Electronic Supplementary Information for

A 24-Gd Nano-Capsule with Large Magnetocaloric Effect

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Experimental Section:

Materials. Except for isonicotinic acid purchased from Jinan Camolai Trading Company, the other reagents are from Tianjin Guangfu Fine chemical research institute. All were used without further purification.

Measurement techniques. The FT-IR spectra were measured with a Bruker Tensor 27 Spectrophotometer on KBr disks. The elemental analyses (C, H and N) were carried out applying a Perkin-Elmer 240C elemental analyzer; Magnetic properties were measured on a Quantum Design MPMS-XL7 and a PPMS-9 ACMS magnetometer. Diamagnetic correction was made with Pascal's constants for all the constituent atoms.

(1) **Synthesis of Gd_{24}:** 10 mL DMF (N, N-Dimethylformamide) mixture of 0.3 mmol CuO, 0.6 mmol $Ln(NO_3)_3 \cdot 6H_2O$ (Ln= Gd, Dy) and 0.5 mmol isonicotinic acid are sealed in a Teflon lined stainless steel container and heated at 160 □ for 96 h, and then cooled slowly controlled procedures to room temperature during 96 h. Finally, polyhedral crystals were collected with a yield of 67% (calculated based on $Gd(NO_3)_3 \cdot 6H_2O$). **Dy_{24}** were prepared by the same experiment method with a yield of 72% (calculated based on $Dy(NO_3)_3 \cdot 6H_2O$). The crystal structures determined by single crystal X-ray diffraction reveal that the ligand isonicotinic acid does not exist in the structures of two compounds, but it maybe plays an important role in the constructions of **Gd_{24}** and **Dy_{24}** since these compounds can not be obtained under the absence of isonicotinic acid. The N, N'-dimethylcarbamic acid may originate from the oxidation of DMF by CuO as an oxider. In additional, we also tried our best to synthesis the two compound using carbonates, DMC and Ln nitrates, but the target products were not obtained. Anal. Calcd. for $C_{126}H_{232}Gd_{24}N_{36}O_{134}$ (%): C 18.52, H 2.86 , N 6.17. Found: C 18.43, H 2.78, N 6.12. Anal. Calcd. for $C_{126}H_{222}Dy_{24}N_{36}O_{130}$(%): C 18.40, H 2.72, N 6.13. Found: C 18.35, H 2.66, N 6.04. IR (KBr disk, υ cm^{-1}): For **Gd_{24}**; 3428(br), 3149(br), 2994(m), 1632(s), 1551(m), 1440(s), 1080(m), 858(m), 796(w). For **Dy_{24}**, 3420(br), 3155(br), 2990(m), 1638(s), 1556(m), 1442(s), 1085(m), 851(m), 793(w). The IR spectrograms of **Gd_{24}** and **Dy_{24}** are very similar, and only that of **Gd_{24}** is analyzed as representation. Weak absorption peaks on 858 and 796 cm^{-1} can be separately referred to face and out-face deformation vibration absorption of CO_3^{2-} anions, Strong peak of 1440 and 1632 cm^{-1} can be referred to asymmetric

stretching vibration absorption of CO_3^{2-} anions and carboxyl groups, respectively.[1] 2994 cm^{-1} can be identified to the C-H bond stretching vibration of $-CH_3$.

