Supporting Information

Magnetic refrigeration and slow magnetic relaxation in tetranuclear lanthanide cages (Ln = Gd, Dy) with *in situ* ligand transformation.

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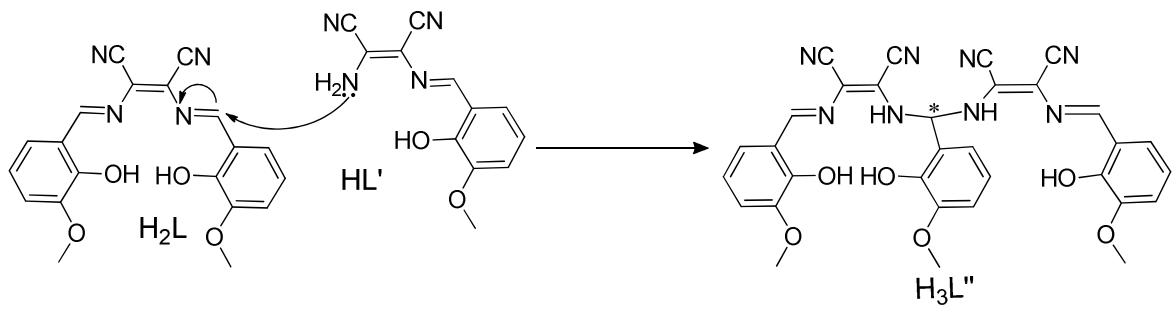
Scheme S1. Mechanism showing in situ ligand transformation



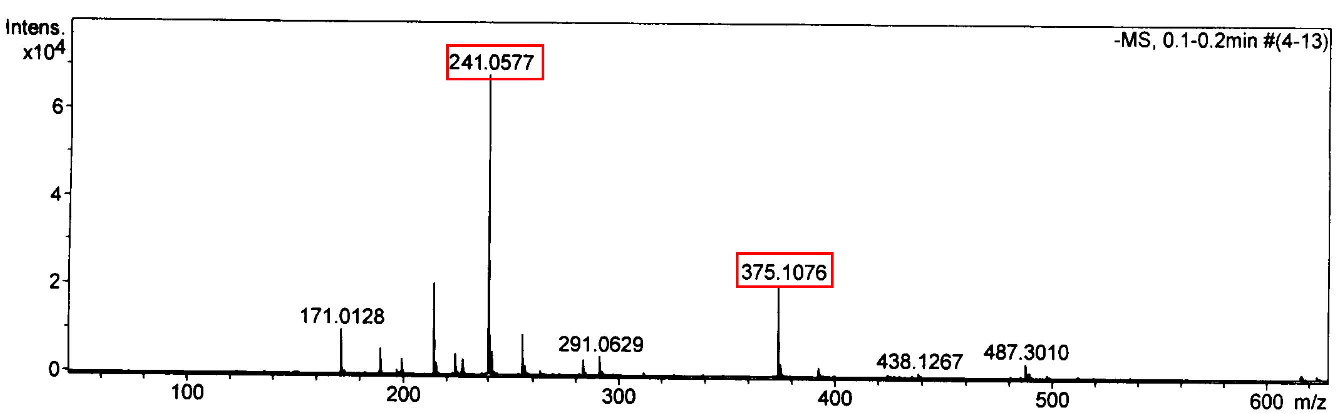


Fig. S1 ESI-MS Spectra of ligand before addition of metal salt. The highlighted peaks match in order with HL_1 and H_2L respectively.

