Supplementary Information for:

Multiple Core-shell Structure in $Cu_{24}Ln_6$ Cluster with Cooler and Slow Magnetization Relaxation

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Experimental Section:

Materials. All of 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. Powder X-ray diffraction was carried on the Rigaku Ultima IV multipurpose X-ray diffraction system. The elemental analyses (C, H and N) were carried out applying a Perkin-Elmer 240C elemental analyzer; TG-DTA analyzer from room temperature to 700 °C under nitrogen atmosphere with heating rate of 10 °C min^{-1}. Energy Dispersive Spectrometer (EDS) test was measurement on the field-emission scanning electron microscopy (SEM, JEOLJSM7500F); The 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]. $\chi_{(L\text{-}ala)}^{D}=4*\chi_{H} + \chi_{N} + 2*\chi_{carboxyl\ O} + 2*\chi_{C} = -(4*2.9 + 5.6 + 2*1.7 + 2*2.6)*10^{-6}= -32.6*10^{-6}cm^{3}mol^{-1}$; $\chi_{total}^{D}= 12*\chi_{(L\text{-}ala)} + \chi_{Na} + 6*\chi_{Ac} + 37*\chi_{OH-} + 12\chi_{NO3-} + 42*\chi_{H_2O} = -(12*32.6 + 6.8 + 6*30 + 37*12 + 12*18.9 + 42*13)*10^{-6} = - 1795.4*10^{-6}cm^{3}mol^{-1}=-1.795*10^{-3}\ cm^{-3}mol^{-1}$. $\chi = \chi_{exp}-\chi_{total}^{D}$.

Syntheses of 1 and 2

A mixture of 2 mmol $Cu(NO_3)_2\cdot 3H_2O$, 0.3 mmol $Gd(NO_3)_3\cdot 6H_2O$, 0.5 mmol *L*-alanine and 0.5 mmol sodium acetate was dissolved in 10 mL deionized water and stirred for 30 min. And then the 0.1 mol/L NaOH aqueous was used to adjust pH value to about 6.8 and then filtered. The filtrate was allowed to evaporate slowly at room temperature, and blue laminar crystals were obtained after about two weeks. The synthesis method of **2** is similar to that of **1**. The yield is 60% and 66% based on rare earth salt for **1** and **2**, respectively. Calcd. for $C_{48}H_{211}Cu_{24}Gd_6N_{24}NaO_{151}$ (%): C 9.56, H 3.53, N 5.57. Found: C 9.40, H 4.10, N 5.30. Anal. Calcd. for $C_{48}H_{211}Cu_{24}Dy_6N_{24}NaO_{151}$ (%): C 9.51, H 3.51, N 5.54. Found: C 9.45, H 4.11, N 5.38. IR (KBr disk): For **1** (cm^{-1}): 3427 (broad and strong peak), 1635 (strong peak), 1397 (strong peak), 1115 (middle strong peak), 859 (middle strong peak), 825 (middle strong peak), 527 (middle strong peak); For **2** (cm^{-1}): 3427 (broad and strong peak), 1635 (strong peak), 1397 (strong peak), 1115 (middle strong peak), 859 (middle strong peak), 825 (middle strong peak), 527 (middle strong peak). There is a broad band at 3427 cm^{-1} resulting from the O-H and N-H vibrations. The strong peak at 1635 cm^{-1} can be attributed to the asymmetric vibration of the carboxyl group. The bands at 1397 and 1450 cm^{-1} are attributed to stretching vibration of NO_3^- ions. The middle strong peak of 1115 cm^{-1} is the characteristic peak of stretching vibration of C-C single bond.

