Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

A series of Cu^{II}–Ln^{III} complexes of an N_2O_3 donor asymmetric ligand and a possible Cu^{II}–Tb^{III} SMM candidate in no bias field

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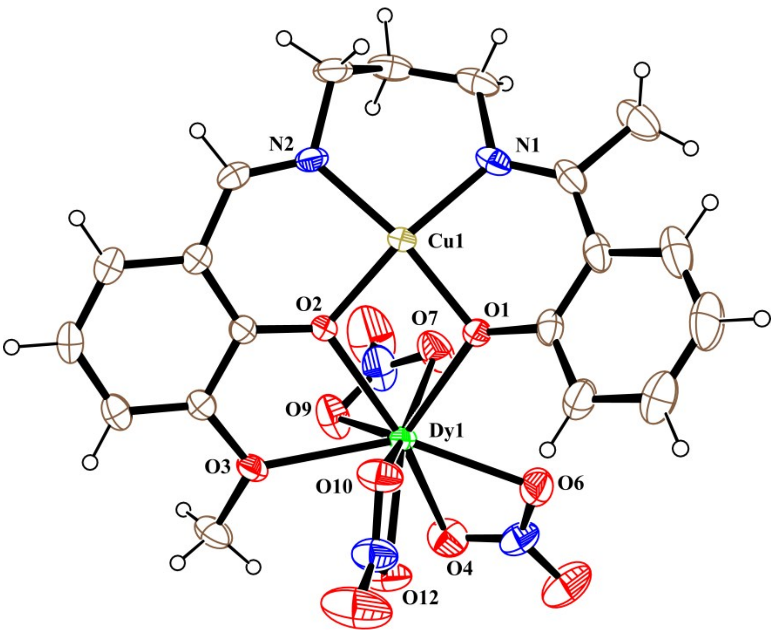


Fig. S1. Structure of complex **2Dy** with 30% thermal ellipsoid probability.

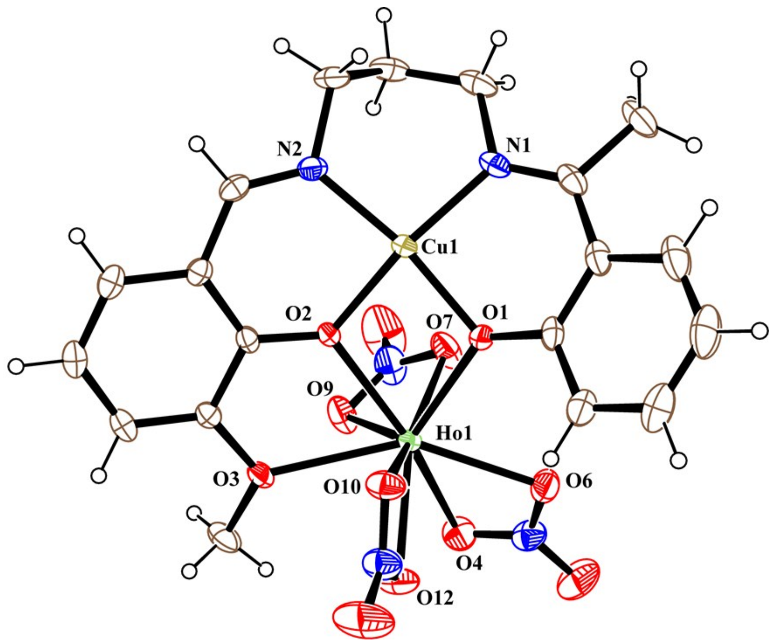


Fig. S2. Structure of complex **3Ho** with 30% thermal ellipsoid probability.

