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

Supporting information

Experimental Section

Synthesis of Compound 1. GeO_2(0.0523g, 0.5mmol) was dissolved in 20mL of water with vigorous stirring, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (1.0g, 0.8mmol) was added into the solution, and this solution was still stirred for 15min. To the former solution was added $ErCl_3\cdot6H_2O$(0.1g, 0.26mmol), then 1M morpholine 1.5mL was added dropwise. The pH of the mixed solution was adjusted to 4.0 with 6M HCl and 0.5M NaOH, then the mixture was heated for 1 h at 90 °C. The yellow-green solution was filtered after it was cooled to room temperature. The yellow-green crystals of complex **1** were obtained after one week. Yield: 0.2845 g (24.56%, based on Ge). Elemental analyses calcd (%): Ge, 3.14; Mo, 45.55; Er, 3.61; C, 8.30; N, 2.42; H, 2.46; Found: Ge, 3.07; Mo, 46.78; Er, 3.73; C, 8.57; N, 2.26; H, 2.61.

Synthesis of Compound 2. Compound **2** was synthesized following a similar procedure to that used for compound **1**, except that $GdCl_3\cdot6H_2O$(0.1g, 0.27mmol) was used instead of $ErCl_3\cdot6H_2O$. The green solution was filtered after it was cooled to room temperature. The green crystals of complex **2** were obtained after one day. Yield: 0.5036g (43.74%, based on Ge). Elemental analyses calcd (%): Ge, 3.15; Mo, 45.83; Gd, 3.41; C, 8.34; N, 2.43; H, 2.43; Found: Ge, 3.20; Mo, 46.75; Gd, 3.53; C, 8.50; N, 2.60; H, 2.58.

Synthesis of Compound 3. Compound **3** was synthesized following a similar procedure to that used for compound **1**, except that $DyCl_3·6H_2O$(0.1g, 0.26mmol) was used instead of $ErCl_3·6H_2O$. The green solution was filtered after it was cooled to room temperature. The green crystals of complex **3** were obtained after one day. Yield: 0.4127g (35.53%, based on Ge). Elemental analyses calcd (%): Ge, 3.13; Mo, 45.42; Dy, 3.50; C, 8.27; N, 2.41; H, 2.49; Found: Ge, 3.19; Mo, 46.52; Dy, 3.65; C, 8.36; N, 2.56; H, 2.55.

Synthesis of Compound 4. Compound **4** was synthesized following a similar procedure to that used for compound **1**, except that $TbCl_3·6H_2O$ (0.1g, 0.27mmol) was used instead of $ErCl_3·6H_2O$. The green solution was filtered after it was cooled to room temperature.The green crystals of complex **4** were obtained after three days. Yield: 0.4779g (41.33%, based on Ge). Elemental analyses calcd (%): Ge, 3.14; Mo, 45.64; Tb, 3.44; C, 8.31; N, 2.42; H, 2.46; Found: Ge, 3.23; Mo, 46.87; Tb, 3.65; C, 8.48; N, 2.34; H, 2.62.

X-Ray crystallography. For single crystal structure determination, crystal data of **1-4** were measured on a CrysAlisPro CCD (Oxford Diffraction) using MoKα radiation (λ = 0.71073 Å) at 293(3) K. The structures were solved with the direct methods (SHELXS-97) and refined on F^2 by full-matrix least-squares (SHELXL-97). Anisotropic thermal parameters were used to refine all non-hydrogen atoms, with the exception for some oxygen atoms. Those hydrogen atoms attached to lattice water molecules and morpholine molecules were not located. Crystallization water molecules were estimated by thermogravimetry and only partial oxygen atoms of water molecules were achieved with the X-ray structure analysis. The crystal data and structure refinement results of **1-4** are summarized in Table 1. CCDC no. 991332 for **1**, CCDC no. 991333 for **2,** CCDC no. 991334 for **3,** CCDC no. 991335 for **4**.

