dy(1)-O(2)	2.352(5)
Dy(1)-O(5)	2.323(5)	Dy(1)-O(1)	2.349(5)
Zn(1)-O(10)	1.966(6)	Zn(1)-O(13)	1.979(5)
Zn(1)-O(11)	2.057(6)	Zn(1)-O(14)	1.965(5)
Zn(1)-O(12)	2.076(5)	O(8)-N(2)	1.261(8)
N(3)-O(9)	1.271(9)	O(15)-N(4)	1.274(8)
O(14)-N(5)	1.300(7)	Dy(1)-O(7)-Dy(1)#1	111.5(2)
O(7)-Dy(1)-O(7)#1	68.5(2)	O(1)-Dy(1)-O(2)	72.3 (2)
O(3)-Dy(1)-O(4)	72.4(2)	O(5)-Dy(1)-O(6)	72.2(2)
N(5)-O(14)-Zn(1)	116.7(4)	O(10)-Zn(1)-O(11)	90.8(3)

Table S3. SHAPE analysis for the Ln coordination spheres for **1-3**.

Complex	SAPR-8	TDD-8	BTPR-8	JBTPR-8
1 Gd	**0.585**	1.454	1.549	2.144
2 Dy	**0.498**	1.515	1.654	2.276
3 Dy	**0.469**	1.755	2.208	2.832

SAPR-8: Square antiprism; TDD-8: Triangular dodecahedron; BTPR-8: Biaugmented trigonal prism; JBTPR-8: Biaugmented trigonal prism.

Table S4. Best fitted parameters (χ_T, χ_S, τ, α) with the Debye model for complex **2** from fitting of ac data at 0 Oe in the temperature range 2-11 K

T/ K	χ_S / cm^3mol^{-1}	χ_T / cm^3mol^{-1}	τ/s	α
1.9	6.76(1)	0.59(2)	0.0038(3)	0.33(2)
2.2	7.17(5)	0.93(6)	0.00379(3)	0.33(3)
2.5	6.51(7)	0.38(8)	0.00328(1)	0.32(1)
3.0	6.22(4)	0.36(6)	0.00249(5)	0.31(1)
3.5	6.04(5)	0.56(6)	0.00221(6)	0.29(2)
4.0	6.15(2)	1.11(5)	0.0015(6)	0.24(2)
4.5	5.48(2)	1.02(6)	0.00125(7)	0.23(2)
5.0	4.89(1)	0.64(4)	8.35(1)E-4	0.20(1)
6.0	5.12(7)	0.37(5)	4.45(9)E-4	0.17(1)
7.0	4.88(8)	1.62(7)	2.56(6)E-4	0.15(1)
8.0	4.63(2)	1.86(3)	1.53(1)E-4	0.14(1)
9.0	4.41(6)	2.25(1)	9.57(3)E-5	0.12(2)
10.0	4.07(3)	1.91(2)	3.62(2)E-5	0.16(6)
11.0	3.67(1)	2.99(4)	8.64(7)E-5	0.026(3)

Table S5. Best fitted parameters ($\Delta\chi_1$, $\Delta\chi_2$, τ_1, τ_2, α_1, α_2) with the modified Debye model for complex **3** from fitting of ac data at 0 Oe in the temperature range 2-11 K

