Supporting Information

Preparation:

$[Er_4(salen)_6]\cdot 13H_2O$ [**1**$\cdot 13H_2O$; salen = N,N'-ethylenebis(salicylideneiminato) dianion]: $Er(NO)_3\cdot 5H_2O$ (89 mg, 0.2 mmol) dissolved in MeOH (10 mL) was mixed with H_2salen in MeCN (10 mL). NEt_3 (0.14 mL, 1.0 mmol) was added to the resulting solution, which was heated at 70 °C for 2 h. The mixture was filtered, slowly evaporated in the dark, and dried in air. Yield: 35%. The number of water molecules was checked by TGA in which dehydration was completed at 110 °C (Fig. S1). Elemental analysis (%) calcd for $C_{96}H_{110}Er_4N_{12}O_{25}$: C 46.10, H 4.43, N 6.72; Found: C 45.85, H 4.29, N 7.16. $[Gd_4(salen)_6]\cdot 6H_2O$ (**2**$\cdot 6H_2O$) was prepared with the identical procedure to compound **1** except for using $Gd(NO)_3\cdot 6H_2O$ instead of Er(III). Yield: 35%. Elemental analysis (%) calcd for $C_{96}H_{96}Gd_4N_{12}O_{18}$: C 49.38, H 4.14, N 7.20; Found: C 49.00, H 3.78, N 7.23.

Physical Measurements:

Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of Sogang University. Infrared spectra were obtained from KBr pellets with a Bomen MB-104 spectrometer. Magnetic susceptibilities for complexes **1** and **2** were carried out using a Quantum Design SQUID susceptometer (dc) and a PPMS magnetometer (ac). Diamagnetic corrections of all samples were estimated from Pascal's Tables. Thermogravimetric analyses were carried out at a ramp rate of 10 °C/min in a N_2 flow using a Scinco TGA N-1000 instrument.

Crystallographic Structure Determination:

X-ray data for **1** and **2** were collected on a Bruker SMART APEXII diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å). Preliminary orientation matrix and cell parameters were determined from three sets of ϕ scans at different starting angles. Data frames were obtained at scan intervals of 0.5° with an exposure time of 10 s per frame. The reflection data were corrected for Lorentz and polarization factors. Absorption corrections were carried out using SADABS. The structures were solved by direct methods and refined by full-matrix least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXTL program. All hydrogen atoms were calculated at idealized positions and refined with the riding models. Lattice solvent molecules are significantly disordered and could not be modelled properly, thus the program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. Crystal data of **1**: Mr = 2266.79, triclinic, space group P-1, a = 13.4526(5) Å, b = 13.9702(6) Å, c = 15.7336(6) Å, α = 68.813(2)°, β = 78.546(2)°, γ = 63.379(2)°, V = 2462.38(17) Å^3, Z = 1, D_{calc} = 1.529 g cm^{-3}, μ = 3.435 mm^{-1}, T = 100(2) K, 39657 reflections collected, 12005 unique (R_{int} = 0.0767), $R1$ = 0.0455, $wR2$ = 0.1143 [$I > 2\sigma(I)$]. Crystal data of

2: Mr = 2226.75, triclinic, space group *P*-1, a = 13.4952(10) Å, b = 14.1163(9) Å, c = 15.6159(11) Å, α = 69.947(4)°, β = 79.251(5)°, γ = 63.093(4)°, V = 2490.2(3) Å^3, Z = 1, D_{calc} = 1.485 g cm^{-3}, μ = 2.690 mm^{-1}, T = 100(2) K, 20852 reflections collected, 11840 unique (R_{int} = 0.0729), $R1$ = 0.0827, $wR2$ = 0.0827 [$I > 2\sigma(I)$].

Table S1. Results of the continuous shape measure analysis.