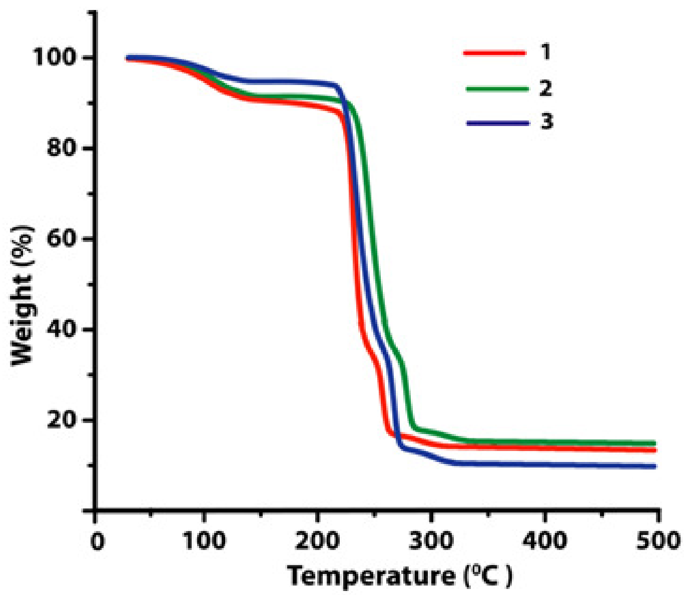


Fig S2. TGA plots for complexes **1-3**

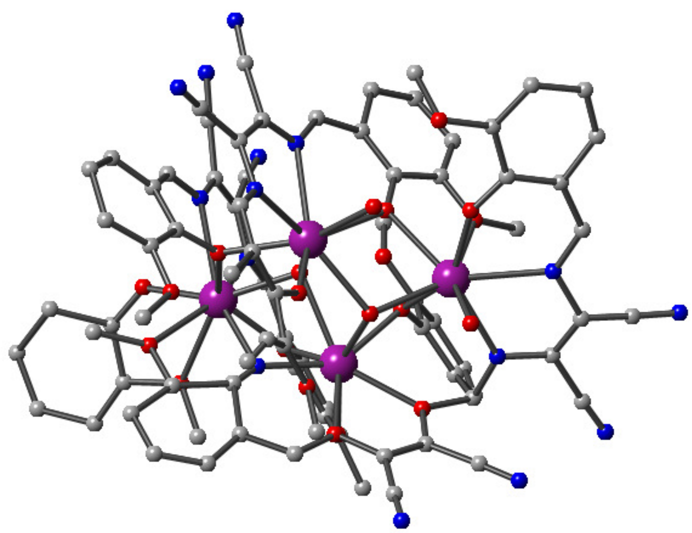


Fig. S3 Ball & stick model showing molecular structure of **2** in the crystal. Colour code: purple, Dysprosium; blue, nitrogen; red, oxygen; gray, carbon; Hydrogen atoms are omitted for clarity