T/K	$\chi_{s,tot}$/cm^3mol^{-1}	$\Delta\chi_1$/cm^3mol^{-1}	$\Delta\chi_2$/cm^3mol^{-1}	τ_1/s	α_1	τ_2/s	α_2
1.9	2.61(6)	3.91(6)	3.27(4)	0.05(2)	0.27(6)	1.77(1)E-4	0.67(1)
2.2	2.19(2)	3.83(1)	2.92(9)	0.042(3)	0.25(6)	1.50(5)E-4	0.65(5)
2.5	2.39(8)	3.62(2)	2.77(5)	0.035(8)	0.23(7)	1.31(1)E-4	0.62(2)
3	1.82(2)	4.06(1)	2.22(5)	0.024(5)	0.22(7)	9.78(3)E-5	0.60(8)
3.5	1.83(1)	3.14(3)	2.36(8)	0.018(1)	0.20(7)	7.80(2)E-5	0.55(1)
4	1.93(3)	2.18(1)	2.56(1)	0.011(1)	0.19(2)	5.79(2)E-5	0.52(6)
4.5	1.72(1)	2.09(3)	2.28(2)	0.0079(7)	0.21(8)	4.50(1)E-5	0.51(1)
5	1.71(1)	1.80(3)	2.09(5)	0.0050(5)	0.15(8)	3.25(1)E-5	0.38(2)
6	1.54(6)	1.50(5)	1.83(5)	0.0028(3)	0.12(5)	2.09(1)E-5	0.30(1)
7	1.37(8)	1.97(2)	0.96(1)	0.00138(2)	0.11(3)	1.59(1)E-5	0.076(1)
8	1.29(4)	0.87(4)	1.67(4)	9.77(1)E-4	0.13(6)	1.29(1)E-5	0.16(6)
9	1.23(6)	1.63(4)	0.63(8)	6.26(7)E-4	0.10(5)	1.10(7)E-5	0.31(1)
10	1.58(8)	1.18(2)	0.58(2)	3.72(3)E-4	0.13(4)	1.06(8)E-5	0.082(1)
11	0.82(3)	1.19(4)	0.15(8)	2.50(2)E-4	0.09(1)	1.50(3)E-5	0.079(2)

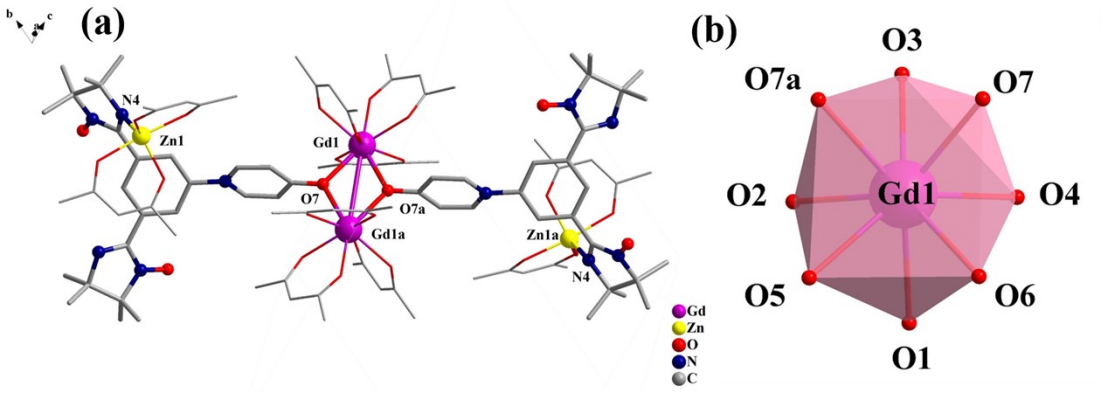

Figure S1. (a) The tetranuclear structure of **1** (H atoms and F atoms are not shown). (b) Coordination polyhedron around Gd^{III} in **1**.

