Electronic Supplementary Information for

Facile and Environment Friendly Synthesis of Two Heterometallic Dumbbell-Shaped $M^{II}_5Ln^{III}_4$ (M = Co, Ni; Ln = Eu, Gd, Dy) Clusters as Cryogenic Magnetic Coolants and Molecular Magnets

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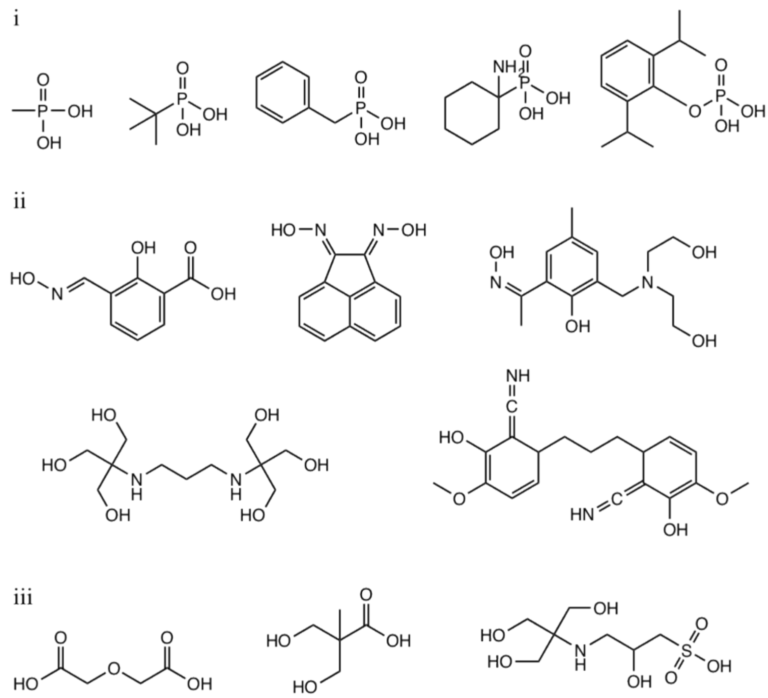
EXPERIMENTAL DETAILS

General. Unless otherwise stated, all starting materials were obtained commercially and were used without further purification. Elemental analyses for C, H, N were performed on a Vario EL III elemental analyser. IR spectra were recorded in range of 400 – 4000 cm^{-1} on a Nicolet 5DX spectrometer (KBr pellets). X-ray diffraction data were collected on Oxford Gemini S Ultra or RAXIS-RAPID diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Magnetic data were collected using a Quantum Design MPMS XL7 SQUID magnetometer. Magnetic susceptibility data under 0.5 T applied field were collected using a Quantum Design MPMS XL7 SQUID magnetometer.

Single Crystal X-ray Diffraction Studies. The crystal data collection and refinement parameters are given in the Table S1 and Table S2. CCDC 1864142-1864147 contains the crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/Requestastructure. X-ray diffraction data were collected by using an Oxford Gemini S Ultra diffractometer or RAXIS-RAPID with graphite-monochromated MoK$_\alpha$ radiation. These crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and protective agent, normally, the crystal would be flash frozen in a nitrogen gas stream at 100 K, and then heated up to 173 K for measurements. (see table S1 and S2) The structures were solved by direct methods using SHELXS-97[1, 2] and refined against F^2 by full-matrix least-squares techniques using SHELXL-97[1, 2] or SHELXL-2018[3] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX.

Magnetic Measurements. The direct-current (dc) and alternating-current (ac) magnetic susceptibility measurements were performed on powdered samples that were mulled in eicosane to prevent torqueing of the samples in high applied magnetic fields on a Quantum Design MPMS-XL7 SQUID magnetometer operating with a working temperature range of 1.8 – 300 K and dc-applied fields ranging from –7 to 7 T. The crystals were taken out form the mother solution, then immediately blotted, wrapped using the diamagnetic film and put in the capsule for the SQUID measurement. The capsule was then inserted into a clear plastic drinking straw. Holes were punched into the straw to allow air to escape. Diamagnetic corrections were applied for the sample holder from previous direct measurements, and molar diamagnetic susceptibilities were calculated from Pascal's constants. Ac susceptibility measurements were carried out under an oscillating-drive field of 3 Oe and ac frequencies ranging between 0.1 and 1500 Hz within a dc magnetic field.



Scheme S1. Some organic ligands carried out in the syntheses of molecular magnetic coolants and/or SMMs. i. ligands of organic phosphorus; ii. ligands of nitrogenous compounds; iii. ligands of organic acids. [4-25]

Syntheses. All the reaction mixture was prepared and put into oven at 90 ºC, please be careful, all the reaction field calculated based on the lanthanide salts.

$$M(OAc)_2 + Ln(NO_3)_3 \xrightarrow{MeOH} [M^{II}_5Ln^{III}_4(OH)_m(OMe)_{8-m}(OAc)_{10+n}(NO_3)_{4-n}(MeOH)_6](MeOH)_4$$

Scheme S2 The route of syntheses of two M_5Gd_4 complexes.