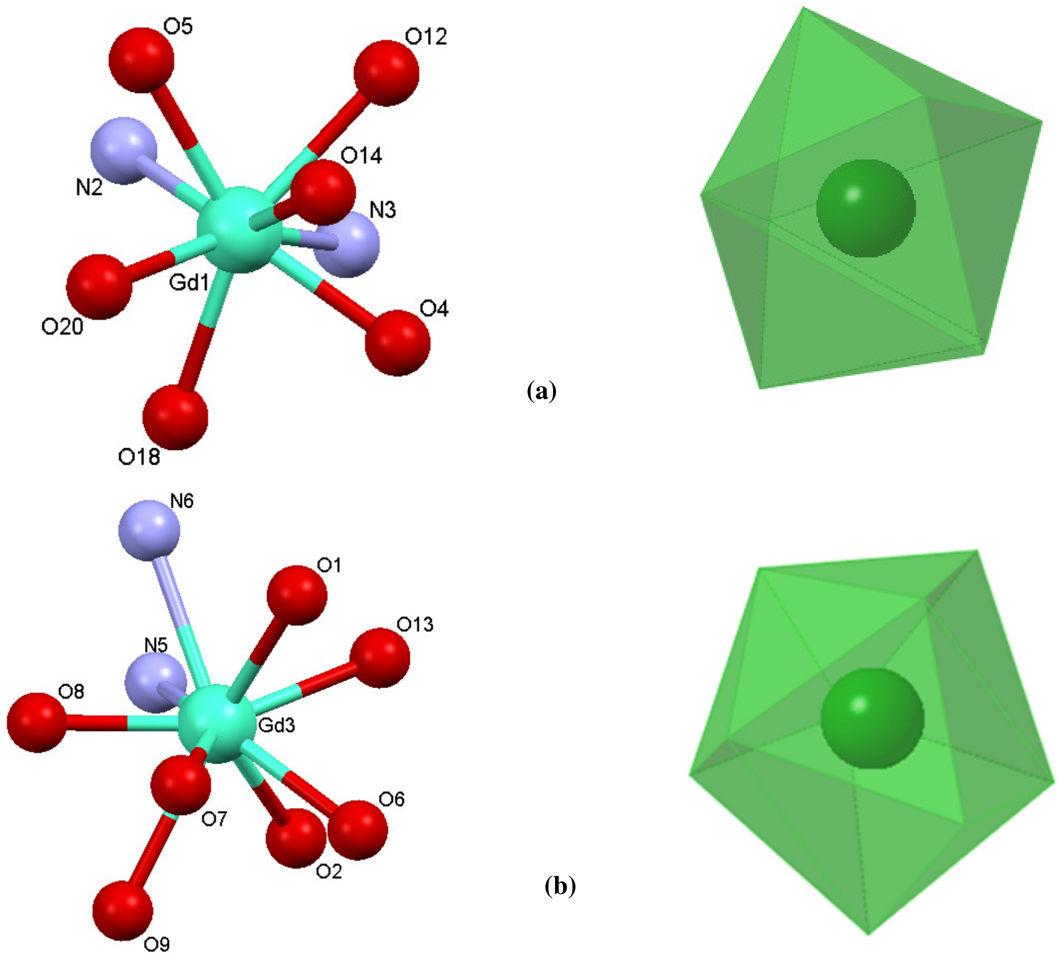


Fig. S4 Illustration of coordination environment and geometry around two types of Ln^{III} centres in **1,** (a) Square antiprismatic, (b) Trigonal prismatic**.** Exactly similar coordination environment is found in **2.**

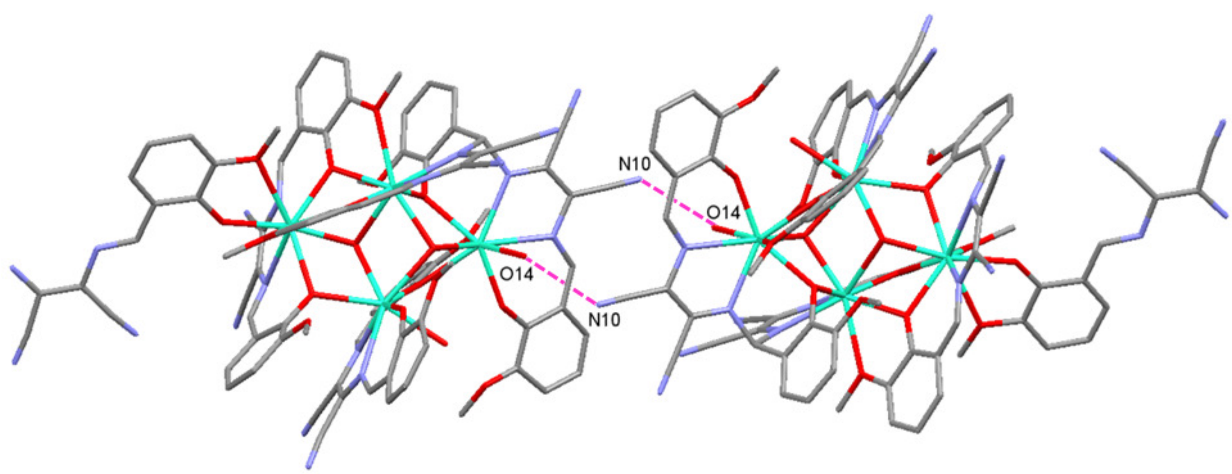


Fig. S5 Capped stick view showing intermolecular interactions in Complex **2.** Colour code: Green, Metal; blue, nitrogen; red, oxygen; gray, carbon; Hydrogen atoms are omitted for clarity