Crystallographic Study

A suitable single crystal of **1** and **2** was selected and settled on a SuperNova Single Crystal Diffractometer equipped with graphite-monochromatic Mo-Ka radiation (λ = 0.71073 Å) using the ω - φ scan technique, respectively. The crystal was kept at about 123 K during data collection. Using Olex2[2], the structure was solved with the XS[3] structure solution program using Direct Methods and refined with the XL[3] refinement package using Least Squares minimisation. Some carbon and nitrogen atoms of L-Ala ligands, which exhibit unbearable isotropic displacement parameters, are split two parts according to suitable site occupancy. So some restricted instructions were employed when splitting these atoms, for example, ISOR and EADP. All the hydrogen atoms were riding on carbon atoms geometrically except for those of the uncoordinated water molecules and disorder methyl carbon atoms. In additional, it is different to adjust the sites of hydrogen atoms on the free water molecules and hydroxyl groups, so these hydrogen atoms are not added rationally and omitted. For **1** and **2**, The highest peak and deepest hole are very closed to the core Na^+ with the distance of about 1.2 Å, which can be accounted for the series termination errors. The existence of Na^+ in **1** was characterized by EDS (Figure S1), but due to the low content (0.38%) of Na^+ in **1** caused the weak energy spectrum signal. The combination the results of EDX and single-crystal data and raw materials in syntheses experiment can confirm the existence of Na^+ in **1** without doubt as well as in **2**. Details of the crystal parameters, data collection, and refinements for **1** and **2** are summarized in Table S1. CCDC: 920370 for **1** and 920369 for **2** 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 refinements for complexes **1** and **2**.

Empirical formula	$C_{48}H_{211}Cu_{24}Gd_6N_{24}NaO_{151}$	$C_{48}H_{211}Cu_{24}Dy_6N_{24}NaO_{151}$
Formula weight	6032.86	6064.36
Temperature/K	123.3(3)	125.2(4)
Crystal system	triclinic	triclinic
Space group	*P*-1	*P*-1
a/Å	17.0801(7)	17.0946(8)
b/Å	17.8312(7)	17.8122(9)
c/Å	17.9410(5)	17.9557(9)
α/°	87.087(3)	87.212(4)
β/°	71.317(3)	71.420(4)
γ/°	64.441(4)	64.470(5)
Volume/$Å^3$	4645.2(3)	4651.2(4)
Z	1	1
$\rho_{calc}mg/mm^3$	2.157	2.165
m/mm^{-1}	4.915	5.179
F(000)	2966	2978
Crystal size/mm^3	0.3 × 0.25 × 0.2	0.3 × 0.25 × 0.2

2θ range for data collection	5.86 to 50.02°	6.06 to 50.02°
Index ranges	$-20 \le h \le 20$, $-18 \le k \le 21$, $-21 \le l \le 21$	$-20 \le h \le 20$, $-21 \le k \le 21$, $-18 \le l \le 20$
Reflections collected	35765	34547
Independent reflections	16310[R(int) = 0.0281]	16326[R(int) = 0.0371]
Data/restraints/parameters	16349/424/1254	16326/678/1363
Goodness-of-fit on F^2	1.018	1.087
Final R indexes [I>=2σ (I)]	$R_1 = 0.0644$, $wR_2 = 0.1875$	$R_1 = 0.0684$, $wR_2 = 0.1887$
Final R indexes [all data]	$R_1 = 0.0747$, $wR_2 = 0.1964$	$R_1 = 0.0812$, $wR_2 = 0.2018$
Largest diff. peak/hole / e Å^{-3}	2.098/-1.219	2.61/-1.324

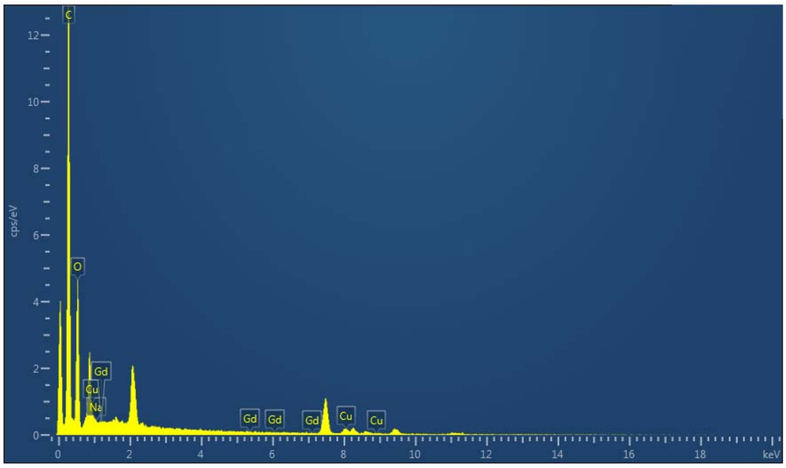


Figure S1. The EDS spectrum of **1**.