Metal center	Shape Measures(S_X) relative to SAPR	DD	BTP
Er1	3.54463	1.54198	4.02701
Gd1	4.62896	1.78539	4.55054

Metal center	Shape Measures(S_X) relative to PBPY	OCF	TPRS
Er2	4.47431	2.67756	1.95965
Gd2	4.44323	2.88335	2.26373

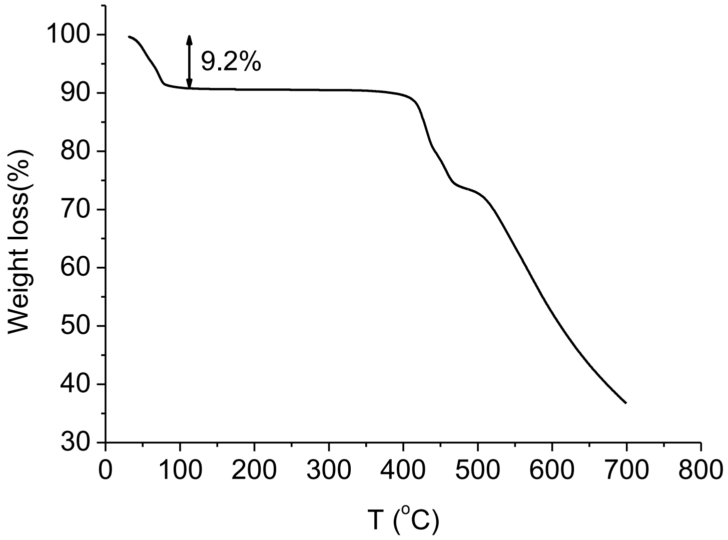

Fig. S1. TGA of **1**·13H_2O. The weight loss (9.2%) in the temperature range 30 – 110 °C corresponds to that of 13 H_2O (9.4%).

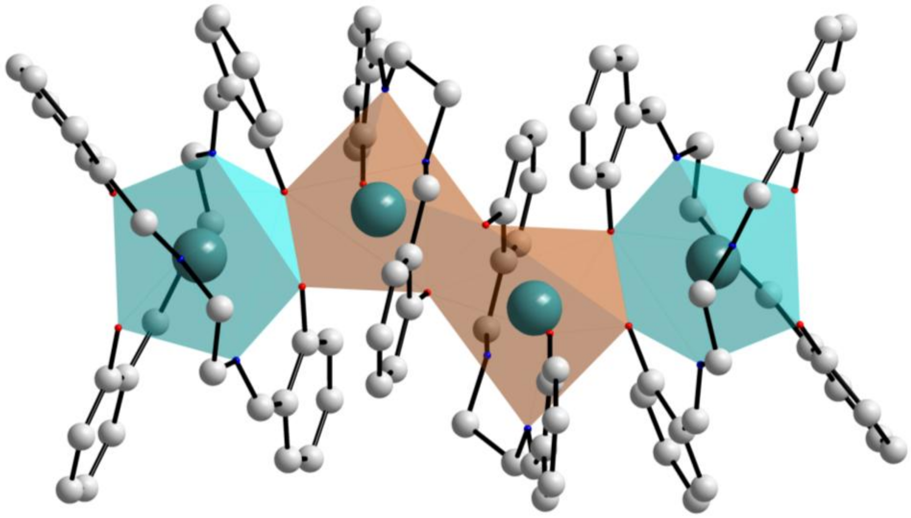

Fig. S2. Polyhedral representation of the tetranuclear core showing seven-(orange) and eight-coordination (turquoise).

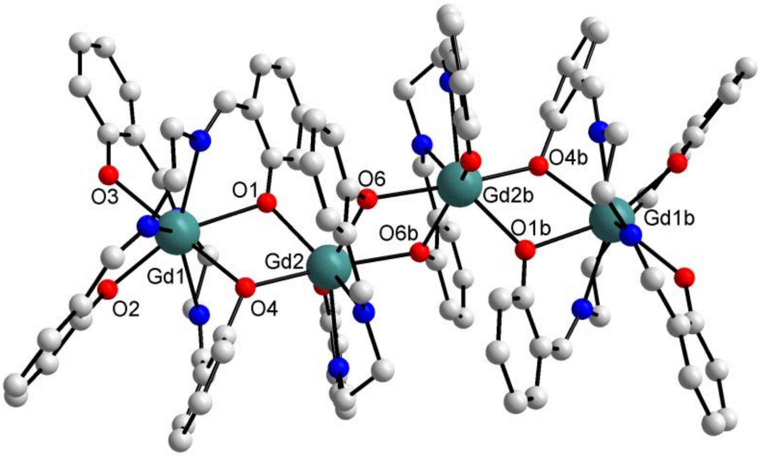

Fig. S3. Molecular view of **2**. Symmetry transformation used to generate equivalent atoms (b = 1-x, 1-y, -z).