Physical Measurements. Elemental analysis (Ge, Mo, Ln) were determined by a Leaman inductively coupled plasma (ICP) spectrometer. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Infrared spectra of solid samples were obtained on a BRUKER Vertex 70 FTIR spectrometer in the 400–4000 cm^{-1} region with a KBr pellet. The UV electronic spectra were obtained on a Varian Cary 50 Conc UV-Vis spectrophotometer. TGA was performed with a Perkin–Elmer TGA7 instrument in a flow of N_2 at a heating rate of 10℃·min^{-1}. XRD was performed on a Philips X'Pert-MPD instrument with CuKα radiation (λ = 1.54056 Å) in the range 2θ = 5–50° at 293 K. Magnetic susceptibility measurements (300–2 K) were performed on polycrystalline samples at a field strength of 1000 Oe using a Quantum Design MPMS XL-5 SQUID magnetometer.

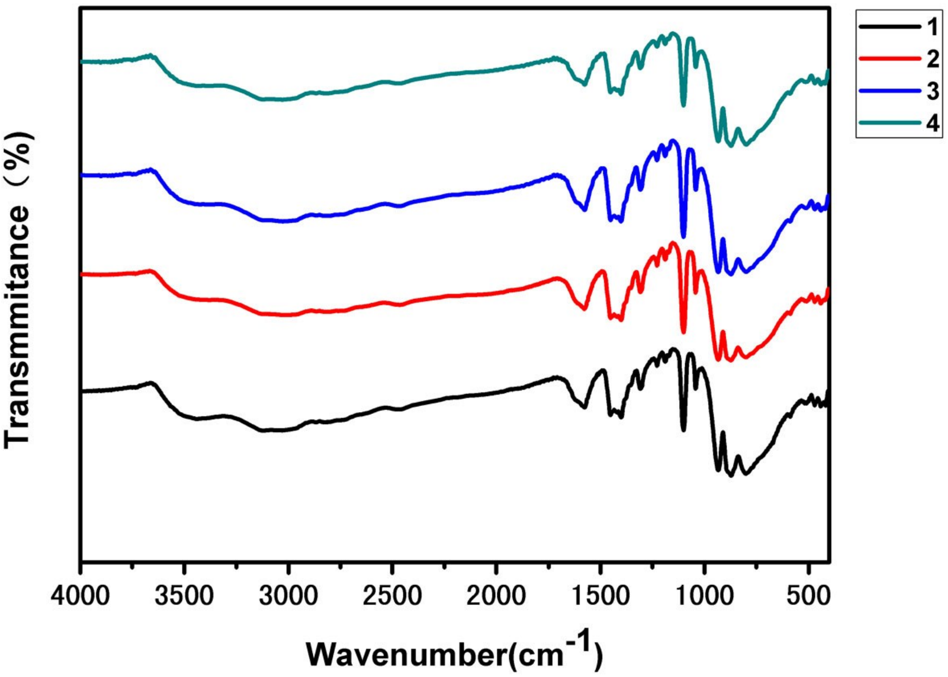


Fig. S1 IR spectra of compounds **1**-**4**.

The characteristic peaks of the different bonds in **1**–**4** assigned to ν(Mo-O_d), ν(Mo-O-Mo), and ν(Ge-O_a) appear at 933, 871, and 800cm^{-1} for **1**; 933, 875, and 802cm^{-1} for **2**; 933, 877, and 800cm^{-1} for **3**; 933, 869, and 798cm^{-1} for **4**, respectively. The wave numbers are similar to the reported polyanion $[Ln(PMo_{11}O_{39})_2]^{11-}$,[19] which suggests that the polyanion of complex **1-4** possesse the comparable sandwich-type structure based on monolacunary germanomolybdate fragment. The bands at 3416 and 3027 cm^{-1} (**1**), 3467 and 3047 cm^{-1} (**2**), 3492 and 3025 cm^{-1} (**3**), 3492 and 3029 cm^{-1} (**4**) can be ascribed to the ν(NH_2) and ν(CH_2) stretching vibration modes of the morpholine molecules, while the peaks at 1579 and 1230 cm^{-1} (**1**), 1577 and 1226 cm^{-1} (**2**), 1577 and 1228 cm^{-1} (**3**), 1575 and 1228 cm^{-1} (**4**) can be assigned to the characteristic peaks of the morpholine molecules. Furthermore, the broad peak at about 3500 cm^{-1} is attributed to the vibration band of the lattice water molecules.