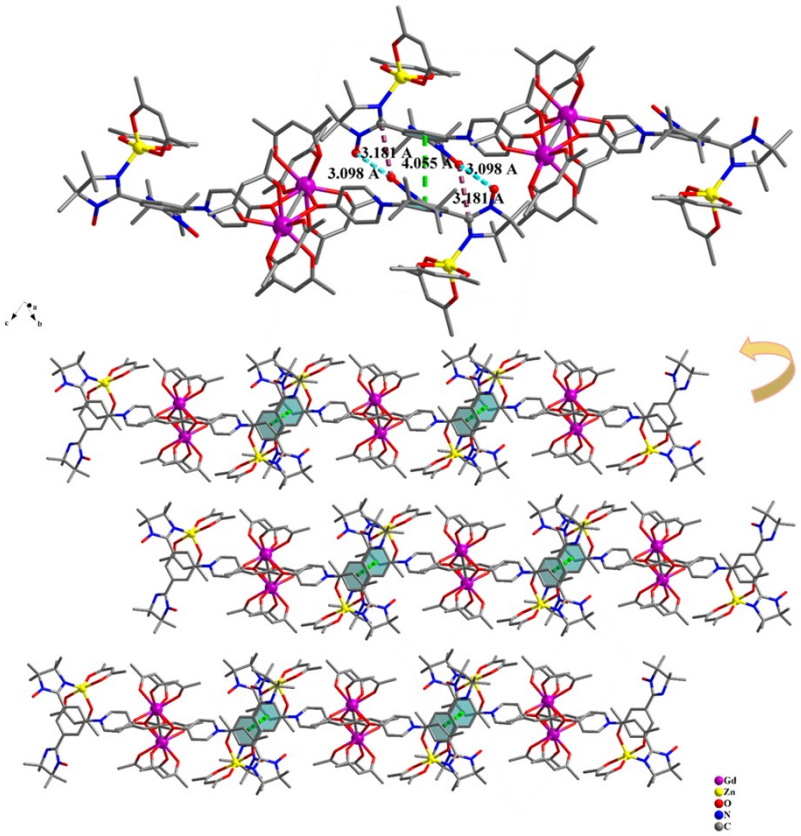

Fig.S2. Packing diagram of complex **1**. H and F atoms are not shown for clarity.

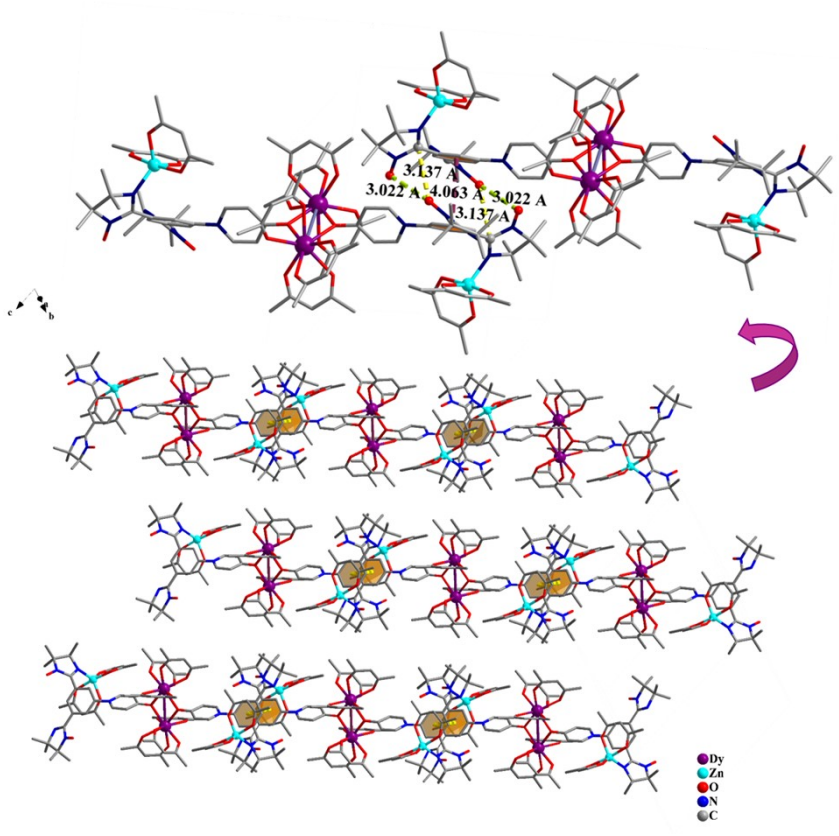

Fig.S3. Packing diagram of complex **2**. H and F atoms are not shown for clarity.