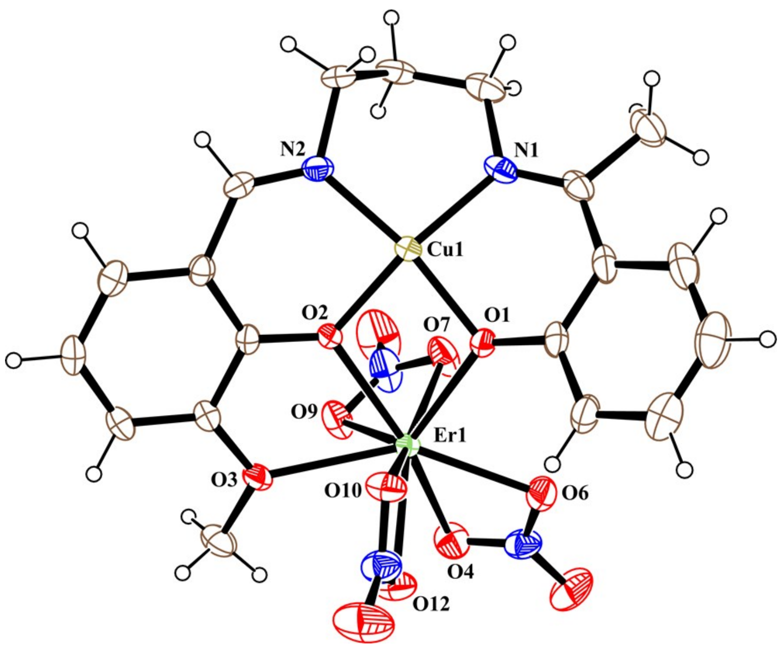


Fig. S3. Structure of complex **4Er** with 30% thermal ellipsoid probability.

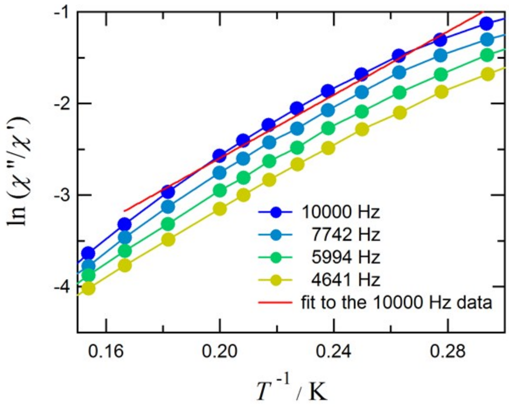


Fig. S4. The natural logarithm of the ratio of χ'' over χ' *vs* $1/T$ for the zero-bias data of **1Tb**. The Arrhenius parameters were estimated by fitting the experimental χ''/χ' data as $U_{\text{eff}}/k_{\text{B}}$ = 17.3(7) K and $\tau_0 = 3.7(6)\times10^{-8}$ s.