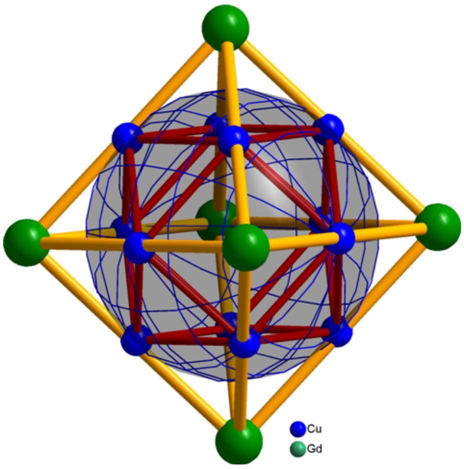


Figure S2. The metal skeleton of the first and second shell in **1**.

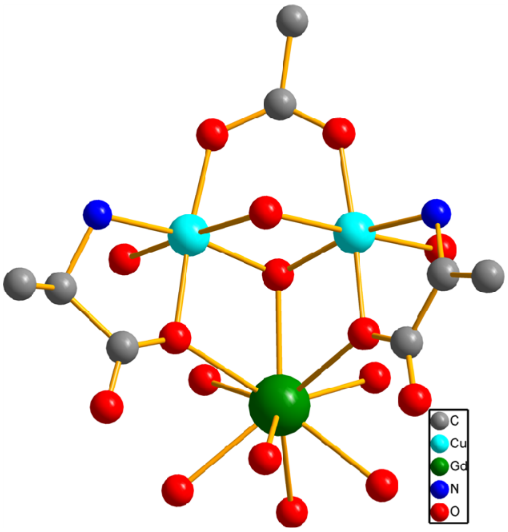


Figure S3. The [Cu_2] dimer on the third shell.

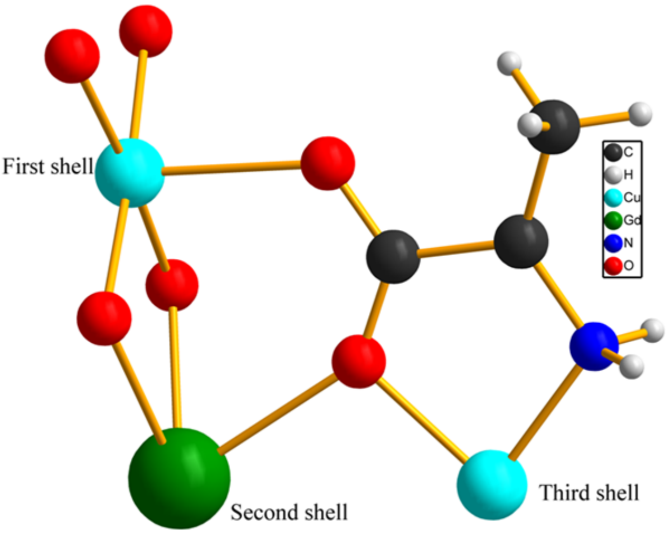


Figure S4. The coordination mode of ligand *L*-Ala.

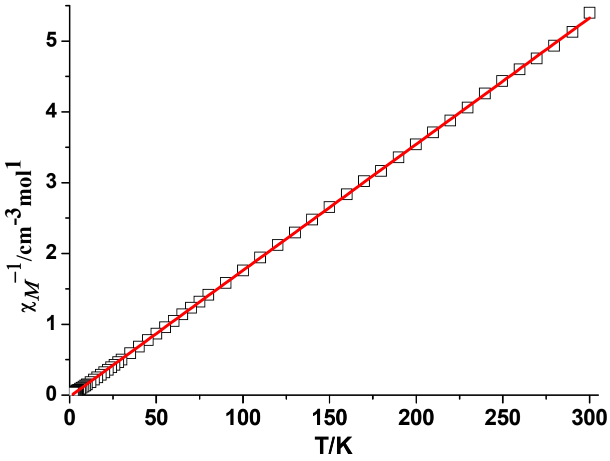


Figure S5. χ_M^{-1} vs T curve for **1.** The red line is the best fitting using Curie-Weiss law.