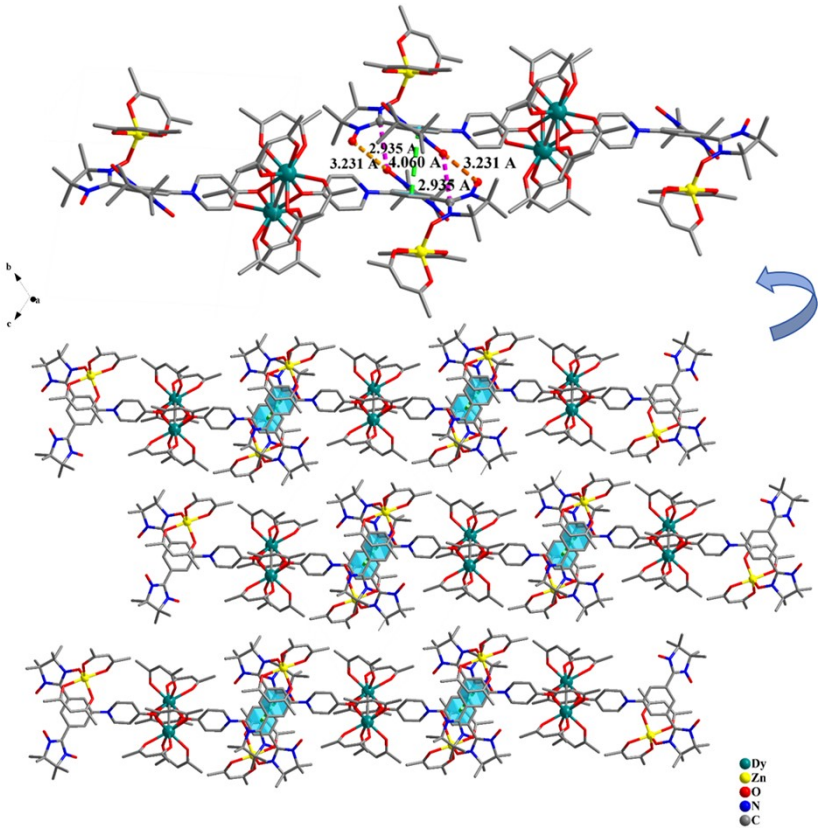

Fig.S4. Packing diagram of complex **3**. H and F atoms are not shown for clarity.

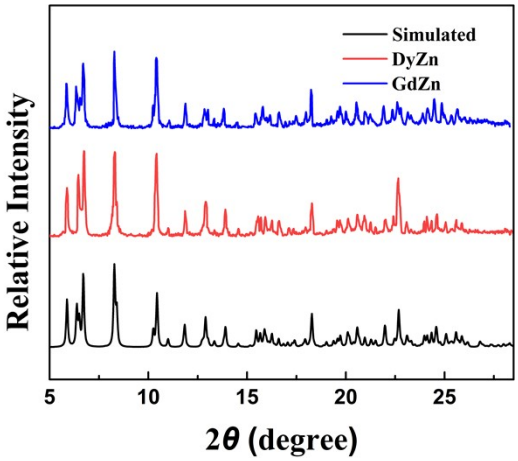

Fig.S5. The Powder X-ray diffraction (PXRD) patterns for complexes **1** and **2** at room temperature.

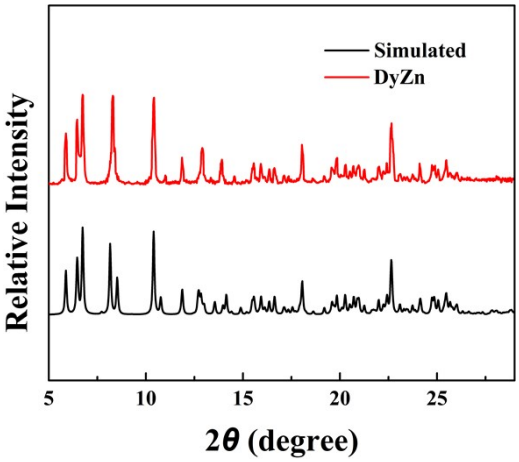

Fig.S6. The Powder X-ray diffraction (PXRD) pattern for complex **3** at room temperature.

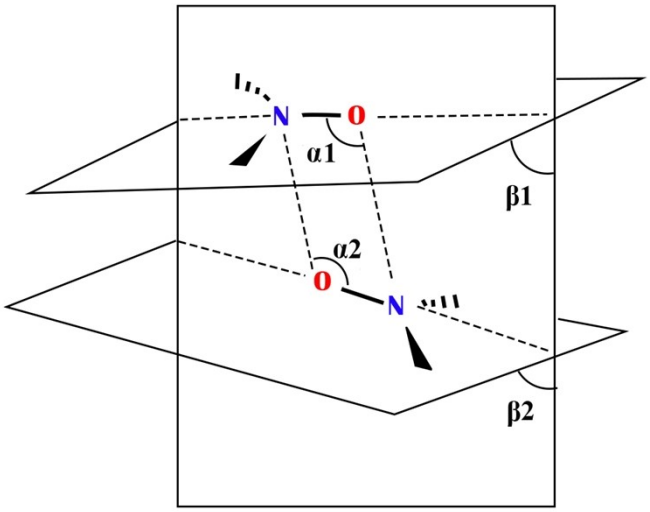

Fig.S7. Definition of the parameters used in the discussion of two nitroxide groups interactions.