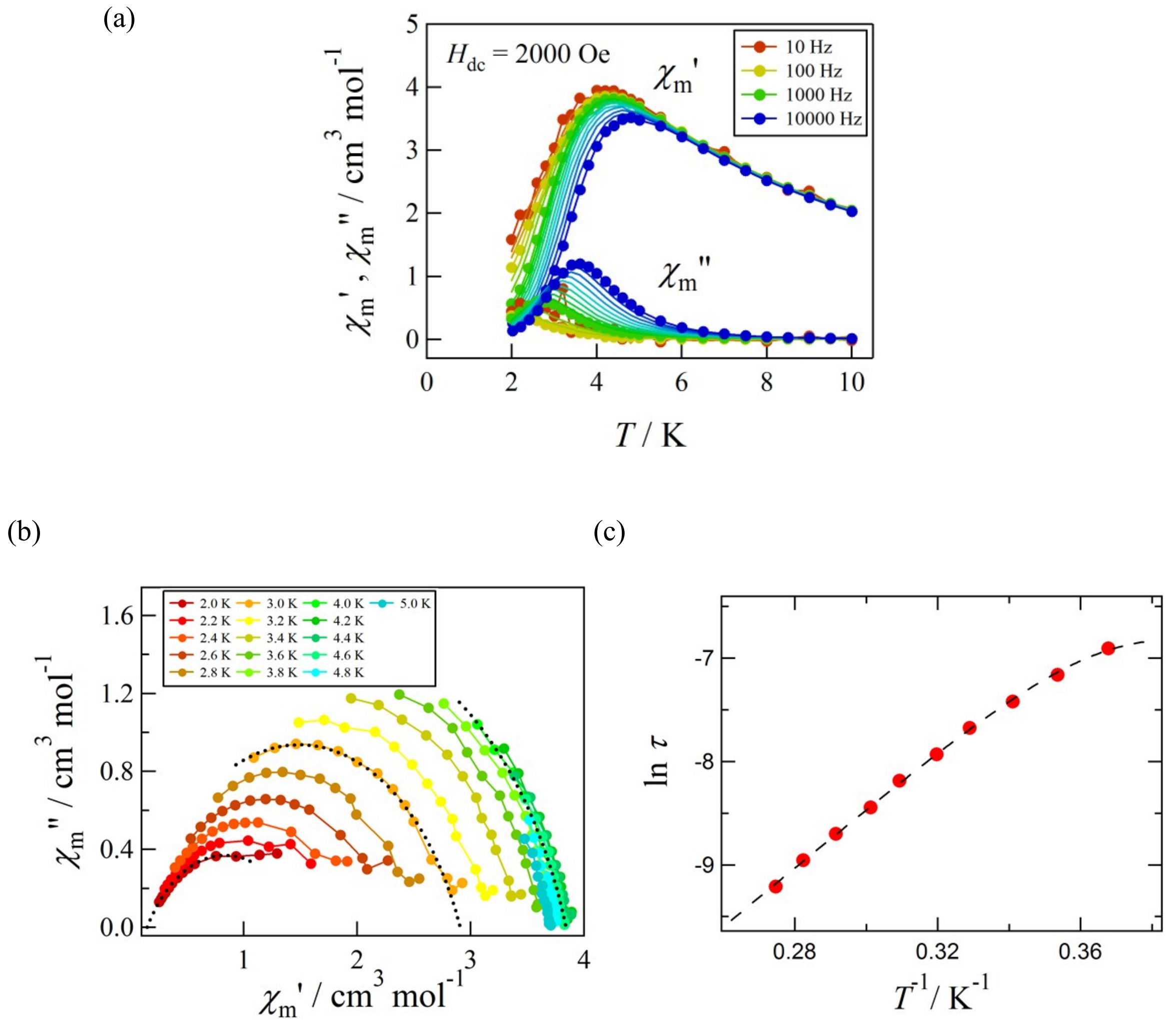
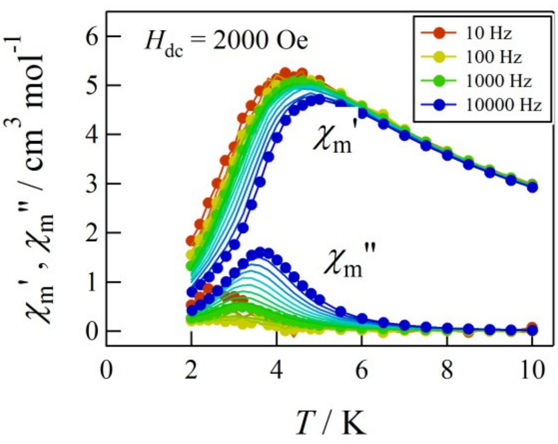
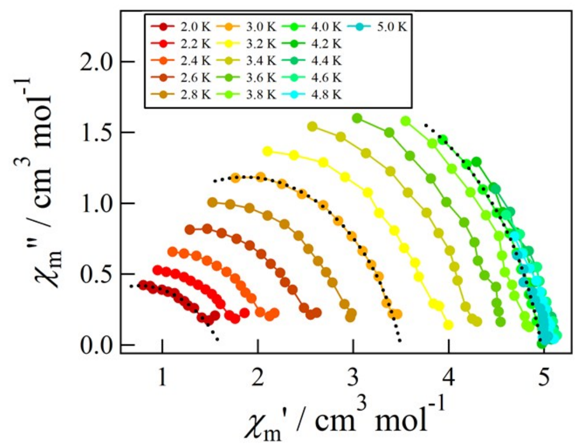


Fig. S5. (a) Ac magnetic susceptibilities of **1Tb**, measured at an applied dc field of 2000 Oe. (b) The Cole-Cole plot for **1Tb**. Dotted lines stand for calculation curves based on the Debye model. The optimized α values are 0.22(3), 0.26(2), and 0.370(3) at 4.0, 3.0, and 2.0 K, respectively. The equation $\chi(\omega) = \chi_S + (\chi_T - \chi_S)/(1 + (i\omega\tau)^{1-\alpha})$ was applied, where χ_T and χ_S are the isothermal and adiabatic magnetic susceptibilities, respectively.[1] Note that the relatively small α values support a narrow distribution of relaxation times. (c) The Arrhenius plot for **1Tb**. A broken line stands for calculation based on a modified Arrhenius equation, $\tau^{-1} = CT^n + \tau_0^{-1} \exp(-U_{eff}/k_BT)$, where the first and second terms imply the Raman and Orbach mechanisms, respectively.[2] The optimized parameters are: U_{eff} = 28.5(5) K and τ_0 = 4.1(6)×10^{-8} s.