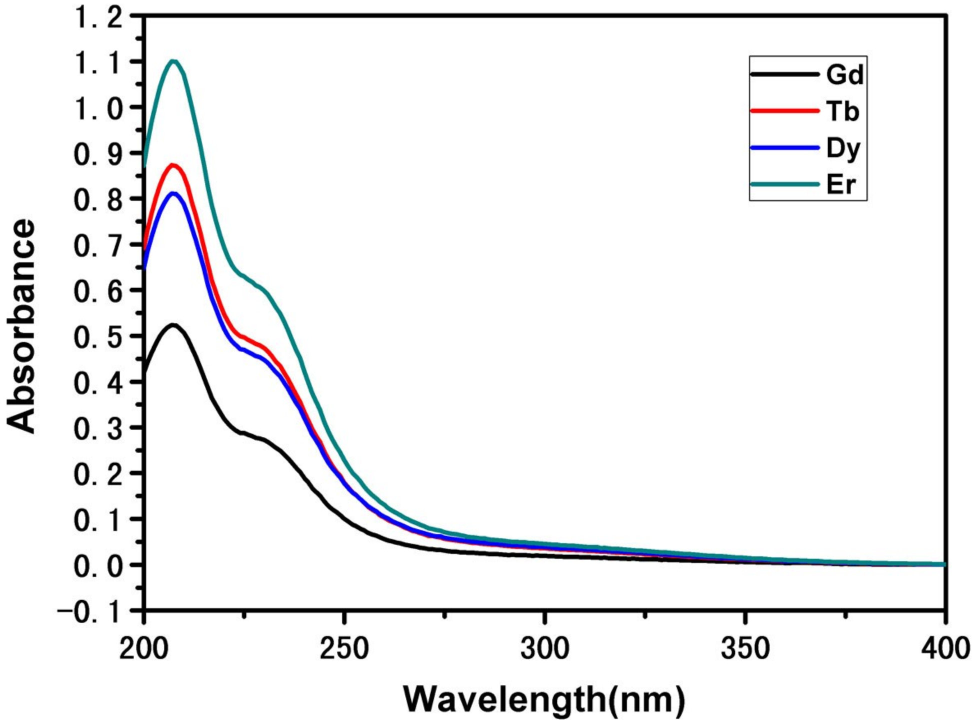
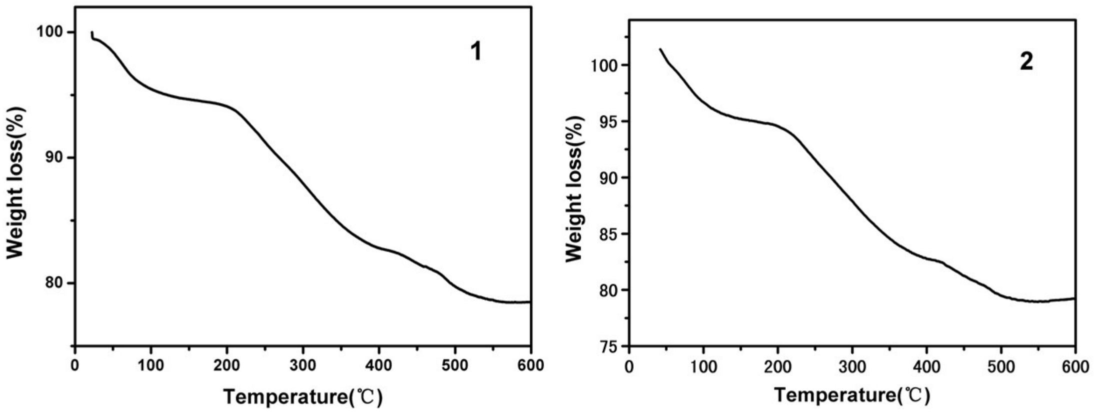


Fig. S2 UV spectra of compounds **1-4**.