$[Co_5Eu_4(OMe)_8(OAc)_{12}(NO_3)_2(MeOH)_6]\cdot4MeOH$ (1):

A solution of $Co(OAc)_2\cdot4H_2O$ (374 mg, 1.5 mmol) and $Eu(NO_3)_3\cdot6H_2O$ (446 mg, 1.0 mmol) in methanol (24 mL) was stirred for 10 min, and then sealed in flask and heated to 90 ºC for 7 days. Orange crystals of **1** were collected by filtration. Yield: 68%. The crystals were dried in air to give samples for characterization, elemental analysis and magnetic measurements. Elem Anal. Calc.: C 21.90 H 4.38 N 1.22; Found: C 19.78 H 4.07 N 1.27. That may owe to the MeOH in lattice replaced by H_2O in air. $[Co_5Eu_4]\cdot8H_2O$: C 19.67 H 4.34 N 1.21. IR (KBr pellet, cm^{-1}): 3415 (m), 2432 (m), 1555 (s), 1421 (m), 1384 (m), 1027 (m), 673 (s), 616 (s).

$[Co_5Gd_4(OMe)_8(OAc)_{12}(NO_3)_2(MeOH)_6]\cdot4MeOH$ (2):

A solution of $Co(OAc)_2\cdot4H_2O$ (374 mg, 1.5 mmol) and $Gd(NO_3)_3\cdot5H_2O$ (433 mg, 1.0 mmol) in methanol (24 mL) was stirred for 10 min, and then sealed in flask and heated to 90 ºC for 15 days. Orange crystals of **2** were collected by filtration. Yield: 46%. The crystals were dried in air to give samples for characterization, elemental analysis and magnetic measurements. Elem Anal. Calc.: C 21.70 H 4.34 N 1.20; Found: C 20.70 H 4.01 N 1.31. That may owe to the MeOH in lattice replaced by H_2O in air. $[Co_5Gd_4]\cdot2MeOH\cdot4H_2O$: C 20.59 H 4.32 N 1.20. IR (KBr pellet, cm^{-1}): 3438 (m), 2920 (m), 1563 (w), 1384 (m), 1021 (m), 672 (s), 616 (m).

$[Co_5Dy_4(OH)_2(OMe)_6(OAc)_{10}(NO_3)_4(MeOH)_6]\cdot4MeOH$ (3):

A solution of $Co(OAc)_2\cdot4H_2O$ (374 mg, 1.5 mmol) and $Dy(NO_3)_3\cdot5H_2O$ (438 mg, 1.0 mmol) in methanol (24 mL) was stirred for 10 min, and then sealed in flask and heated to 90 ºC for 10 days. Orange crystals of **3** were collected by filtration. Yield: 62%. The crystals were dried in air to give samples for characterization, elemental analysis and magnetic measurements. Elem Anal. Calc.: C 18.61 H 3.90 N 2.41; Found: C 16.87 H 3.83 N 2.31. That may owe to the MeOH in lattice replaced by H_2O in air. $[Co_5Dy_4]\cdot8H_2O$: C 16.43 H 3.88 N 2.39. IR (KBr pellet, cm^{-1}): 3433 (m), 2920 (m), 1562 (w), 1384 (m), 1024(m), 670 (s), 615 (m).

$[Ni_5Eu_4(OMe)_8(OAc)_{12}(NO_3)_2(MeOH)_6]\cdot4MeOH$ (4):

A solution of $Ni(OAc)_2\cdot4H_2O$ (374 mg, 1.5 mmol) and $Eu(NO_3)_3\cdot6H_2O$ (446 mg, 1.0 mmol) in methanol (24 mL) was stirred for 10 min, and then sealed in flask and heated to 90 ºC for 5 days. Blue crystals of **4** were collected by filtration. Yield: 71%. The crystals were dried in air to give samples for characterization, elemental analysis and magnetic measurements. Elem Anal. Calc.: C 21.91 H 4.38 N 1.22; Found: C 19.43 H 4.41 N 1.89%. That may owe to some MeOH in lattice replaced by H_2O in air and some OAc^- coordinated to Eu^{3+} ions may be NO_3^-.

If [{Ni_5Eu_4}(OAc)(NO_3)$_3$]·2MeOH·4H_2O: C 19.73 H 4.23N 1.82. IR (KBr pellet, cm^{-1}): 3434 (m), 2369 (m), 1562 (s), 1421 (m), 1385 (m), 1029 (m), 676 (s), 616 (s).