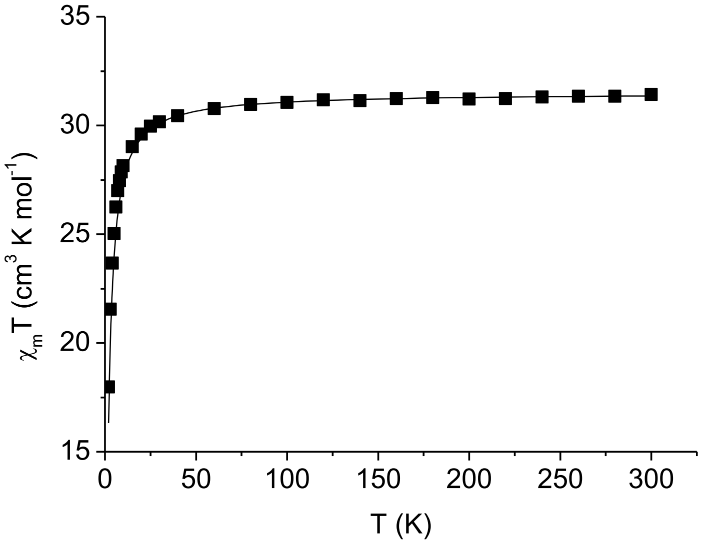

Fig. S4. Plots of $\chi_m T$ versus T for **2**·6H_2O at 1000 G.

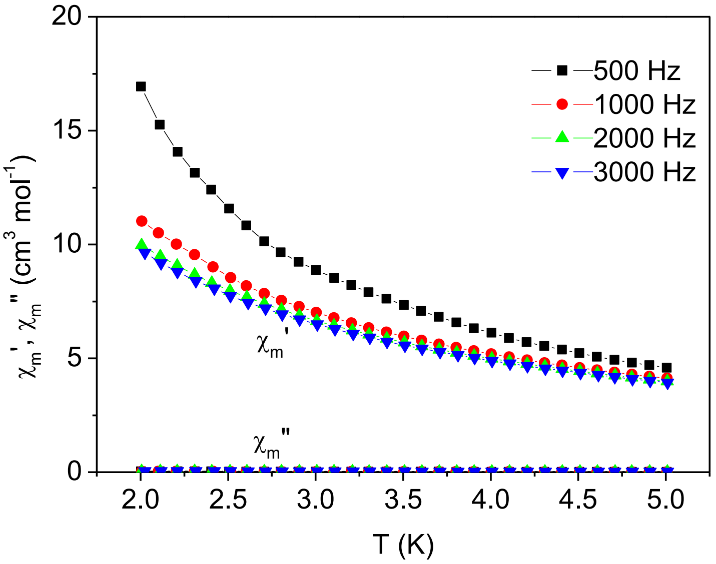

Fig. S5. Plots of χ_m' and χ_m'' signals versus T for **1**·13H_2O at zero dc field, an ac field of 5 G, and several frequencies.