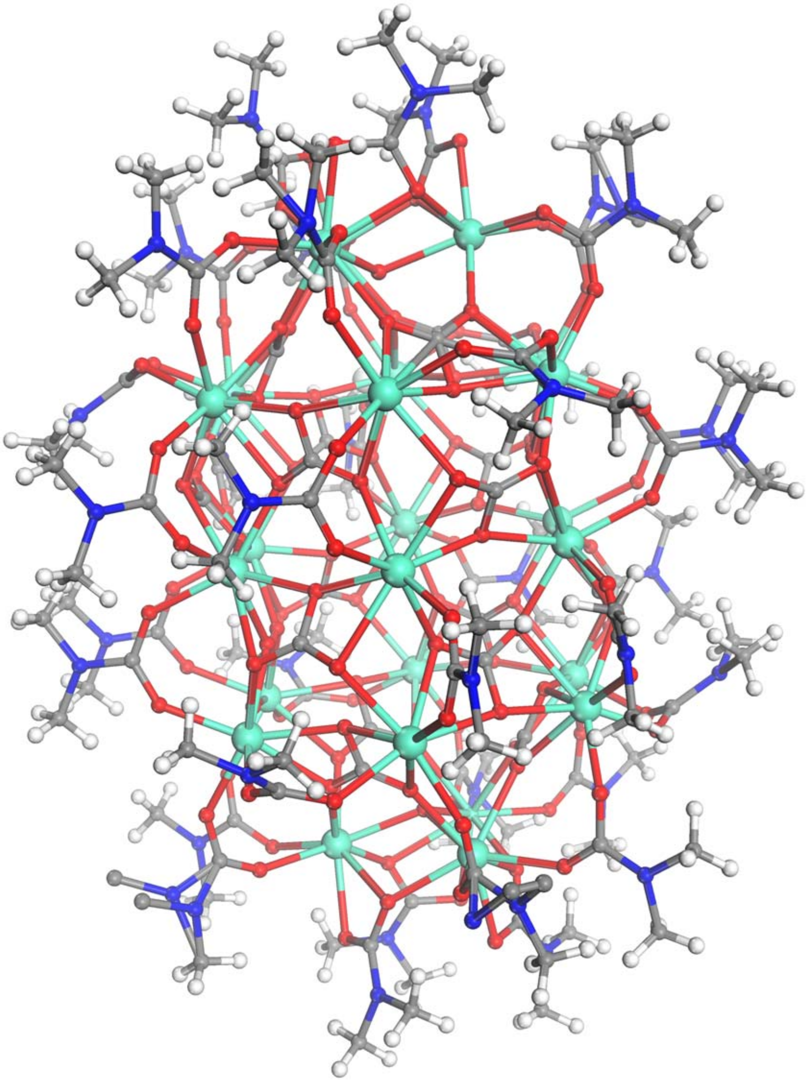
Crystallographic Study

Crystallographic data of **Gd_{24}** and **Dy_{24}** collected on a SuperNova Single Crystal Diffractometer equipped with graphite-monochromatic Mo-Ka radiation (λ = 0.71073 Å) using the ω - φ scan technique. The data integration and empirical absorption corrections were carried out by SAINT programs.[2] The structures were solved by direct methods (SHELXS 97).[3] All the non-hydrogen atoms were refined anisotropically on F^2 by full-matrix least-squares techniques (SHELXL 97).[3] Some ligand atoms and solvent molecules, which exhibit unbearable isotropic displacement parameters, were split two parts according to suitable site occupancy. Therefore, some restrain instructions ISOR, EADP and DFIX were used and listed in the "_refine_special_details" section of the CIF. Hydrogen atoms were riding on carbon atoms geometrically except for those of the uncoordinated water molecules and disorder methyl carbon atoms. During refining the structures of **Gd_{24}** and **Dy_{24}**, we did not use "SQUEEZE" program. However, a considerable void volume was calculated by PLATON program. Actually, when refining the structures, there were not valid residual peaks to be assigned to the solvent molecules, and the higher electronic intensity peaks almost attached the metal center and/or the cluster. Details of the crystal parameters, data collection, and refinements for **Gd_{24}** and **Dy_{24}** are summarized in TableS1. CCDC: 885748 for **Gd_{24}** and 885747 for **Dy_{24}** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic Data and Structure Refinement for Complexes **Gd_{24}** and **Dy_{24}**.

Empirical formula	$C_{126}H_{232}Gd_{24}N_{36}O_{134}$	$C_{126}H_{222}Dy_{24}N_{36}O_{130}$
Formula weight	8169.48	8221.40
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1
Unit cell dimensions	a =18.5577(7) Å, α = 70.309(3)° b = 18.6531(7) Å, β = 71.744(3)° c =24.5481(9) Å, γ = 62.202(4)°	a = 18.4912(7) Å ,α = 70.008(3)°. b = 18.7881(7) Å, β= 71.465(3)° c = 24.6429(6) Å, γ = 62.324(4)°
Volume	6951.9(4) A^3	6993.5(4) A^3
Z, Calculated density	1, 1.951 Mg/m^3	1, 1.952 Mg/m^3
Absorption coefficient	5.723 mm^{-1}	6.408 mm^{-1}

F(000)	3848	3854
Crystal size	0.25 × 0.20 × 0.20 mm	0.16 x 0.12 x 0.10 mm
Theta range for data collection	4.76 to 25.01°	2.32 to 25.01°
Limiting indices	$-22 \leq h \leq 22$, $-22 \leq k \leq 19$, $-29 \leq l \leq 29$	-21<=h<=21, -22<=k<=21, -29<=l<=23
Reflections collected / unique	49758/24456[R(int) = 0.0313]	48840 / 24554 [R(int) = 0.0387]
Completeness to theta = 25.01	99.8%	99.6%
Data / restraints / parameters	23452 / 452 / 1681	24554 / 462 / 1690
Goodness-of-fit on F^2	1.084	1.064
Final R indices [I>2sigma(I)]	$R_1 = 0.0384$, $wR_2 = 0.0981$	R1 = 0.0495, wR2 = 0.1157
R indices (all data)	$R_1 = 0.0504$, $wR_2 = 0.1041$	R1 = 0.0701, wR2 = 0.1320