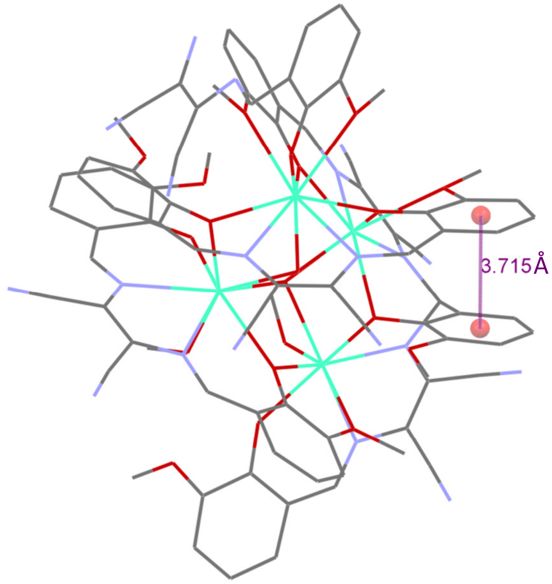
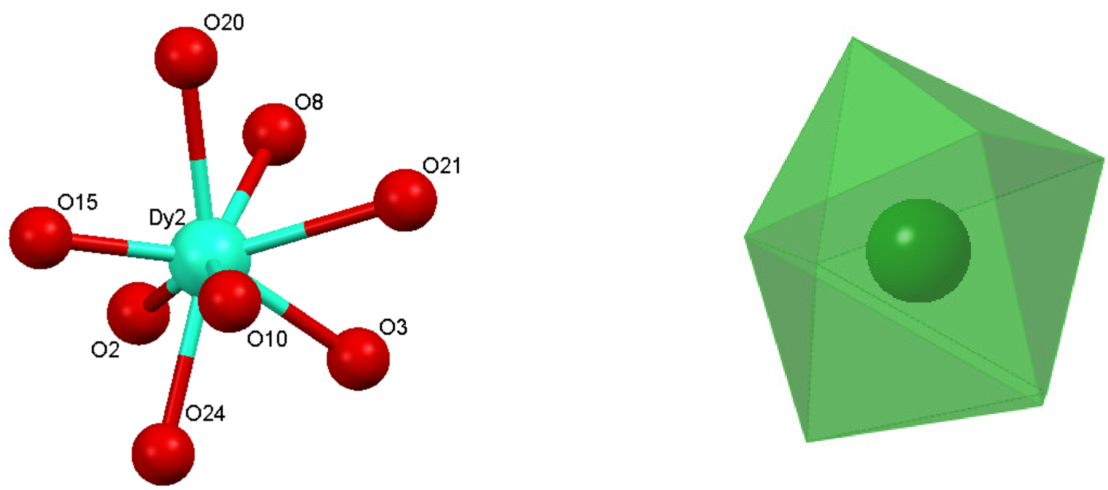
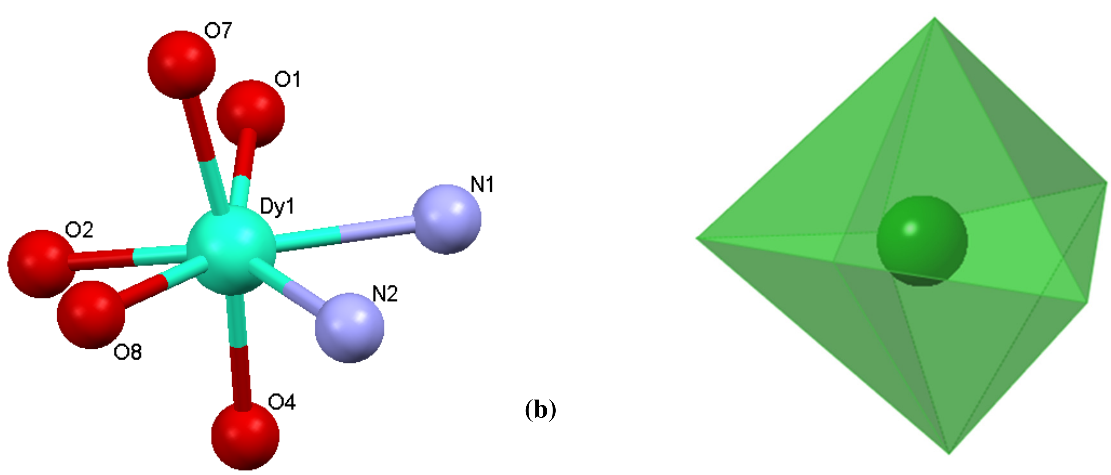


Fig. S6 Wireframe view displaying π-π interactions between O-vanilin rings in Complex **1** or **2.** Colour code: Same as Fig. S4**.**



(a)



(b)

Fig. S7 Illustration of coordination environment and geometry around two types of Ln^{III} centres in **3,** (a) Square antiprismatic**,** (b) Distorted Pentagonal bipyramidal

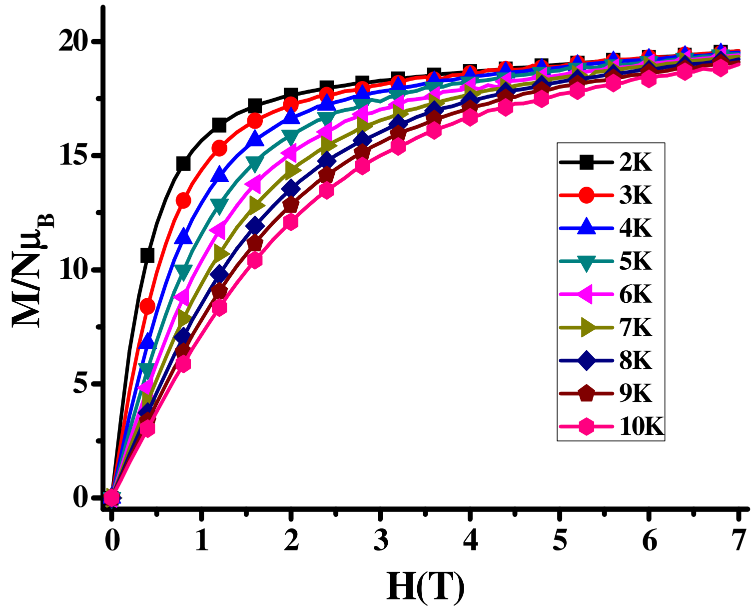


Fig. S8. Field-dependencies of isothermal normalized magnetizations for complex **2** collected for temperatures ranging from 2-10 K.