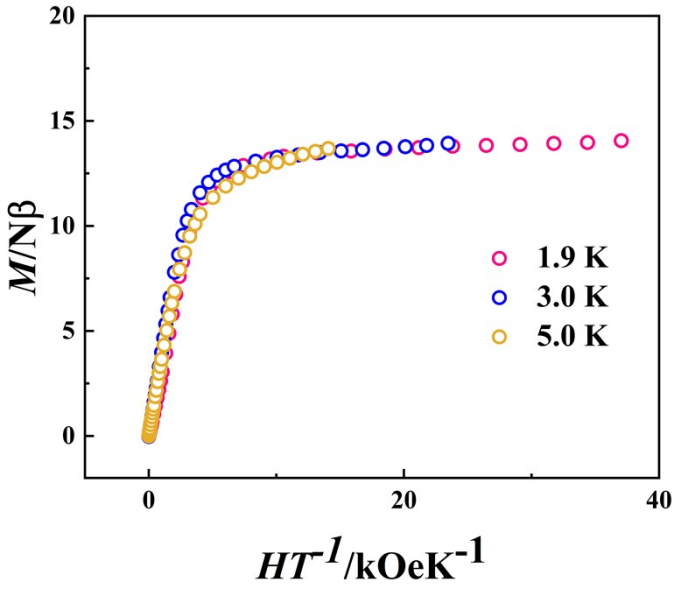

Fig.S8. Plots of *M* vs. *H*/*T* between 0 and 70 kOe at temperatures 1.9, 3.0 and 5.0 K for **2**

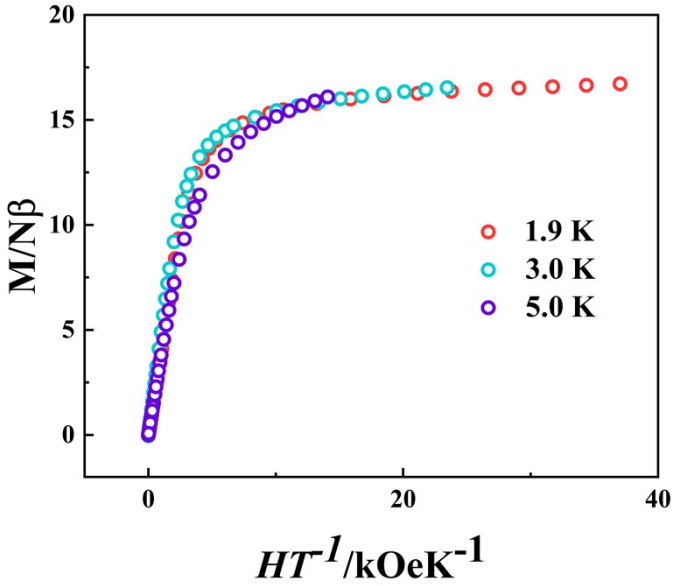

Fig.S9. Plots of *M* vs. *H*/*T* between 0 and 70 kOe at temperatures 1.9, 3.0 and 5.0 K for **3**

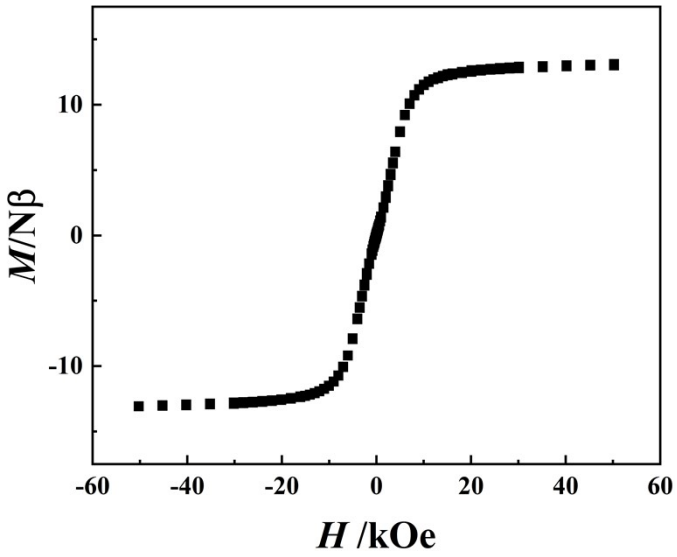

Fig.S10. Magnetization plot of complex **2** at 1.9 K.