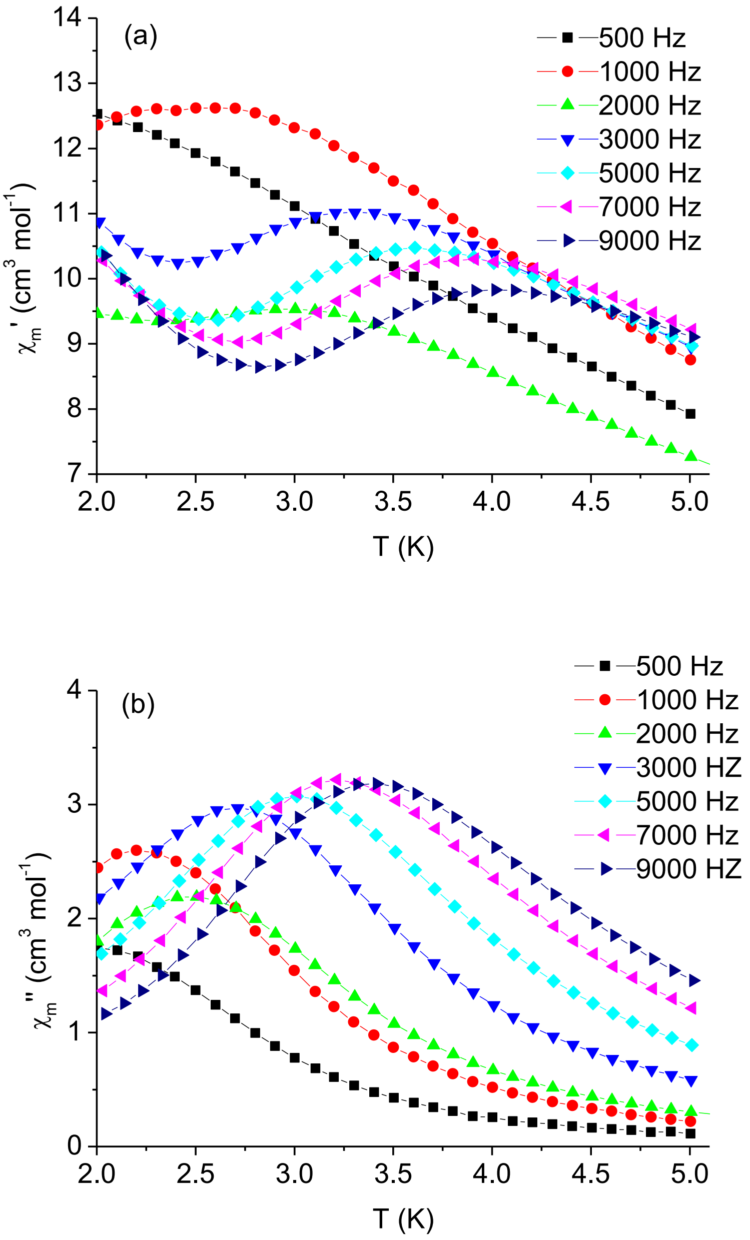

Fig. S6. Plots of (a) χ_m' and (b) χ_m'' versus T for **1**·13H$_2$O at H_{dc} = 1.0 kG, an ac field of 5 G, and several frequencies. The solid lines are eye-guides.

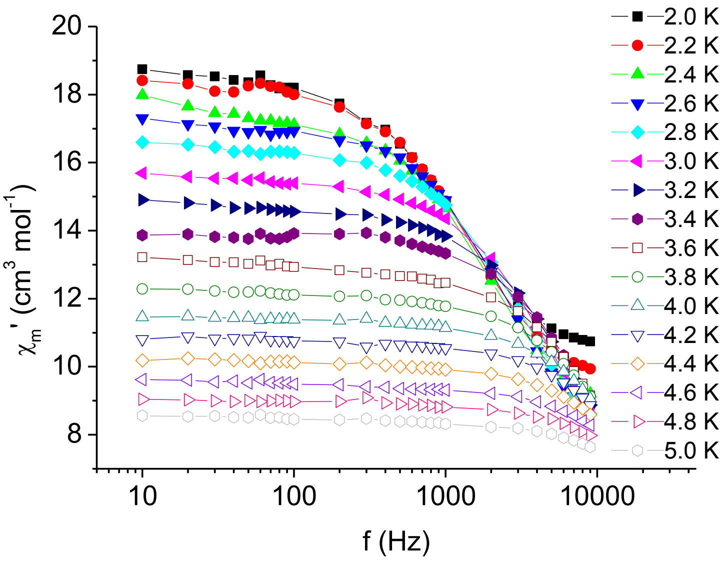

Fig. S7. Plots of χ_m' versus *f* for **1**·13H_2O at H_{dc} = 1.0 kG, an ac field of 5 G, and several temperatures.