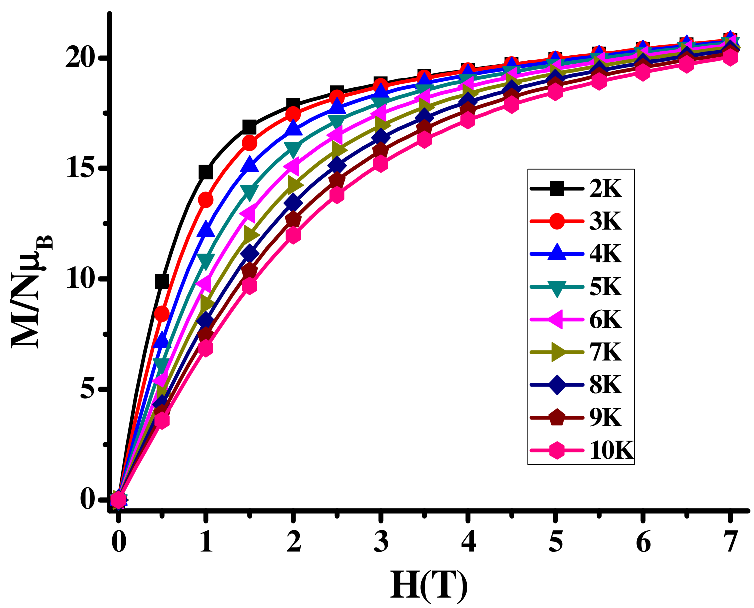


Fig. S9. Field-dependencies of isothermal normalized magnetizations for complex **3** collected for temperatures ranging from 2-10 K.

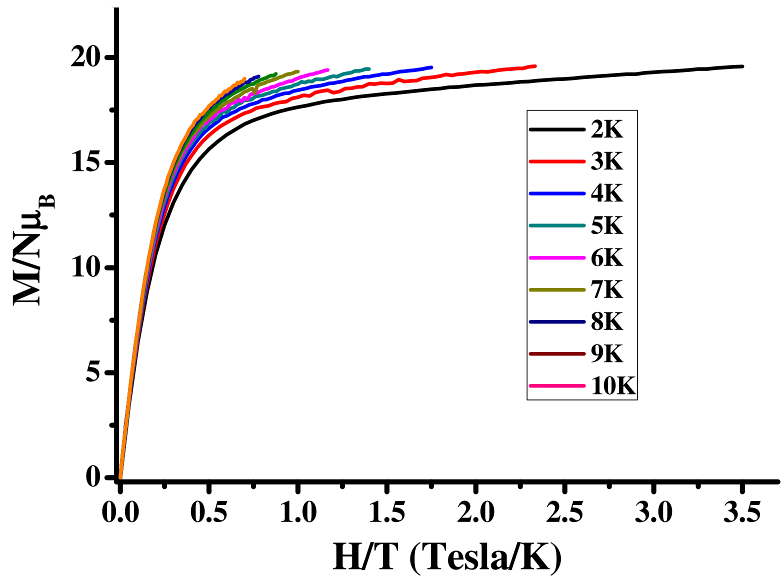


Fig. S10. M/NμB vs H/T plots for complex **2** at 2-10 K.

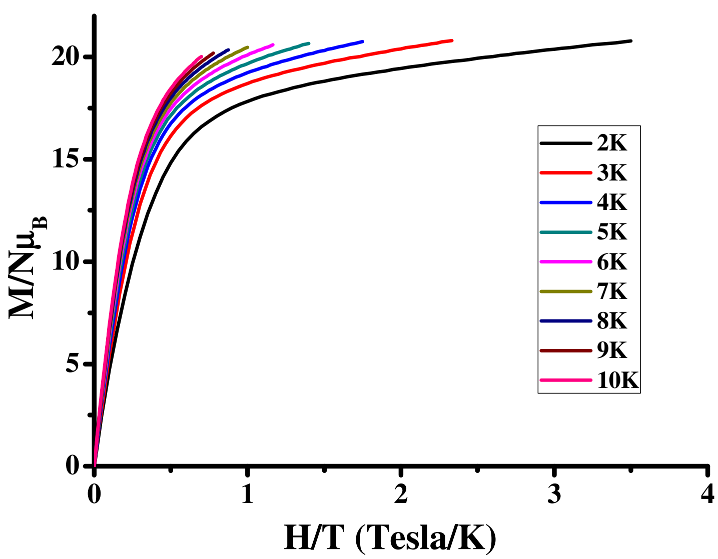


Fig. S11. M/NμB vs H/T plots for complex **3** at 2-10 K.