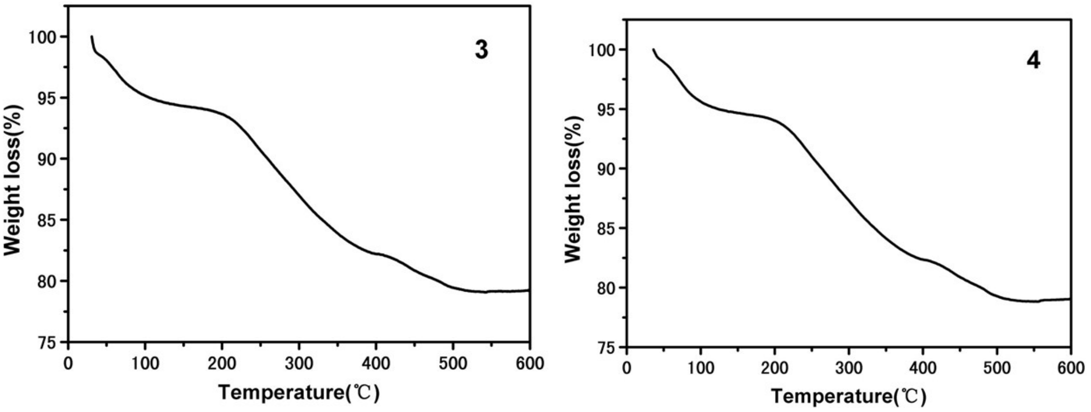
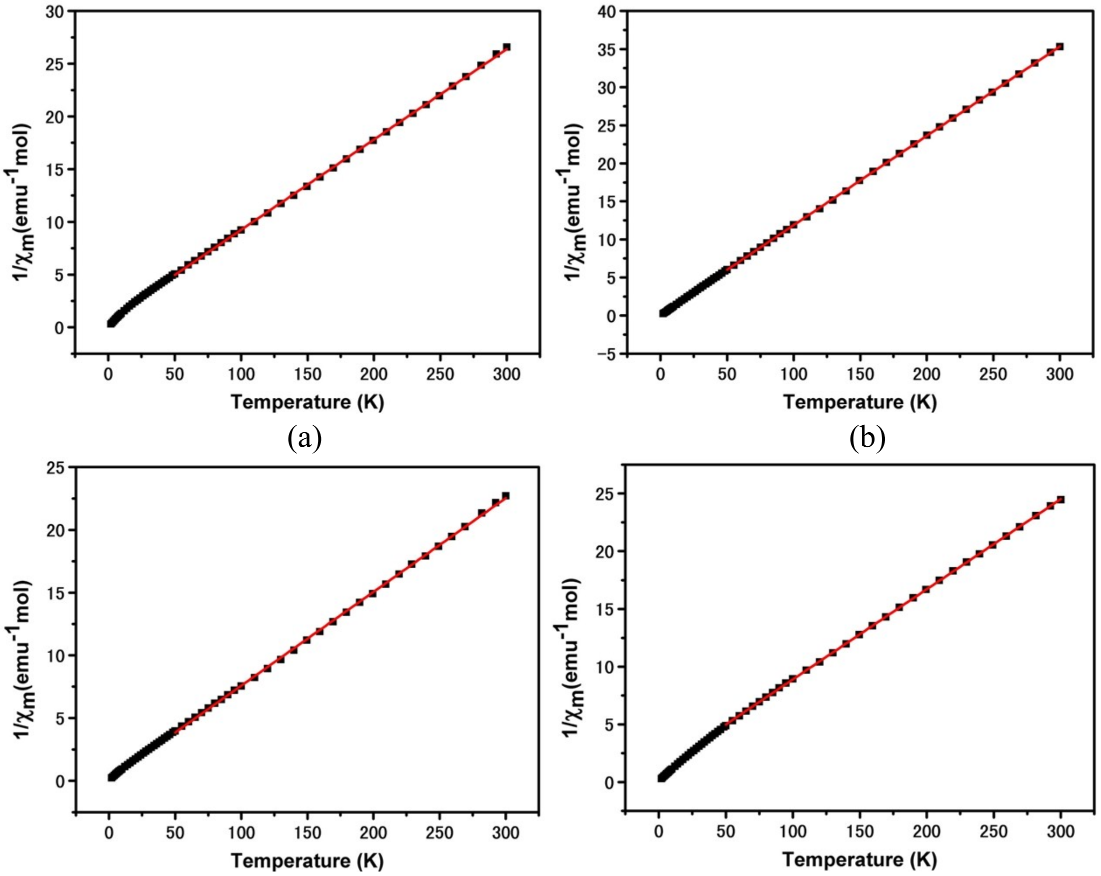