[$Ni_5Gd_4(OH)_2(OMe)_6(OAc)_{10}(NO_3)_4(MeOH)_6$]·4MeOH (5):

A solution of $Ni(OAc)_2$·4H_2O (374 mg, 1.5 mmol) and $Gd(NO_3)_3$·5H_2O (433 mg, 1.0 mmol) in methanol (24 mL) was stirred for 10 min, and then sealed in flask and heated to 90 ºC for 7 days. Blue crystals of **5** were collected by filtration. Yield: 56%. The crystals were dried in air to give samples for characterization, elemental analysis and magnetic measurements. Elem Anal. Calc.: C 18.79 H 3.94 N 2.43; Found: C 20.19 H 4.48 N 1.22. That may owe to the MeOH in lattice replaced by H_2O in air and some NO_3^- coordinated to Gd^{3+} ions may be OAc^-. If [{Ni_5Gd_4}$(OAc)_2(NO_3)_2$]·2MeOH·4H_2O: C 19.81 H 4.20N 1.22. IR (KBr pellet, cm^{-1}): 3431 (m), 2918 (m), 1562 (w), 1421 (m), 1022(m), 673 (s), 615 (m).

[$Ni_5Dy_4(OMe)_8(OAc)_{11}(NO_3)_3(MeOH)_6$]·4MeOH (6):

A solution of $Ni(OAc)_2$·4H_2O (374 mg, 1.5 mmol) and $Dy(NO_3)_3$·5H_2O (438 mg, 1.0 mmol) in methanol (24 mL) was stirred for 10 min, and then sealed in flask and heated to 90 ºC for 3 days. Blue crystals of **6** were collected by filtration. Yield: 57%. The crystals were dried in air to give samples for characterization, elemental analysis and magnetic measurements. Elem Anal. Calc.: C 20.46 H 4.16 N 1.79; Found: C 20.42 H 4.13 N 1.22. That may owe to the MeOH in lattice replaced by H_2O in air and some NO_3^- coordinated to Dy^{3+} ions may be OAc^-. If [{Ni_5Gd_4}$(OAc)_2(NO_3)_2$]·2MeOH·4H_2O: C 20.42 H 4.28N 1.19. IR (KBr pellet, cm^{-1}): 3430 (m), 2919 (m), 1561 (w), 1421 (m), 1384 (m), 1018 (m), 676 (s), 615 (m).

Table S1 Crystal data for **1-3**

	1	**2**	**3**
formula	$C_{42}H_{100}N_2O_{48}Co_5Eu_4$	$C_{42}H_{100}N_2O_{48}Co_5Gd_4$	$C_{36}H_{90}N_4O_{50}Co_5Dy_4$
M_r	2303.7501	2324.8941	2323.7627
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
T (K)	173(2)	173(2)	173(2)
a (Å)	13.3061(3)	13.366(3)	14.5001(3)
b (Å)	28.4606(8)	28.431(6)	17.702(4)
c (Å)	21.2498(8)	21.262(4)	29.025(6)
α (°)	90	90	90
β (°)	100.866(3)	101.450(8)	92.740(8)
γ (°)	90	90	90
V (Å^3)	7903.0(4)	7919.0(3)	7442(3)
Z	4	4	4
ρ_{calcd} (g·cm^{-3})	1.926	1.923	2.069
μ (mm^{-1})	4.240	4.412	5.151
F (000)	4604	4492	4508
reflns obsd [$I > 2\sigma(I)$]	15509	18016	14510
GOF on F^2	1.181	1.058	0.797
$R_1[I > 2\sigma(I)]$	0.0866	0.0754	0.0524
wR_2(all data)	0.1560	0.2077	0.1854

Table S2 Crystal data for **4-6**

	4	**5**	**6**
formula	$C_{42}H_{100}N_2O_{48}Ni_5Eu_4$	$C_{36}H_{90}N_4O_{50}Ni_5Gd_4$	$C_{40}H_{97}N_3O_{49}Ni_5Dy_4$
M_r	2302.5511	2301.5638	23247.6560
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
T (K)	173(2)	173(2)	173(2)
a (Å)	13.335(3)	14.4713(5)	13.2406(2)
b (Å)	28.284(6)	17.6015(8)	28.2759(4)
c (Å)	21.178(4)	28.8491(8)	21.0581(5)
α (°)	90	90	90
β (°)	101.850(3)	93.626(4)	101.082(2)
γ (°)	90	90	90
V (Å^3)	7818.0(3)	7367.0(5)	7736.9(2)
Z	4	4	4
ρ_{calcd} (g·cm^{-3})	1.912	2.075	1.944
μ (mm^{-1})	4.431	25.139	22.373
F (000)	4344	4520	4400
reflns obsd [I> 2σ(I)]	14875	11487	11408
GOF on F^2	1.045	1.145	1.314
R_1[I > 2σ(I)]	0.0734	0.0527	0.0810
wR_2(all data)	0.1975	0.1393	0.2267

Table S3 Crystal cell parameters of Co_5Y_4 at 173 K.

a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*V* (Å^3)
14.442(3)	17.744(1)	28.969(6)	90	92.78(3)	90	7414(3)