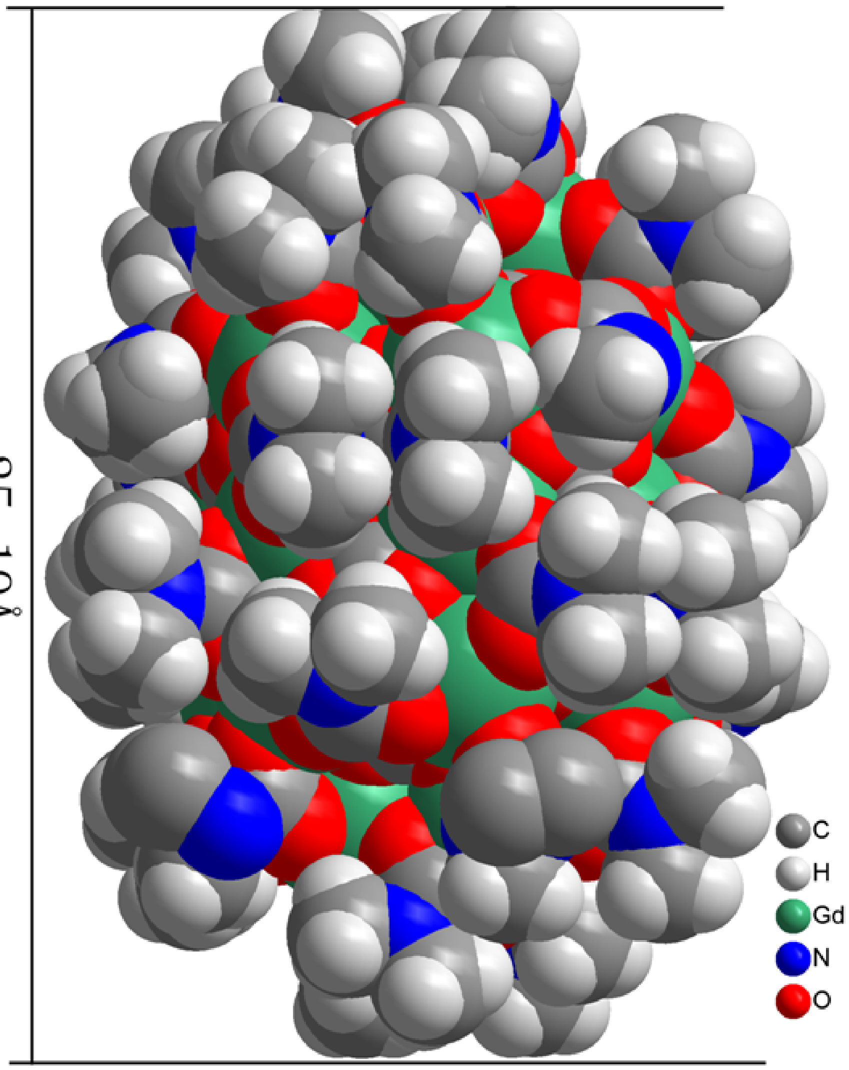


Figure S1 The structure of **Gd$_{24}$** in ball-stick (Top) and space filling (Bottom) modes.

Magnetic Properties

Well known, the fast quantum tunneling, caused no peaks of out-of-phase susceptibility, can be suppressed by appending a static magnetic field. Therefore, 5 kOe external magnetic field was employed during the ac susceptibilities measurements, and the peaks are observed from 6 - 8 K in plots of χ'' *vs* T (Figure S7 in ESI). To obtain the relaxation energy barrier and relaxation time, the peak temperature T_p may be given by the Lorentzian peak function fitting from the plots of χ'' vs T, and the plot of $1/T_p$ *vs* $\ln(2\pi v)$ based on the Arrhénius law $1/T_p=-k_B/\Delta E[\ln(2\pi v)+\ln(\tau_0)]$ obeys a linear correlation (Figure S8), where v is the frequency. The best fitting yields the energy barrier $\Delta E/k_B= 72.84$ K and pre-exponential factor $\tau_0 = 1.92\times10^{-9}$ s, which falls into the normal range of the reported those with $\Delta E/k_B$ from 6.25 to 528 K[9] for Dy-compounds, and τ_0 agrees with expected value of 10^{-6}-10^{-12} s for an SMM.[10] Based on frequency dependences of the ac susceptibilities (FigureS9 in ESI), the cole-cole curves were depicted in the Figure S10 in ESI and fitted using the Debye model[10b], giving distribution coefficient α value of 0.30-0.37 (Table S3 in ESI). The relatively large α value implies a wide distribution of relaxation time[11].