(a)



(b)



(c)

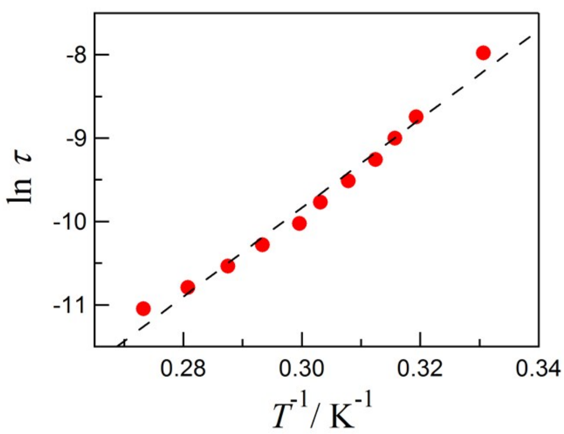


Fig. S6. (a) Ac magnetic susceptibilities of **2Dy**, measured at an applied dc field of 2000 Oe. (b) The Cole-Cole plot for **2Dy**. Dotted lines stand for calculation curves based on the Debye model. The optimized α values are 0.15(2), 0.20(1), and 0.42(3) at 4.0, 3.0, and 2.0 K, respectively. For details, see the caption of Fig. S5. (c) The Arrhenius plot for **2Dy**. A broken line stands for calculation based on the Arrhenius analysis, $\tau^{-1} = \tau_0^{-1} \exp(-U_{eff} / k_B T)$.[3] The optimized parameters are: U_{eff} = 53(2) K and $\tau_0 = 6(5)\times10^{-9}$ s.

(a) (b)

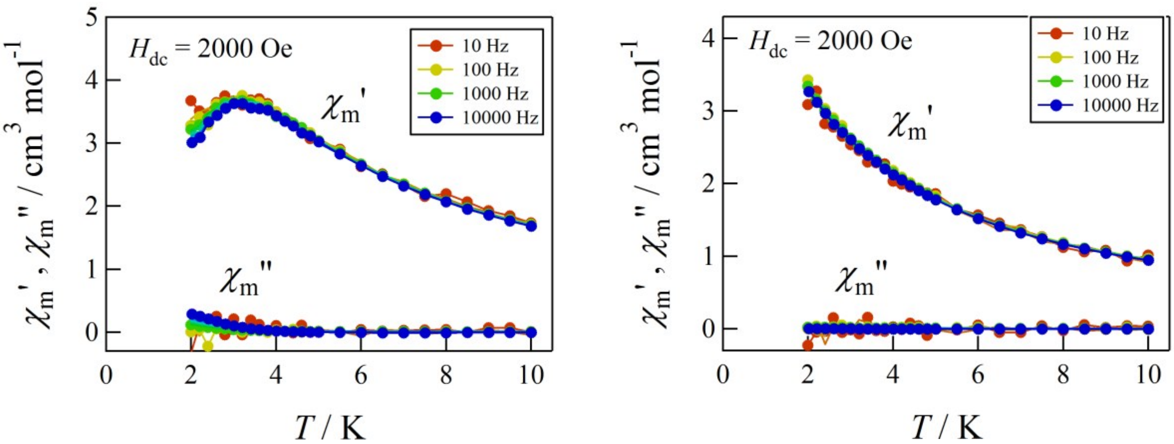


Fig. S7. Ac magnetic susceptibilities as a function of temperature for (a) **3Ho** and (b) **4Er**, measured at an applied dc field of 2000 Oe.

Table S1. Bond distances (Å) and angles (°) for complexes **1Tb–4Er**.