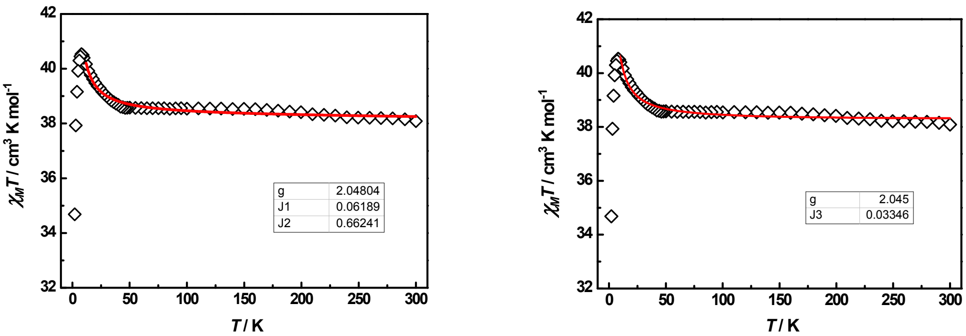


Figure S1. The temperature-dependent magnetic susceptibilities of Ni_5Gd_4 (**5**) measured at 1 kOe and fitting curve range of 300-10 K.

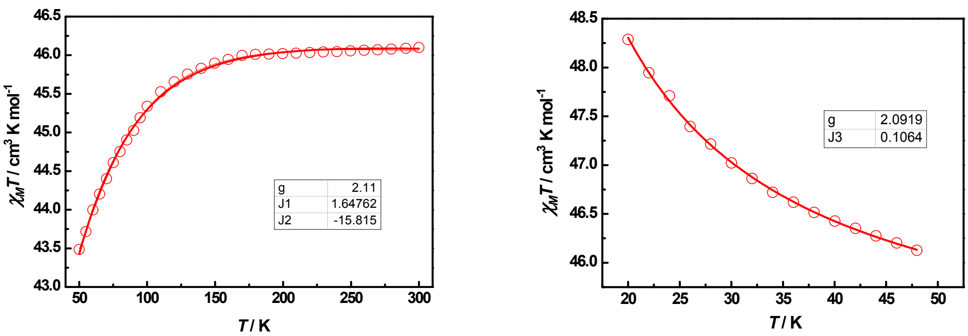


Figure S2. The temperature-dependent magnetic susceptibilities of Co_5Gd_4 (**2**) measured at 1 kOe and fitting curve (left: range of 300-50 K; right: $\chi_M T = \chi_M T_{rt} + \chi_M T_{ex} - \chi_M T_{cal}$ and range of 50-20 K).

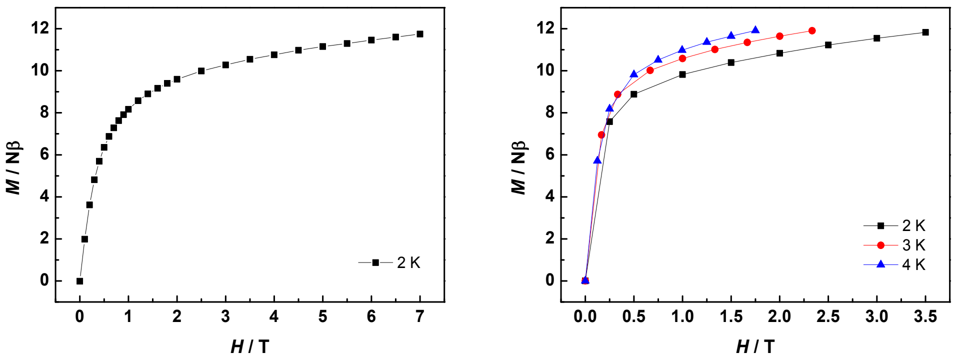


Figure S3. Field dependence of the magnetization for complex Co_5Eu_4 (**1**).

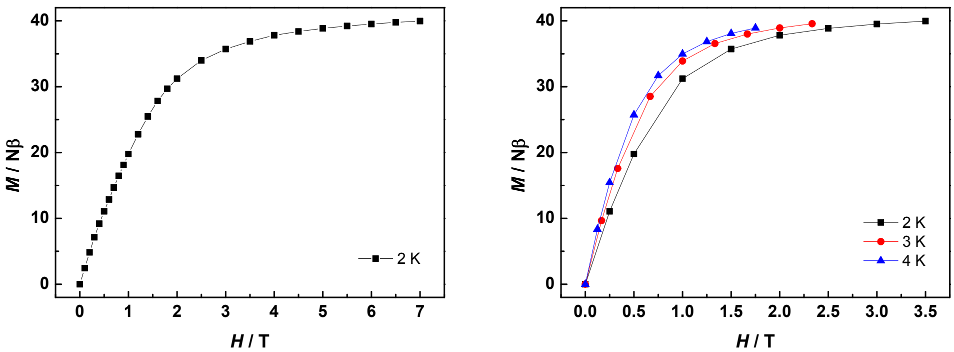


Figure S4. Field dependence of the magnetization for complex Co_5Gd_4 (**2**).