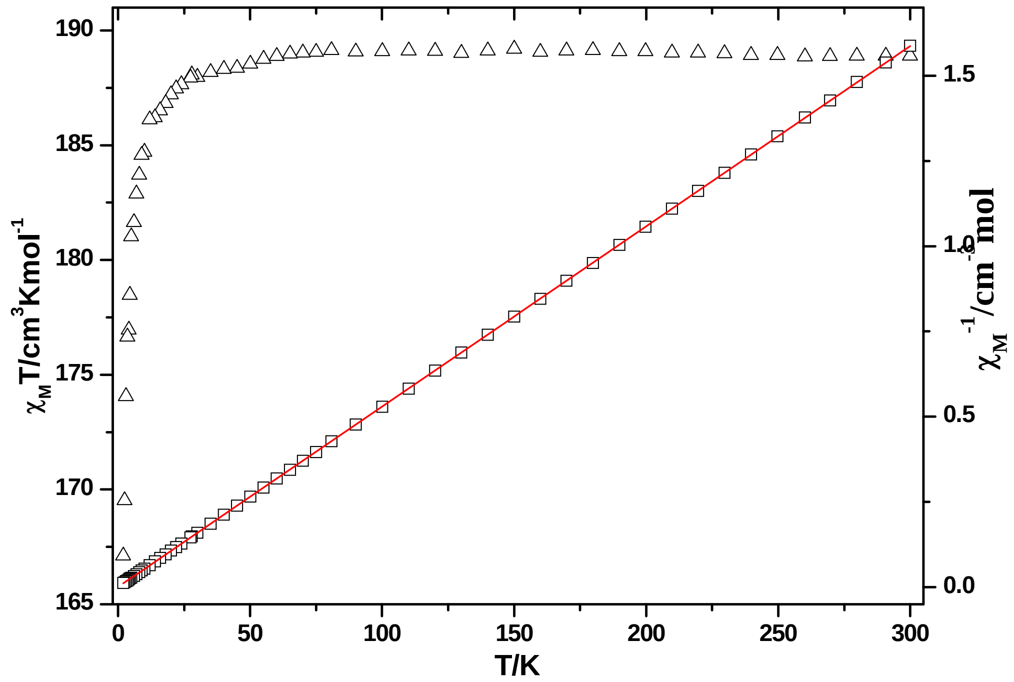


Figure S2. T vs $\chi_M T$ curve (Δ) and T vs χ_M^{-1} curve (□) for **Gd$_{24}$**. The red solid line stands for the best fitting.

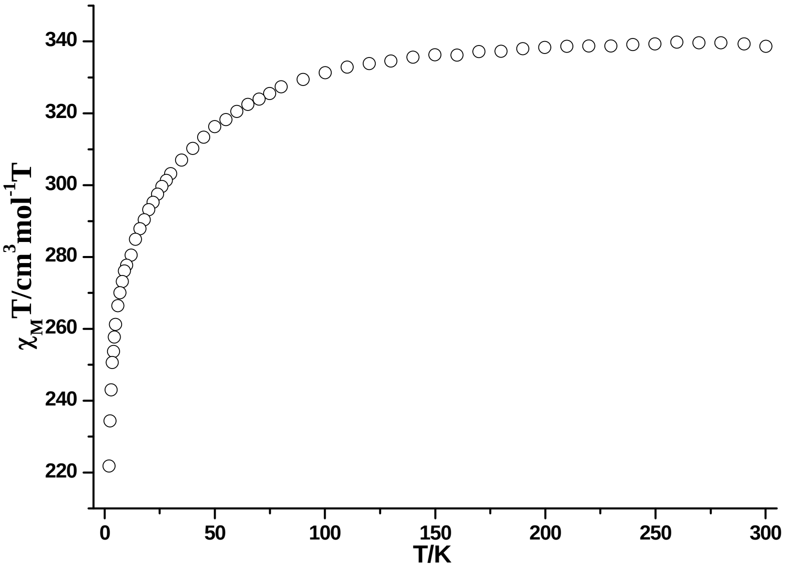
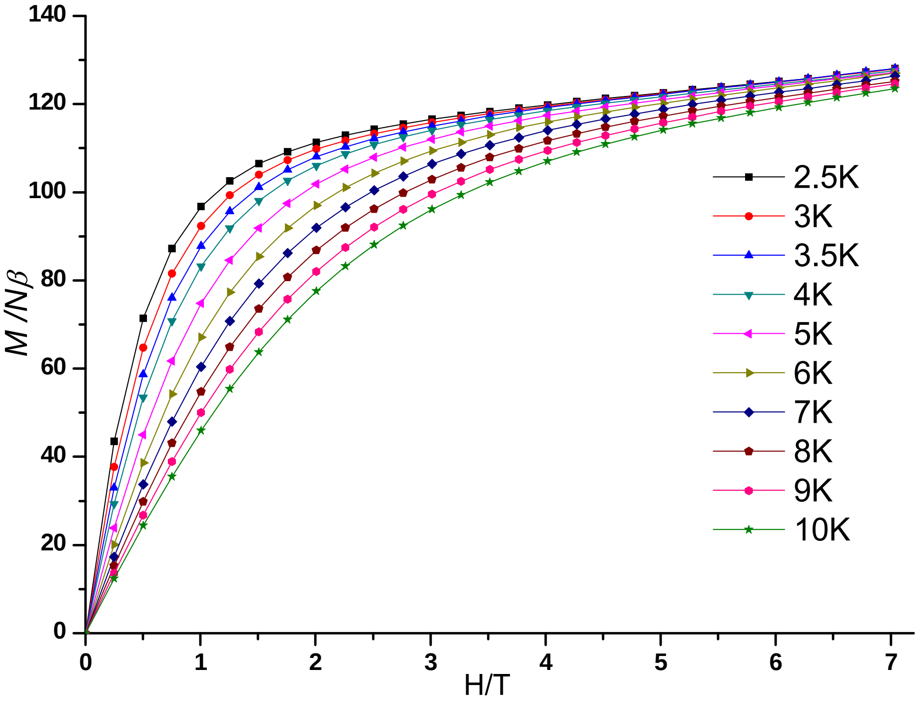


Figure S3. T vs $\chi_M T$ curve (○) for **Dy_{24}**.