Fig. S3 TG curves for compounds **1**–**4**.

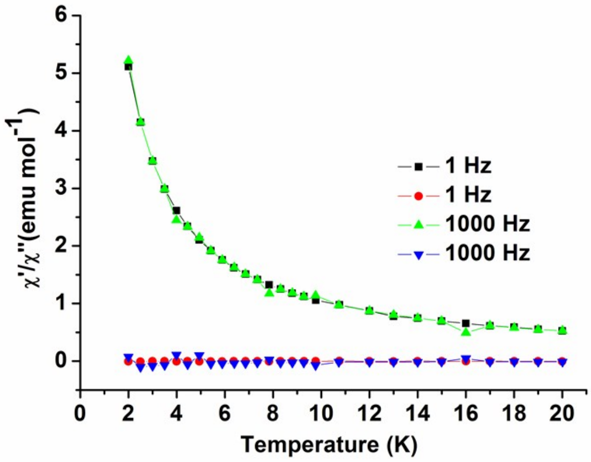
Compound **2** lost 13 water molecules per unit (5.0%, calcd 5.08%) between 42 -172 °C, and 8 morpholine cations per unit (16.0%, calcd 15.31%) between 172-540 °C. Compound **3** lost 15 water molecules per unit (6.0%, calcd 5.81%) between 31-175 °C, and 8 morpholine cations per unit (16.0%, calcd 15.17%) between 175-543 °C; compound **4** lost 14 water molecules per unit (5.5%, calcd 5.45%) between 36-167°C, and 8 morpholine cations per unit (15.5%, calcd 15.24%) between 167-550 °C. These results are in agreement with the aforementioned crystal structures.



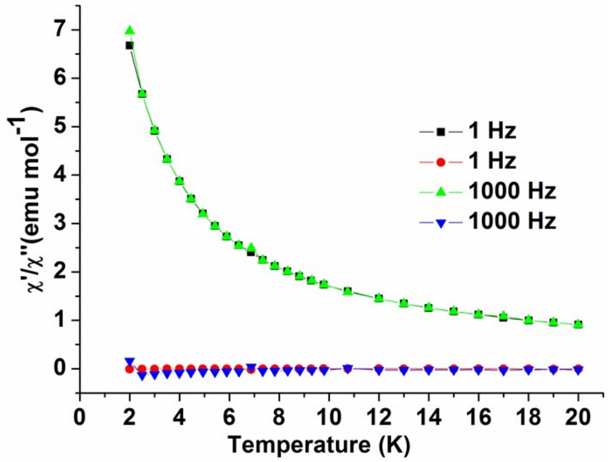
(a) (b)

(c) (d)

Fig. S4 (a) Temperature dependence of $1/\chi_m$ for **1** at 50–300 K. The solid line is the fit of Curie-Weiss law; (b) Temperature dependence of $1/\chi_m$ for **2** at 50–300 K. The solid line is the fit of Curie-Weiss law;(c) Temperature dependence of $1/\chi_m$ for **3** at 50–300 K. The solid line is the fit of Curie-Weiss law;(d) Temperature dependence of $1/\chi_m$ for **4** at 50–300 K. The solid line is the fit of Curie-Weiss law.