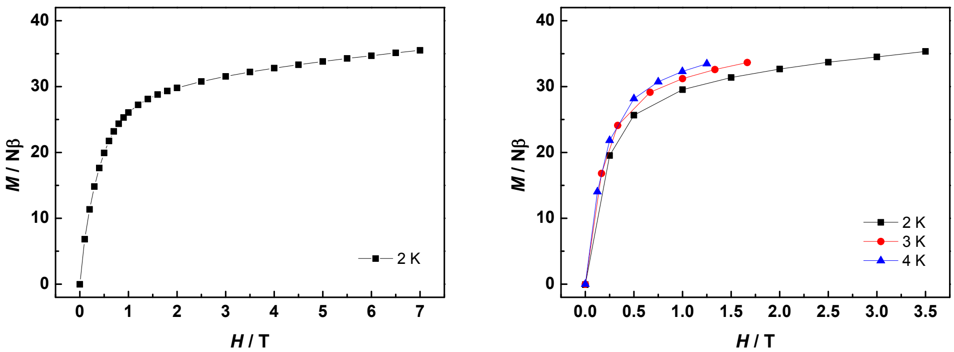


Figure S5. Field dependence of the magnetization for complex Co_5Dy_4 (**3**).

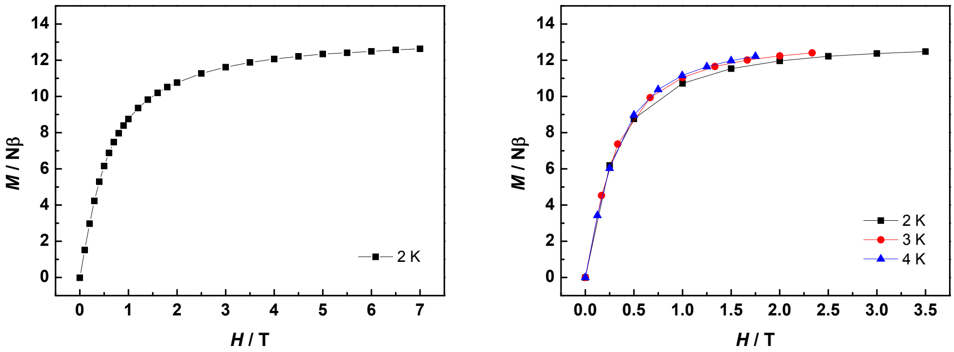


Figure S6. Field dependence of the magnetization for complex Ni_5Eu_4 (**4**).

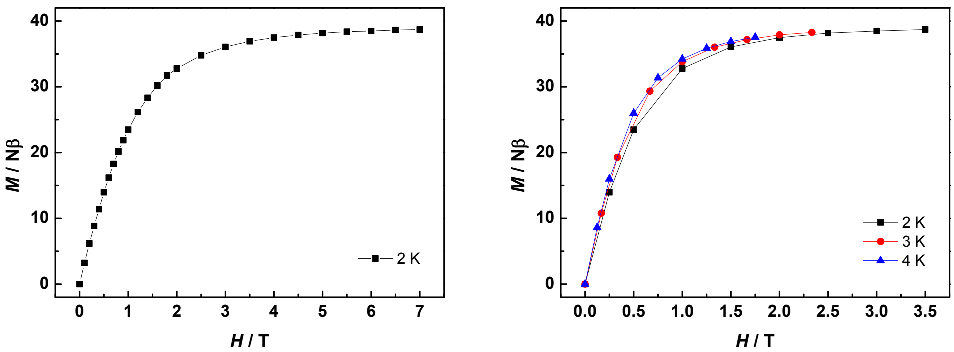


Figure S7. Field dependence of the magnetization for complex Ni_5Gd_4 (**5**).

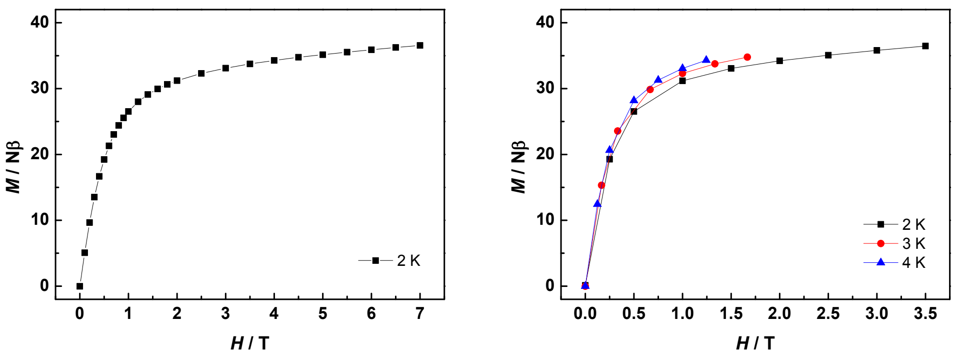


Figure S8. Field dependence of the magnetization for complex Ni_5Dy_4 (**6**).