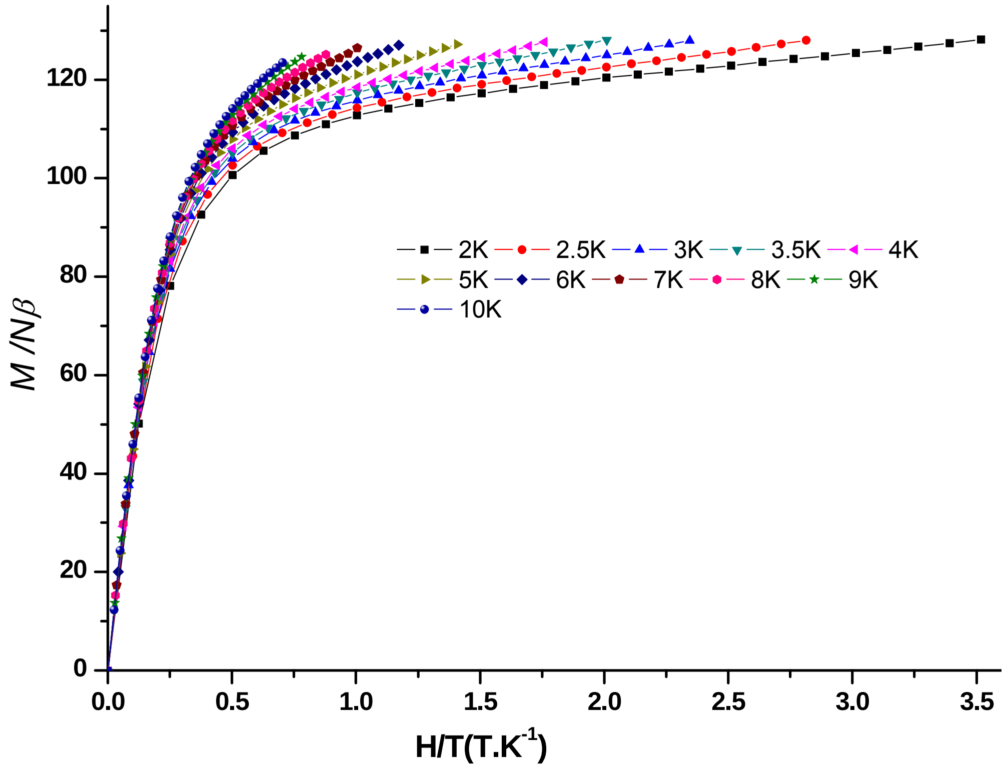


Figure S4. Field dependence of the magnetization drawn as *M* vs *H* (Top) and *M* vs *H/T* (Bottom) plots for **Dy$_{24}$** under different temperatures.

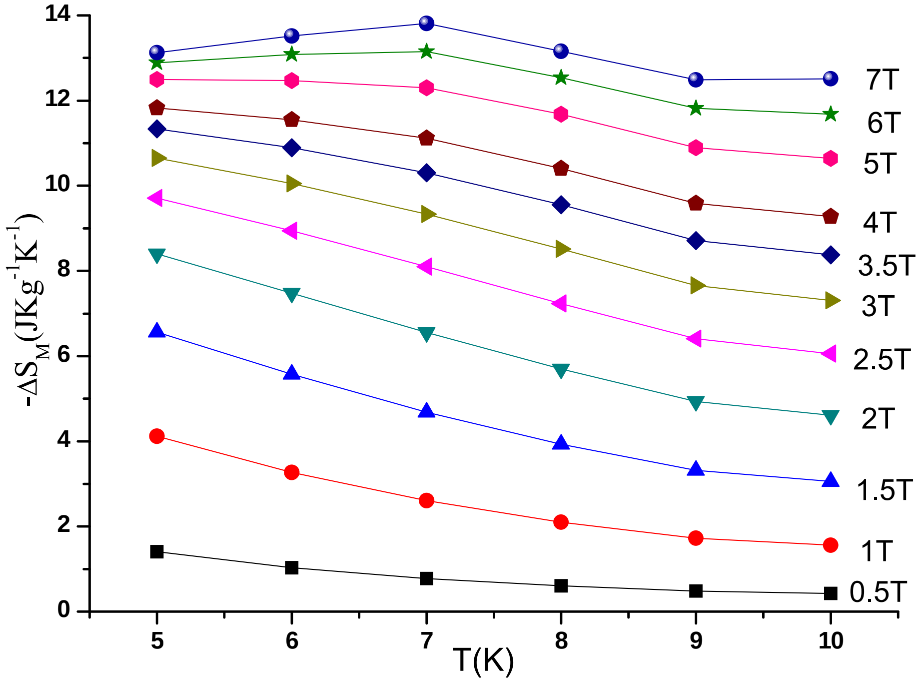


Figure S5. ΔS_m calculated by using the magnetization data of **Dy$_{24}$** at different fields and temperatures.