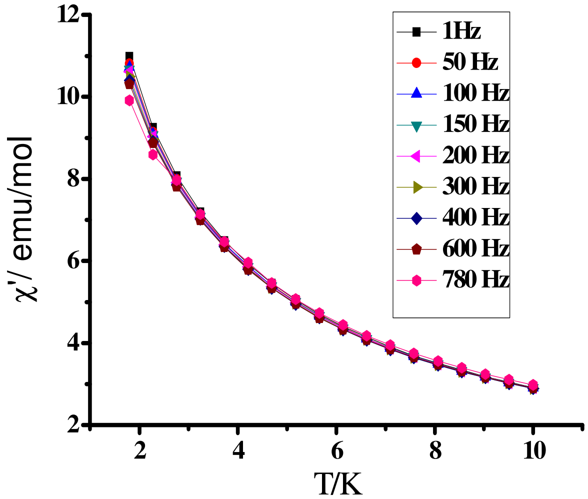


Fig. S12 Temperature dependence of the in phase (χ') ac susceptibility for complex **3** under a zero dc field.

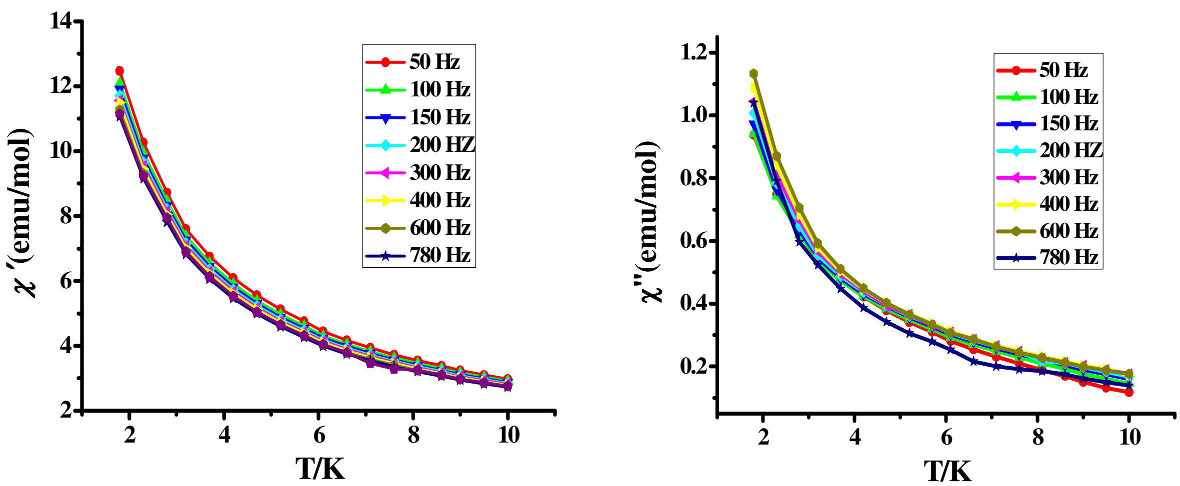


Fig. S13 Temperature dependence of the in phase (χ') (left) and out of phase (χ'') (right) ac susceptibility for complex **2** under a zero dc field.

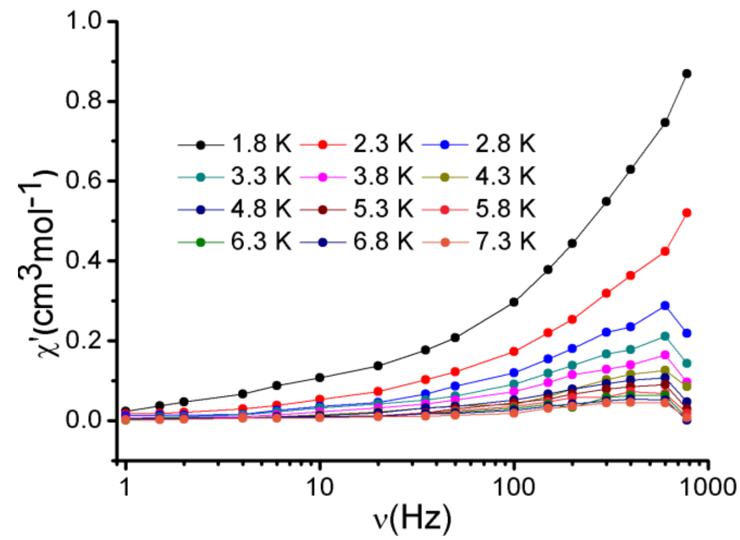


Fig. S14 Frequency dependence of the out of phase (χ'') ac susceptibility for complex **3** under a zero dc field.