	1Tb	**2Dy**	**3Ho**	**4Er**
M(1)–O(1)	2.340(6)	2.326(3)	2.319(3)	2.301(3)
M(1)–O(2)	2.308(5)	2.303(3)	2.285(3)	2.276(4)
M(1)–O(3)	2.510(5)	2.518(3)	2.507(3)	2.493(5)
M(1)–O(4)	2.447(7)	2.438(5)	2.427(3)	2.413(5)
M(1)–O(6)	2.383(6)	2.385(5)	2.375(3)	2.356(5)
M(1)–O(7)	2.416(7)	2.405(5)	2.388(3)	2.378(5)
M(1)–O(9)	2.443(7)	2.444(4)	2.433(3)	2.414(4)
M(1)–O(10)	2.435(6)	2.426(3)	2.419(3)	2.395(4)
M(1)–O(12)	2.431(6)	2.429(4)	2.417(3)	2.401(5)
Cu(1)–O(1)	1.919(5)	1.930(3)	1.919(3)	1.913(3)
Cu(1)–O(2)	1.933(5)	1.937(3)	1.920(2)	1.914(4)
Cu(1)–N(1)	1.966(7)	1.974(4)	1.963(3)	1.957(5)
Cu(1)–N(2)	1.932(7)	1.944(3)	1.926(3)	1.925(5)
O(1)–M(1)–O(2)	65.17(17)	65.46(10)	65.60(8)	65.61(12)
O(1)–M(1)–O(3)	126.23(17)	126.76(10)	127.17(8)	127.36(12)
O(1)–M(1)–O(4)	128.6(2)	128.74(13)	128.36(9)	128.74(13)
O(1)–M(1)–O(6)	79.2(2)	79.21(13)	78.64(10)	78.71(15)
O(2)–M(1)–O(3)	64.78(16)	64.94(11)	65.46(8)	65.79(13)
O(2)–M(1)–O(4)	155.9(2)	154.85(13)	155.24(9)	154.66(15)
O(2)–M(1)–O(6)	144.1(2)	144.29(13)	143.97(10)	143.99(16)
O(3)–M(1)–O(4)	105.2(2	104.48(13)	104.48(9)	103.91(15)
O(3)–M(1)–O(6)	149.7(2)	149.63(14)	149.02(10)	148.77(17)
O(4)–M(1)–O(6)	52.4(2)	52.70(15)	52.98(10)	53.31(16)
O(7)–M(1)–O(9)	51.8(2)	51.94(15)	52.64(10)	52.86(16)
O(7)–M(1)–O(10)	154.3(2)	153.55(14)	154.06(10)	153.69(17)
O(7)–M(1)–O(12)	152.1(2)	152.80(15)	151.40(10)	151.15(17)
O(9)–M(1)–O(10)	142.6(2)	142.30(15)	142.44(9)	142.42(15)
O(9)–M(1)–O(12)	116.6(3)	115.83(15)	116.32(10)	115.96(17)
O(10)–M(1)–O(12)	51.8(2)	52.31(13)	52.32(9)	52.92(15)
O(1)–Cu(1)–O(2)	81.1(2)	80.68(13)	81.01(10)	80.76(14)
O(1)–Cu(1)–N(1)	91.8(2)	91.88(15)	91.62(12)	91.96(17)
O(1)–Cu(1)–N(2)	167.8(3)	167.68(14)	167.92(12)	167.42(17)
O(2)–Cu(1)–N(1)	162.8(3)	162.86(15)	163.14(12)	163.05(18)
O(2)–Cu(1)–N(2)	91.0(2)	90.88(13)	91.07(12)	90.81(17)
N(1)–Cu(1)–N(2)	98.3(3)	98.59(16)	98.34(14)	98.6(2)
M(1)–O(1)–Cu(1)	104.7(2)	104.85(12)	104.32(10)	104.61(13)
M(1)–O(2)–Cu(1)	105.4(2)	105.43(12)	105.57(9)	105.50(14)

Table S2. Continuous SHAPE measures (CShM)[4] for **1Tb–4Er**.

Ideal structure [a]	**1Tb**	**2Dy**	**3Ho**	**4Er**
TCTPR-9	3.24	3.23	2.99	2.91
CSAPR-9	3.32	3.28	3.10	3.01
MFF-9	3.63	3.59	3.42	3.30
JCSAPR-9	4.56	4.53	4.34	4.26

a: JTCTPR-9: tricapped trigonal prism.
CSAPR-9:spherical capped square antiprism.
MFF-9:muffin.
JCSAPR-9:capped square antiprism.

References

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