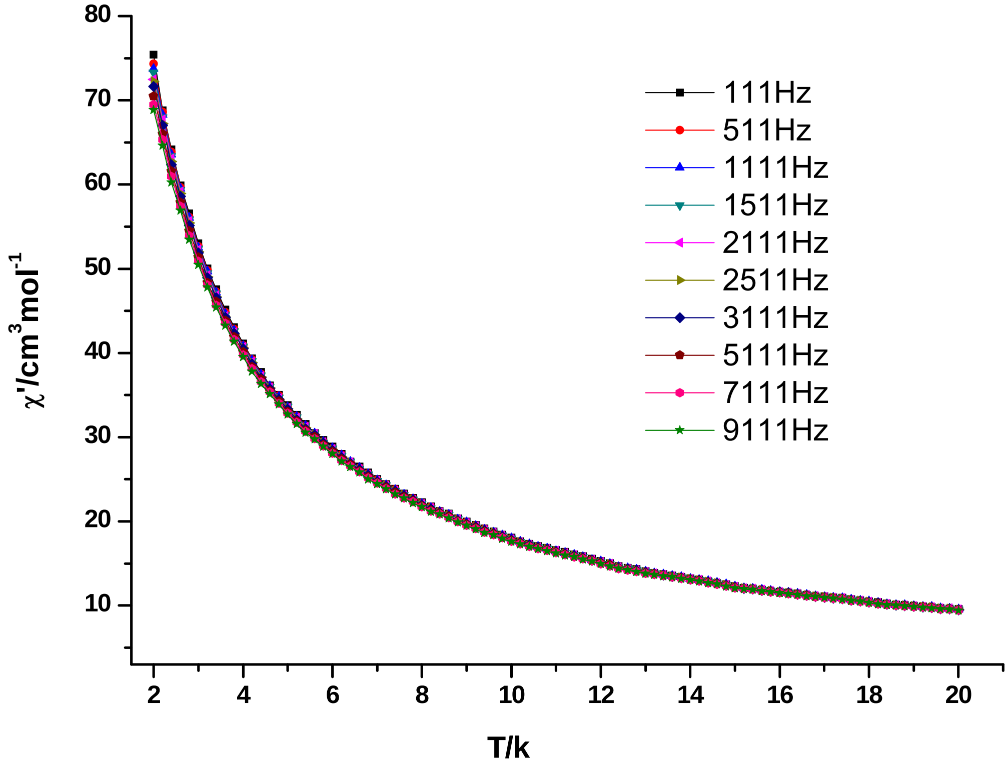
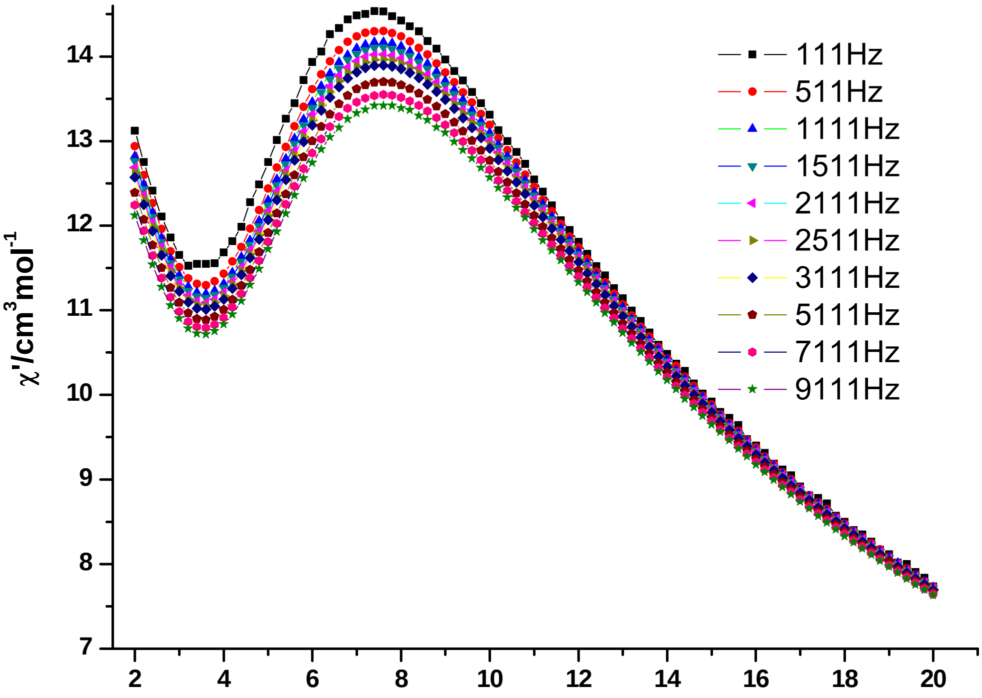


Figure S6. Temperature dependence of the in-phase (χ') ac susceptibility components measured at different frequencies for **Dy$_{24}$** at zero dc field and an oscillation of 3 Oe.