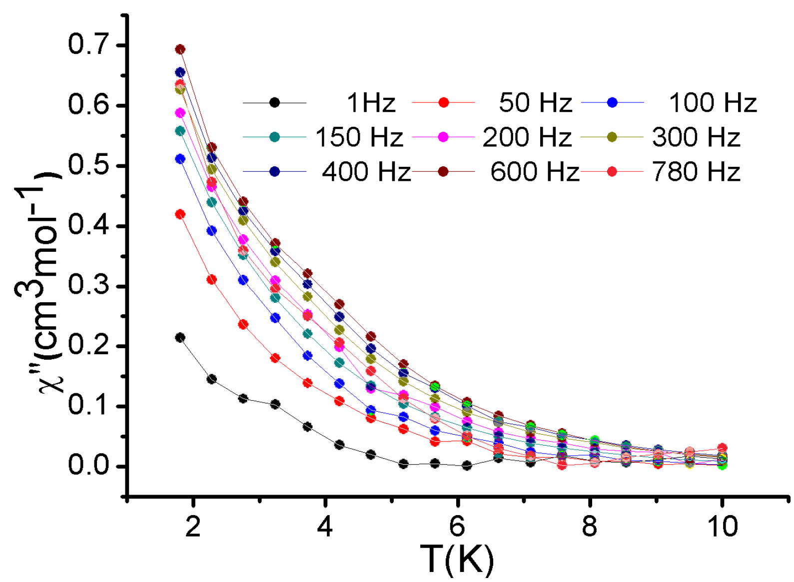


Fig. S15 Temperature dependence of the out of phase (χ'') ac susceptibility for complex **3** under a dc field of 1800 Oe.

Table S1. Selected bond distances (Å) and bond angles (°) around the Ln^{III} centers found in **1**-**3.**