(a)



(b)

Fig. S5 Temperature dependence of AC susceptibility in a zero applied static field with an oscillating field of 3 Oe at a frequency of 1Hz and 1000 Hz for compound **2** (a) and **4** (b). The lines are guides.

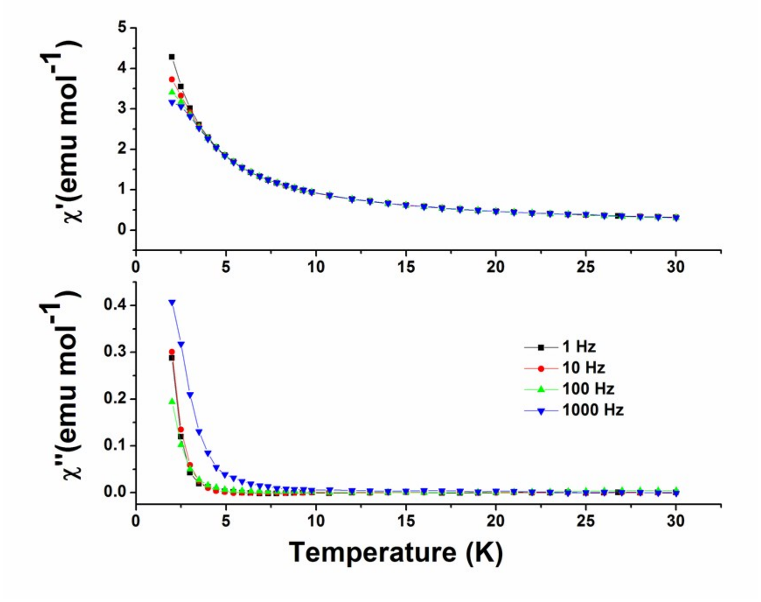


Fig. S6 Temperature dependence of AC susceptibility at 5000 Oe applied static field with an oscillating field of 3 Oe at a frequency of 1–1000 Hz for compound **2**. The lines are guides.

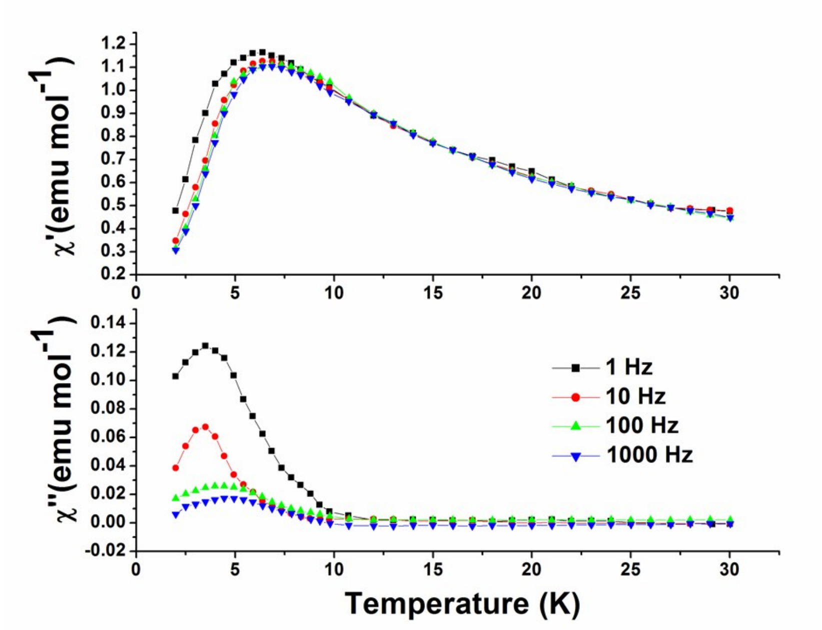


Fig. S7 Temperature dependence of AC susceptibility at 5000 Oe applied static field with an oscillating field of 3 Oe at a frequency of 1–1000 Hz for compound **3**. The lines are guides.