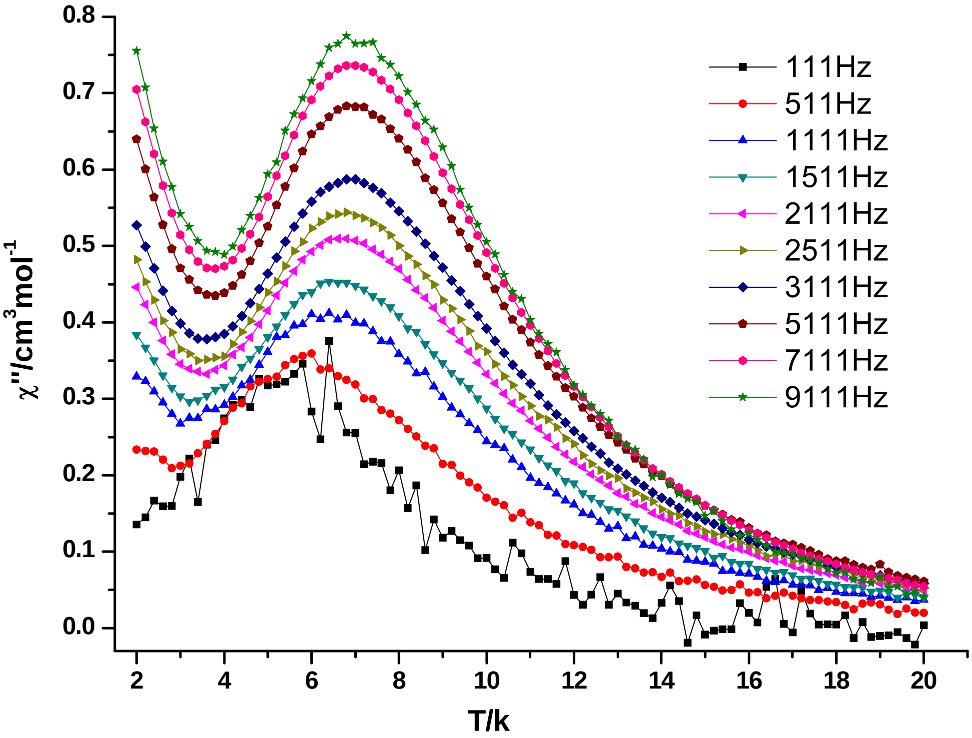


Figure S7. Temperature dependence of the in-phase (χ') and out-of-phase (χ'') ac susceptibilities measured at different frequencies for **Dy_{24}** with 5000 Oe dc field and an oscillation of 3 Oe.

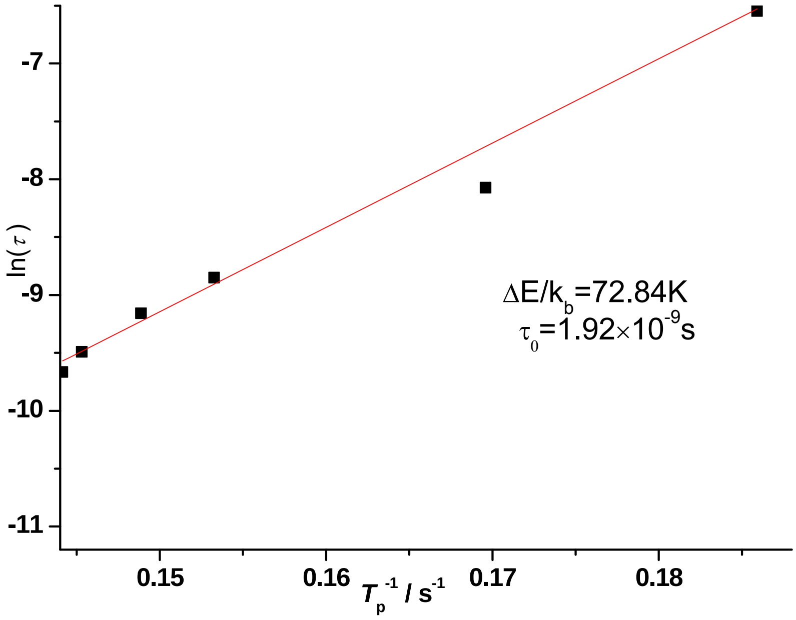


Figure S8. Relaxation time τ of the magnetization for **Dy_{24}** versus inverse temperature at different frequencies under 5000 Oe dc field.