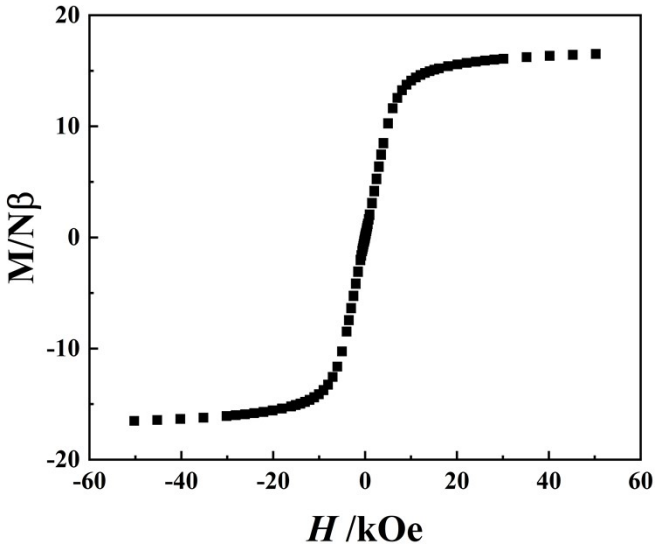

Fig.S11. Magnetization plot of complex **3** at 1.9 K.

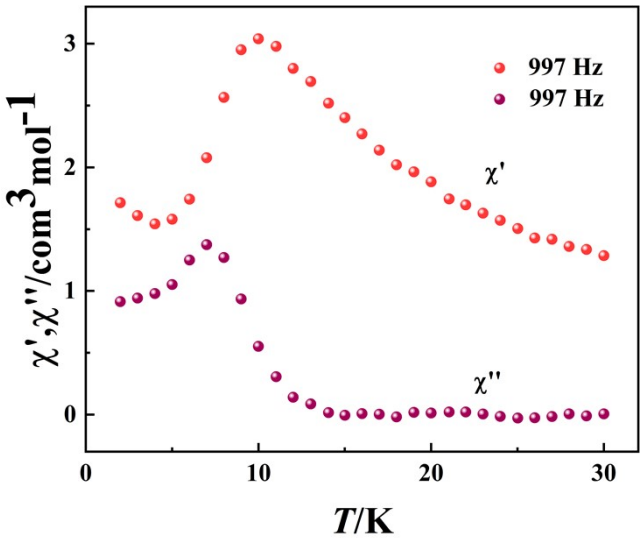

Fig.S12. Temperature dependences of the in-phase and out-of-phase ac susceptibilities under

0Oe dc field for **2**.

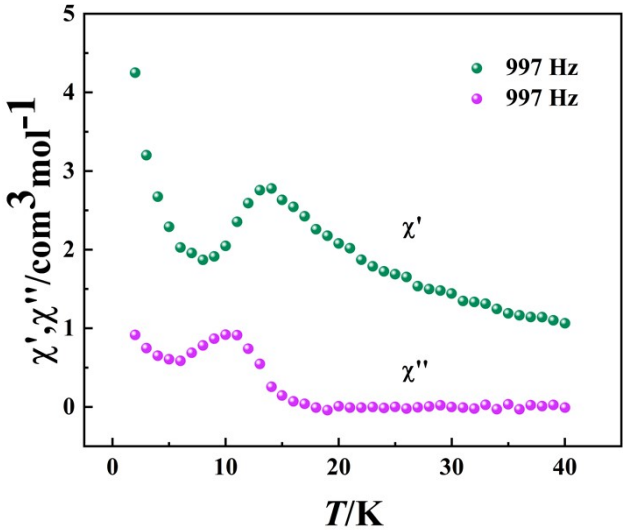

Fig.S13. Temperature dependences of the in-phase and out-of-phase ac susceptibilities under 0Oe dc field for **3**.