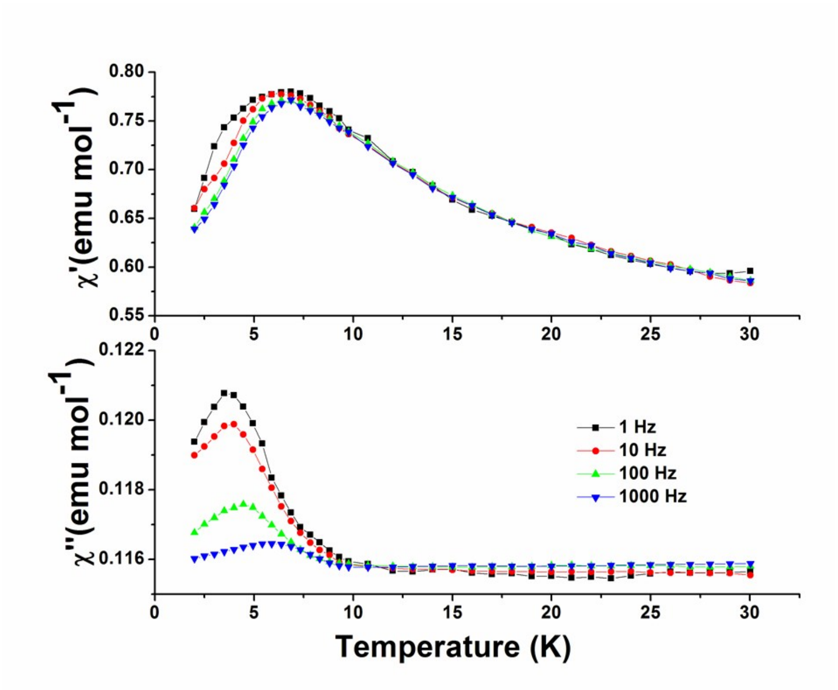
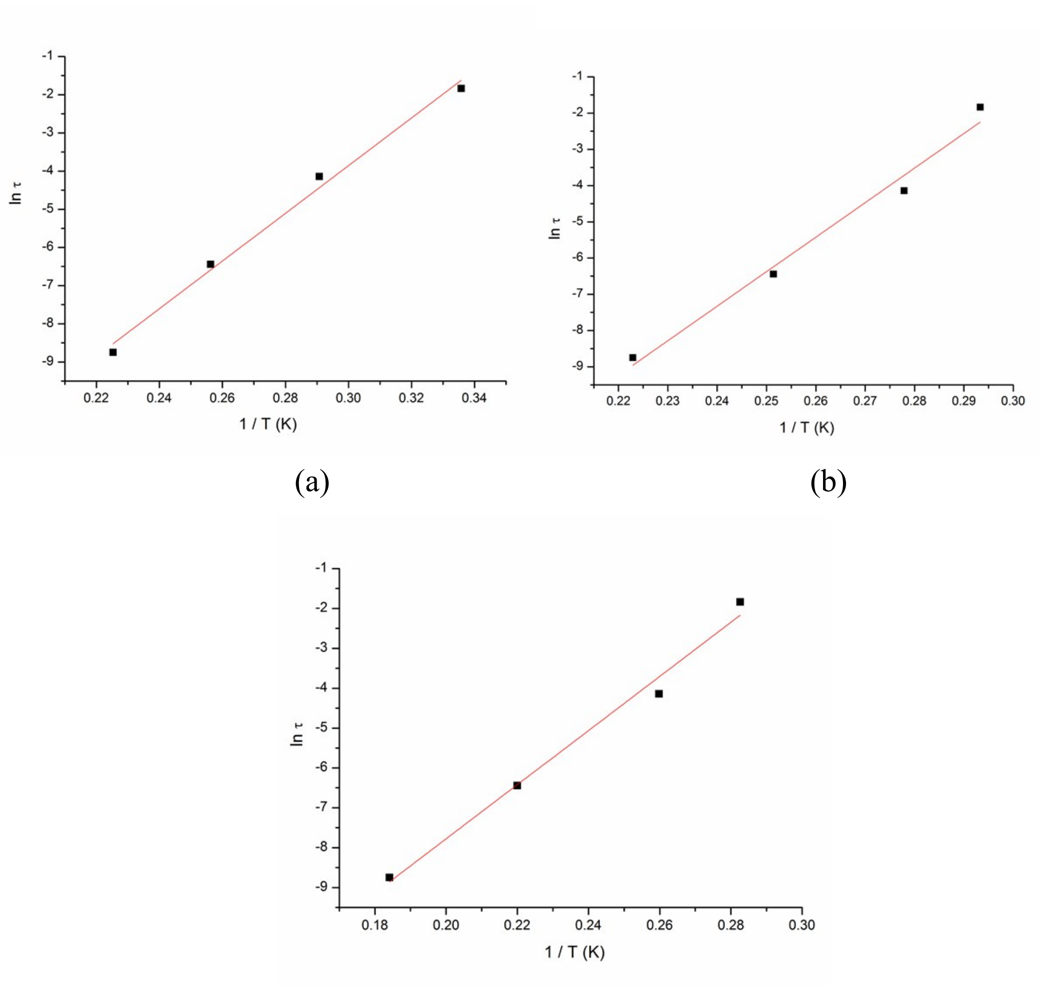