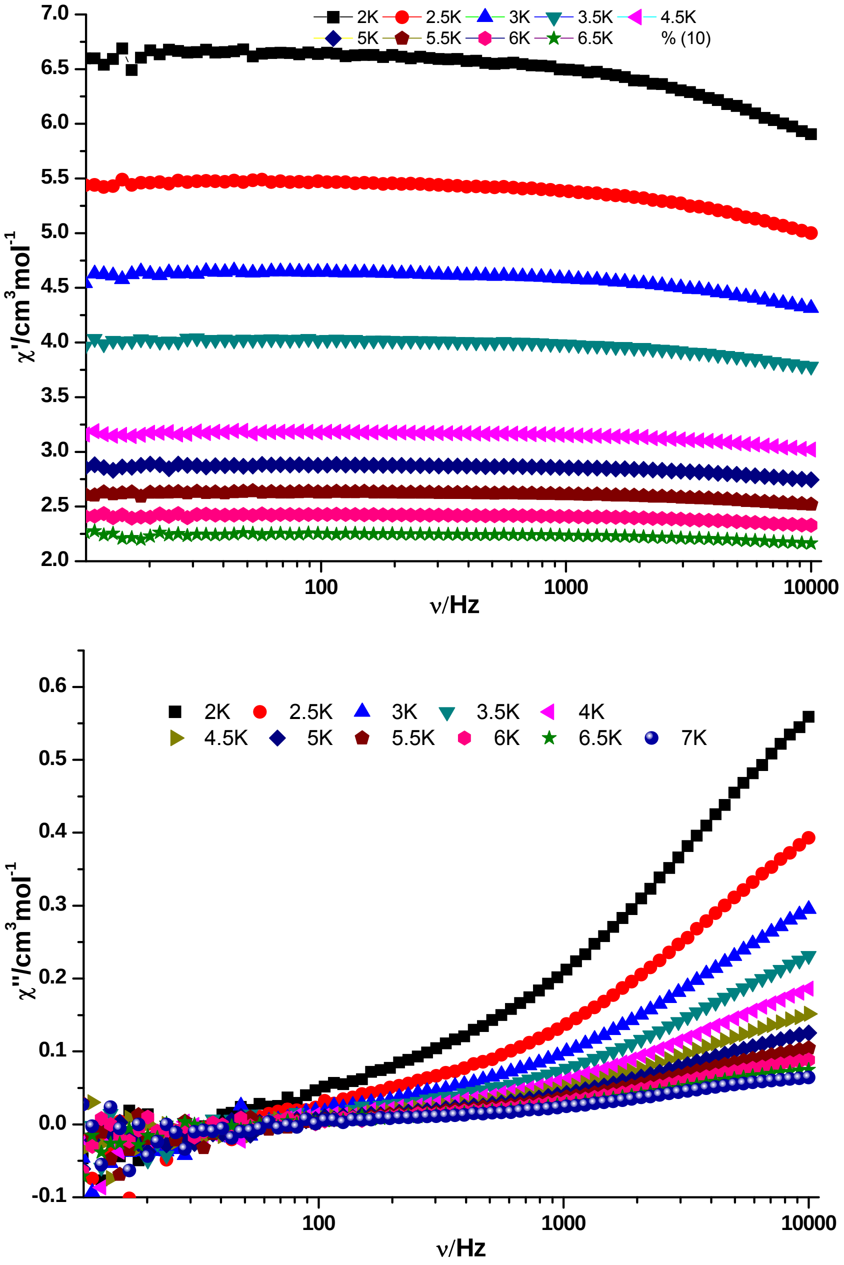


Figure S9. Frequency dependence of in-phase (χ′) and out-of-phase (χ″) susceptibilities under zero dc field at different temperatures of **Dy$_{24}$**。

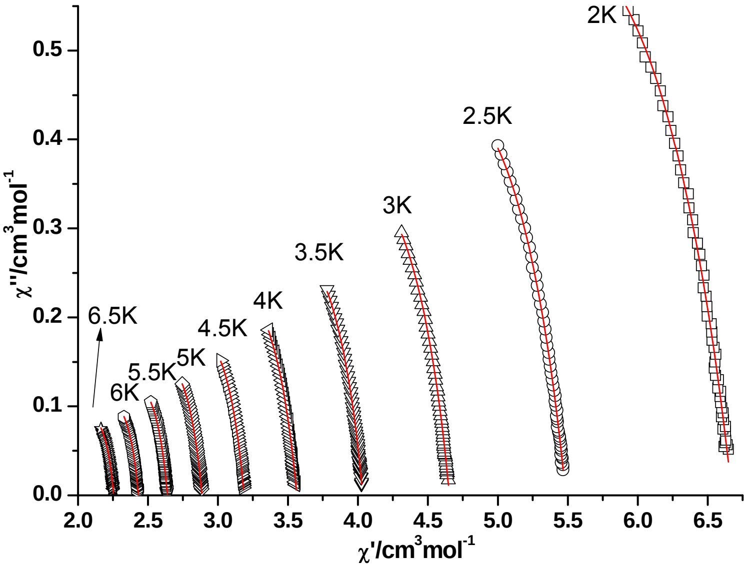


Figure S10. Cole–Cole plots measured at 2-6.5 K under zero dc field; the solid lines are the best fit to the experimental data.

Table S2. -ΔS_m comparison among **Gd_{24}** and selected compounds with the ΔSm value of above 36.0 J kg^{-1} K^{-1} (ΔH = 7T).

Compounds	Dimensionality	-ΔS_m/$JKg^{-1}K^{-1}$ (ΔH=7T)
$[Gd_2(OAC)_3(H_2O)_{0.5}]_n$[4]	1D	47.7
Gd_{24} in this work	0D	46.1
$[Gd(HCOO)(OAc)_2(H_2O)_2]_n$[5]	2D	45.9
$[Gd_2(OAC)_3(MeOH)]_n$[4]	1D	45.0
$[Gd_2(OAC)_6(H_2O)_4]\cdot 4H_2O$[6]	0D	41.6
$\{Co_{10}Gd_{42}\}$[7]	0D	41.26
$\{Ni_{10}Gd_{42}\}$[7]	0D	38.2
$[Gd_4(OAC)_4(acac)_8(H_2O)_4]$[4]	0D	37.7
$\{Ni_{12}Gd_{36}\}$[8]	0D	36.3

Table **S3** The α values obtained from cole-cole plots of **Dy_{24}** using the Debye model.

T(K)	α	T(K)	α
2	0.37	4.5	0.30
2.5	0.34	5	0.32
3	0.33	5.5	0.31
3.5	0.32	6	0.31
4	0.33	6.5	0.32

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