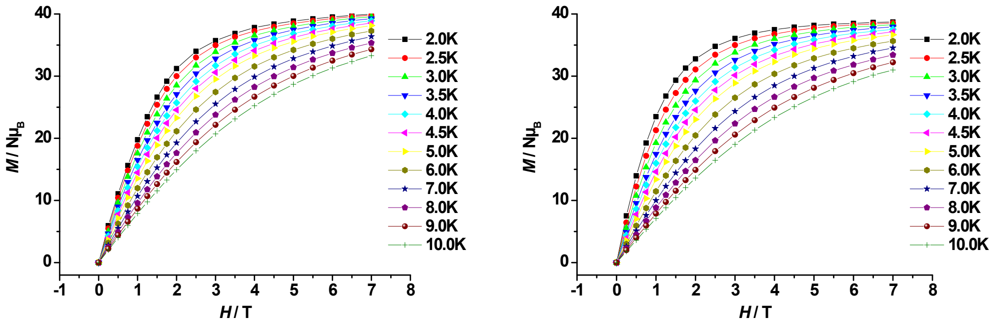


Figure S9. The field-dependent magnetization plots at indicated temperatures for complexes Co_5Gd_4 (**2**) and Ni_5Gd_4 (**5**).

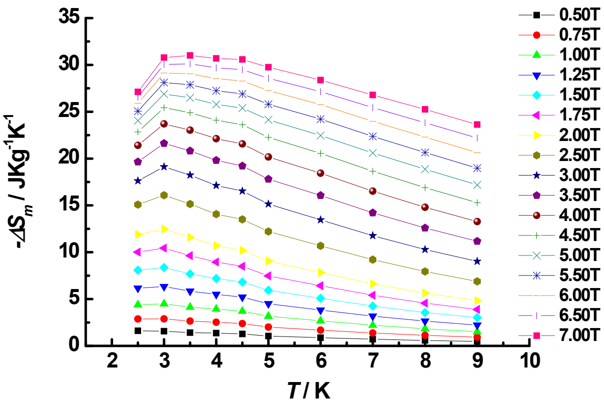


Figure S10. $-\Delta S_m$ calculated by using the magnetization data at various fields and temperatures for complexCo_5Gd_4(**2**).

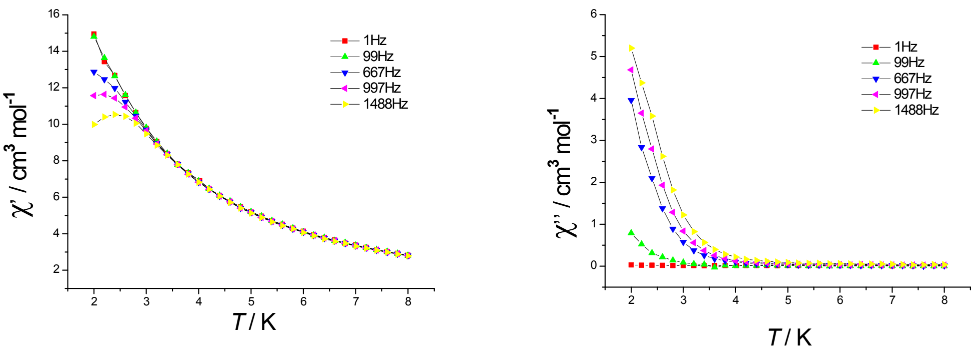


Figure S11. In-phase (left) and out-of-phase (right) ac magnetic susceptibilities at zero dc field for complex Co_5Eu_4 (**1**).

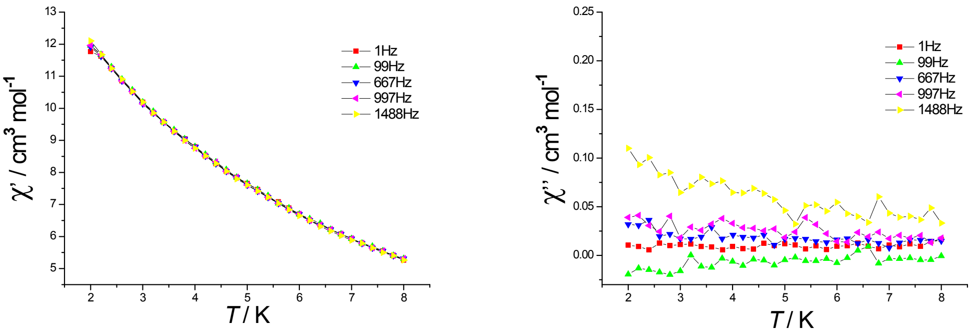


Figure S12. In-phase (left) and out-of-phase (right) ac magnetic susceptibilities at zero dc field for complex Co_5Gd_4 (**2**).

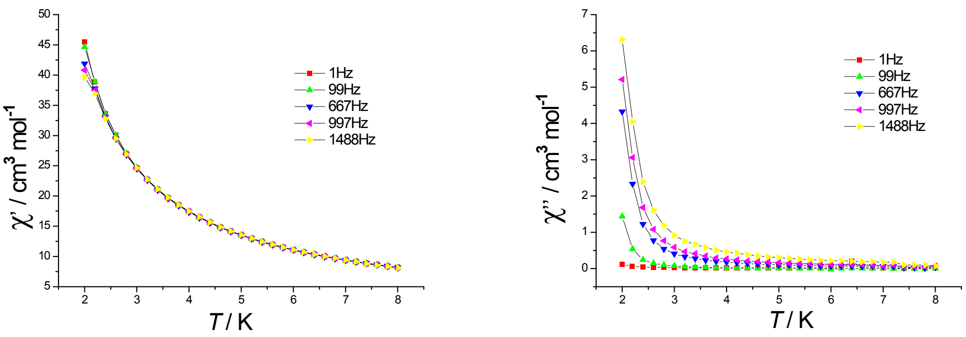


Figure S13. In-phase (left) and out-of-phase (right) ac magnetic susceptibilities at zero dc field for complex Co_5Dy_4 (**3**).