Fig. S8 Temperature dependence of AC susceptibility at 5000 Oe applied static field with an oscillating field of 3 Oe at a frequency of 1–1000 Hz for compound **4**. The lines are guides.



(a)

(b)

(c)

Fig. S9 Relaxation-time fitting to the Arrhenius law in the 1-1000 Hz interval for **1 (a)**, **3 (b)** and **4 (c)**. Best fitting afforded a barrier height (Δ/k_B) of 54.9 K for **1** (68.3 K for **3** and 61.4 K for **4**), and a pre-exponential factor (τ_0) of 1.13×10^{-8} s (R =0.9962) for **1**, 1.90×10^{-9} s (R^2 =0.9918) for **3**, and 3.40×10^{-8} s (R = 0.9942) for **4**, which are in the normal range for SMMs

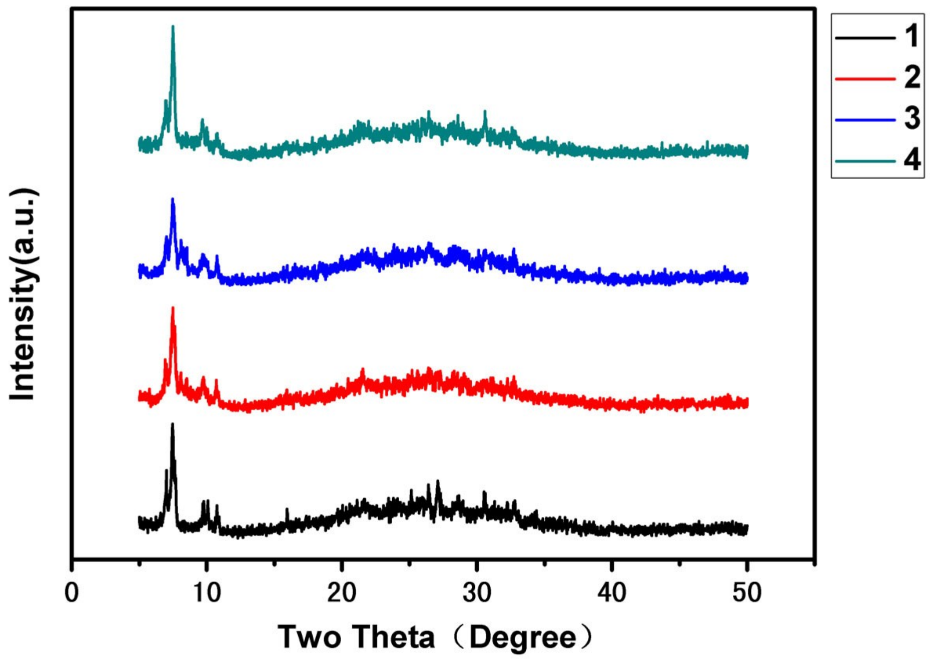


Fig. S10 Experimental PXRD patterns of compounds **1-4**.