1		**2**		**3**	
Gd1- O4	2.23(2)	Dy1- O2	2.27(2)	Dy1- O1	2.40(2)
Gd1- O5	2.39(2)	Dy1- O3	2.58(2)	Dy1- O2	2.35(7)
Gd1- O12	2.46(2)	Dy1- O9	2.31(2)	Dy1- O4	2.38(2)
Gd1- O14	2.45(2)	Dy1- O10	2.47(2)	Dy1- O7	2.34(2)
Gd1- O18	2.40(2)	Dy1- O12	2.38(2)	Dy1- O8	2.31(2)
Gd1- O20	2.36(2)	Dy1- O20	2.33(2)	Dy1- N1	2.44(9)
Gd1- N2	2.43(2)	Dy1- O21	2.50(1)	Dy1- N2	2.42(8)
Gd1- N3	2.65(3)	Dy1- N2	2.29(2)	Dy2- O2	2.22(7)
Gd2- O1	2.44(2)	Dy2- O2	2.37(1)	Dy2- O3	2.29(2)
Gd2- O10	2.21(2)	Dy2- O6	2.42(2)	Dy2- O8	2.28(2)
Gd2- O11	2.38(2)	Dy2- O7	2.19(2)	Dy2- O10	2.49(7)
Gd2- O13	2.33(1)	Dy2- O8	2.44(2)	Dy2- O15	2.18(3)
Gd2- O14	2.42(2)	Dy2- O16	2.43(2)	Dy2- O20	2.49(2)
Gd2- O20	2.44(1)	Dy2- O20	2.34(2)	Dy2- O21	2.59(3)
Gd2- N22	2.55(3)	Dy2- N4	2.59(3)	Dy2- O24	2.42(6)
Gd2- N23	2.49(2)	Dy2- N6	2.45(2)	Dy3- O1	2.43(2)
Gd3- O1	2.40(2)	Dy3- O1	2.56(2)	Dy3- O2	2.18(7)
Gd3- O2	2.35(2)	Dy3- O9	2.35(2)	Dy3- O6	2.28(4)
Gd3- O6	2.42(2)	Dy3- O11	2.39(2)	Dy3- O16	2.22(5)
Gd3- O7	2.55(2)	Dy3- O14	2.20(2)	Dy3- O18	2.58(4)
Gd3- O8	2.24(2)	Dy3- O18	2.59(2)	Dy3- O19	2.49(3)
Gd3- O9	2.62(2)	Dy3- O21	2.28(2)	Dy3- O22	2.41(3)
Gd3- O13	2.35(2)	Dy3- N2	2.42(2)	Dy3- O23	2.48(2)
Gd3- N5	2.70(2)	Dy3- N3	2.59(2)	Dy4- O2	2.31(5)
Gd3- N6	2.60(2)	Dy3- N7	2.63(3)	Dy4- O3	2.33(3)
Gd4- O2	2.36(1)	Dy4- O4	2.38(2)	Dy4- O4	2.25(3)
Gd4- O3	2.59(1)	Dy4- O5	2.24(2)	Dy4- O6	2.27(4)
Gd4- O5	2.30(2)	Dy4- O11	2.39(2)	Dy4- O24	2.72(7)
Gd4- O6	2.32(2)	Dy4- O16	2.47(2)	Dy4- N6	2.62(5)
Gd4- O13	2.50(1)	Dy4- O20	2.43(1)	Dy4- N7	2.31(3)
Gd4- O20	2.38(1)	Dy4- O21	2.29(1)	Dy1-O1-Dy3	96.07(8)
Gd4- N1	2.49(2)	Dy4- N10	2.52(3	Dy1-O2-Dy2	107.4(3)
Gd4- N4	2.45(2)	Dy4- N11	2.55(3)	Dy1-O2-Dy3	104.9(3)
Gd1-O5-Gd4	107.2(7)	Dy1-O2-Dy2	107.1(6)	Dy1-O2-Dy4	100.9(2)
Gd1-O14-Gd2	105.0(7)	Dy1-O9-Dy3	99.5(7)	Dy2-O2-Dy3	130.3(3)
Gd1-O20-Gd2	107.1(6)	Dy1-O21-Dy3	96.0(6)	Dy2-O2-Dy4	99.1(2)
Gd1-O20-Gd4	105.2(6)	Dy1-O21-Dy4	103.3(6)	Dy3-O2-Dy4	110.6(3)
Gd2-O1-Gd3	109.2(7)	Dy1-N2-Dy3	98.1(6)	Dy2-O3-Dy4	96.37(9)
Gd2-O13-Gd3	114.8(7)	Dy2-O20-Dy4	107.4(7)	Dy1-O4-Dy4	101.7(3)
Gd2-O13-Gd4	103.8(7)	Dy2-O16- Dy4	103.5(7)	Dy3-O6-Dy4	109.0(2)
Gd2-O20-Gd4	104.1(6)	Dy3-O11-Dy4	109.2(7)	Dy1-O8-Dy2	106.4(6)
Gd3-O13-Gd4	95.1(6)	Dy3-O21-Dy4	107.0(7)	Dy2-O24-Dy4	84.0(2)
Gd3-O6-Gd4	98.1(6)				
Gd3-O2-Gd4	99.0(6)				

Table S2. $-\Delta S_m$ ($Jkg^{-1} K^{-1}$) value of some discrete compounds and present work (ΔH = 7 T)

Compound	-ΔSm /JKg-1K-1 (ΔH = 7 T)
$[Gd_{24}(DMC)_{36}(\mu_4\text{-}CO_3)_{18}(\mu_3\text{-}H_2O)_2]\cdot nH_2O$[1]	46.1
$[Gd_4(OAc)_4(acac)_8(H_2O)_4]$[2]	37.7
$[Gd_{10}(L)_5(\mu_2\text{-}OH)_6(H_2O)_{22}](Cl)_4\cdot 7H_2O$[3]	37.4
$[\{Gd(OAc)_3(H_2O)_2\}_2]\cdot 4H_2O$[4]	40
$[Gd_3L^1_2(H_2O)_8(Cl)](Cl)_4\cdot 10H_2O$[5]	31.3
$[Gd_6L^2_2(HCO_2)_4(\mu_3\text{-}OH)_4(DMF)_6(H_2O)_2](Cl)_2\cdot 4H_2O$[5]	33.5
$[Gd_{10}(3\text{-}TCA)_{22}(\mu_3\text{-}OH)_8(H_2O)_4]$[6]	31.2
$[Gd_4(\mu_3\text{-}OH)_2(L)_2L_1L_2(HOCH3)_2]\cdot xH_2O$ (x = ~11) (present work)	27.2

References:

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