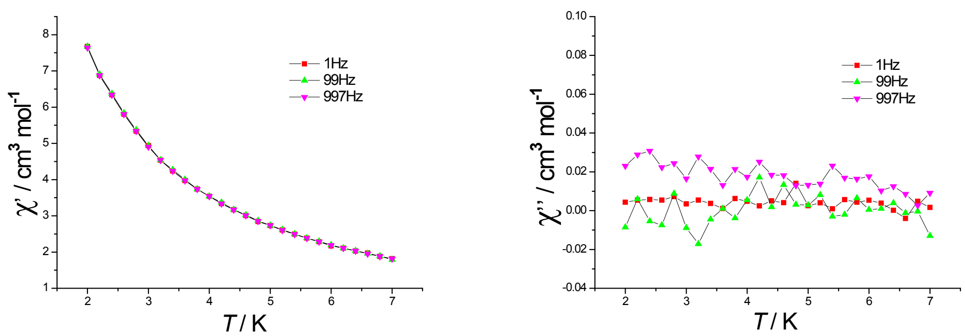


Figure S14. In-phase (left) and out-of-phase (right) ac magnetic susceptibilities at zero dc field for complex Ni_5Eu_4 (**4**).

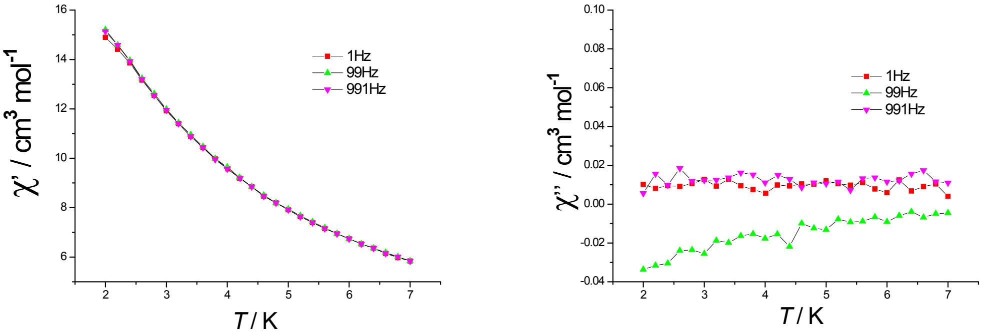


Figure S15. In-phase (left) and out-of-phase (right) ac magnetic susceptibilities at zero dc field for complex Ni_5Gd_4 (**5**).

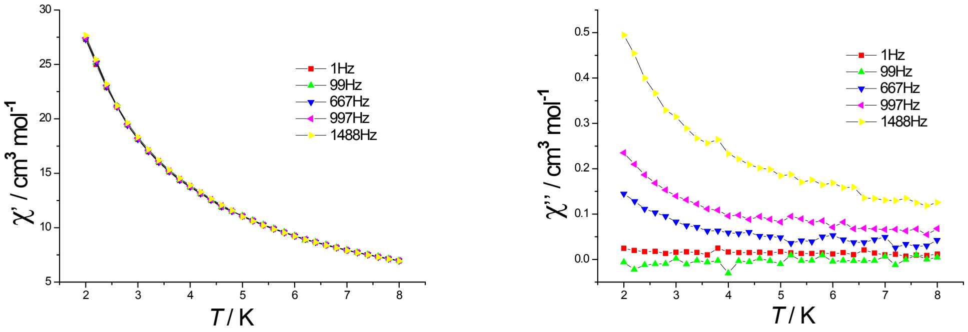


Figure S16. In-phase (left) and out-of-phase (right) ac magnetic susceptibilities at zero dc field for complex Ni_5Dy_4 (**6**).

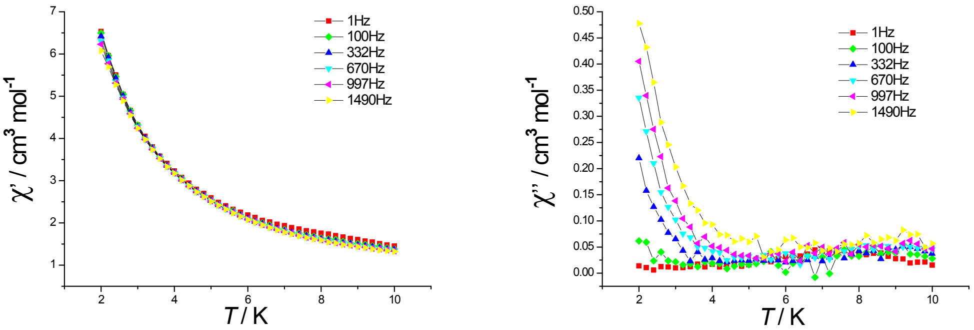


Figure S17. In-phase (left) and out-of-phase (right) ac magnetic susceptibilities at zero dc field for complex Co_5Y_4.

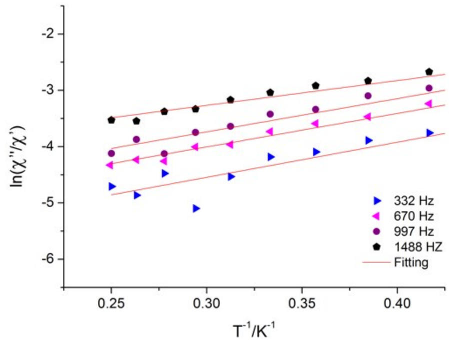


Figure S18. Plots of ln(χ″/χ′) vs. 1/T for **Co_5Y_4**. The solid lines represent the fitting results over the temperature range of 2.0 – 4.0K .

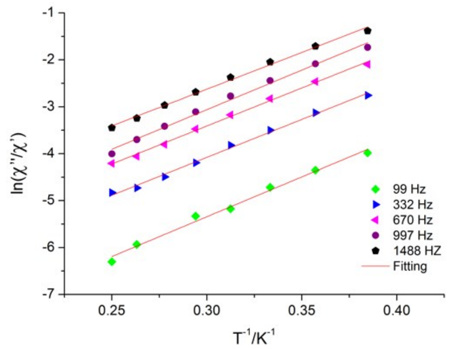


Figure S19. Plots of ln(χ″/χ′) vs. 1/T for **Co_5Eu_4**. The solid lines represent the fitting results over the temperature range of 2.6 – 4.0 K .

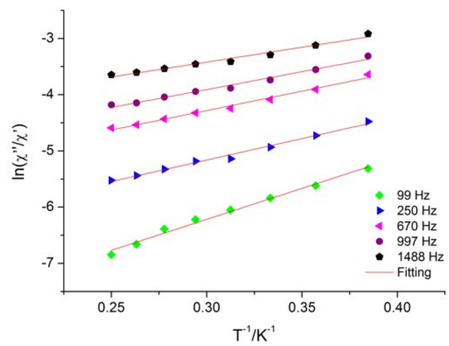


Figure S20. Plots of ln(χ″/χ′) vs. 1/T for **Co_5Dy_4**. The solid lines represent the fitting results over the temperature range of 2.6 – 4.0 K .

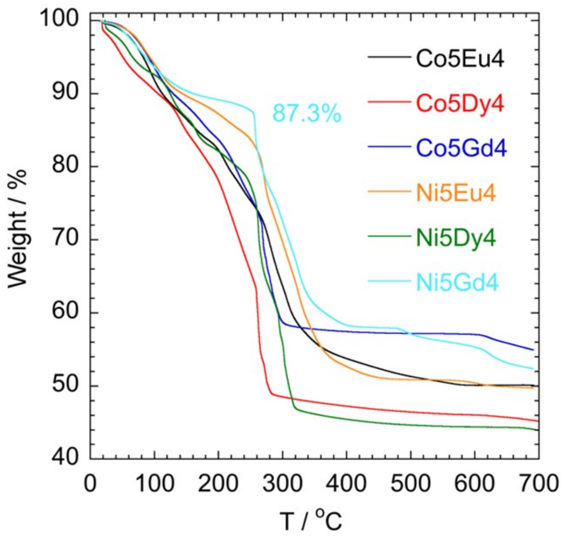


Figure S21. Thermogravimetry analyses (TGA) for complexes **1-6**, only Ni_5Gd_4 one has a good plateau, which is in good agreement of the element analyses result. (Due to the unstable of the clusters, it is difficult to get much better TGA data)

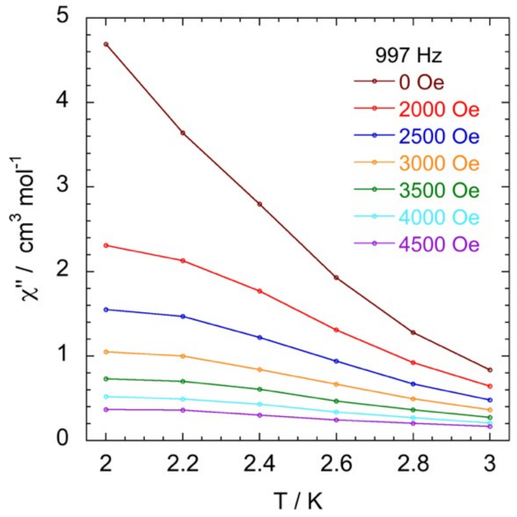


Figure S22. Out-of-phase susceptibility measurements at 997 Hz with a temperature range from 2 to 3 K under various applied dc magnetic fields for complex **1**. (Under 2000 Oe, there is a possibility to see the maximum of out-of-phase susceptibility in a higher frequency, to suppress QTM)

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