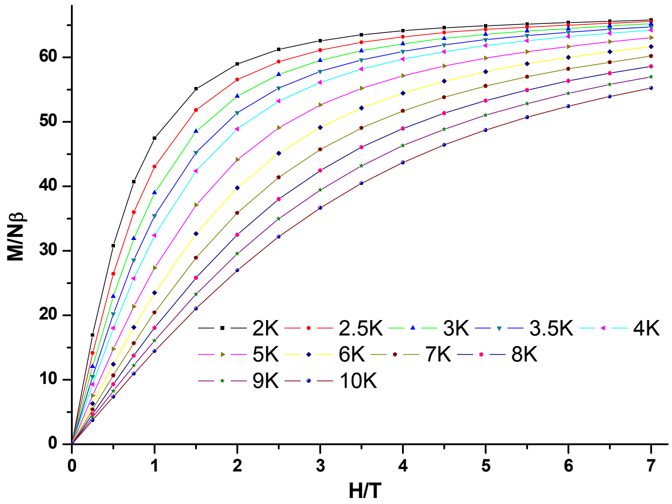


Figure S6. Plots of *M* vs *H* at the temperature of 2-10 K for compound **1**.

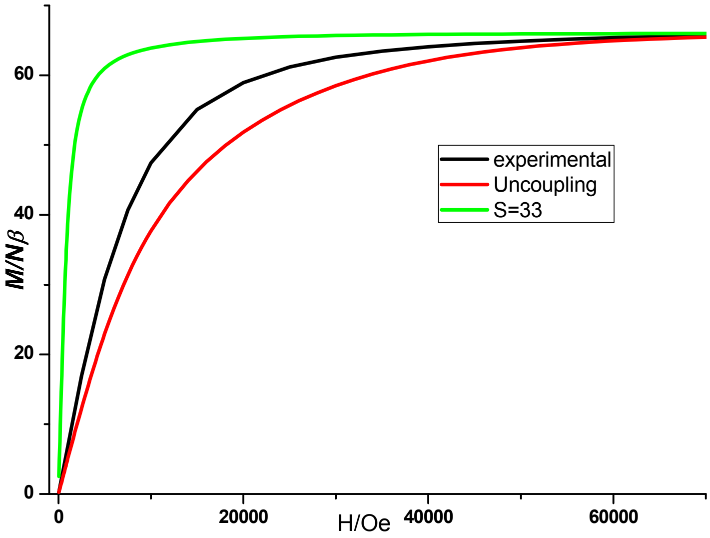


Figure S7. Field-dependent magnetization for **1** at 2 K (black line). The green and red line represents the Brillouin function for **1** six uncoupled Gd and twenty four Cu centers, and an S=33 state, respectively.

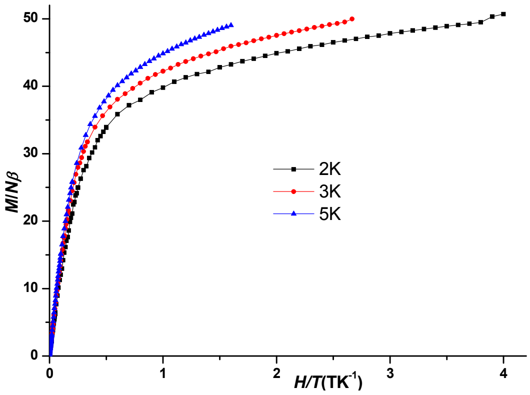


Figure S8. *M* vs *H*/*T* curves under the temperatures of 2, 3 and 5 K for compound **2**.

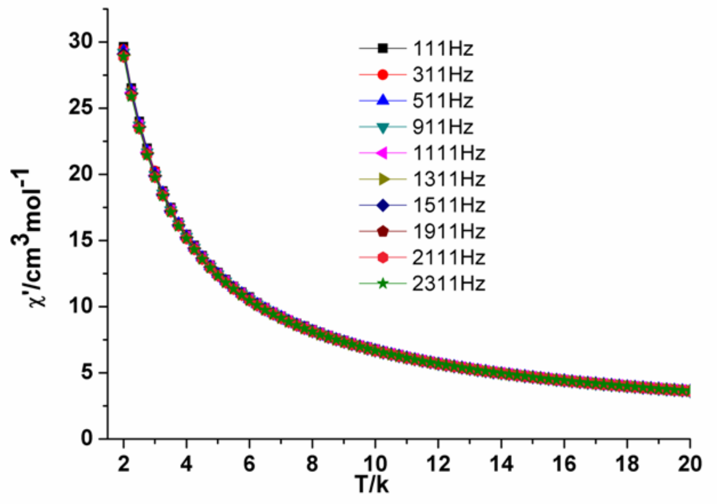


Figure S9. Temperature-dependent of the in-phase (χ') ac susceptibility components at different frequencies for **2** under zero dc field.

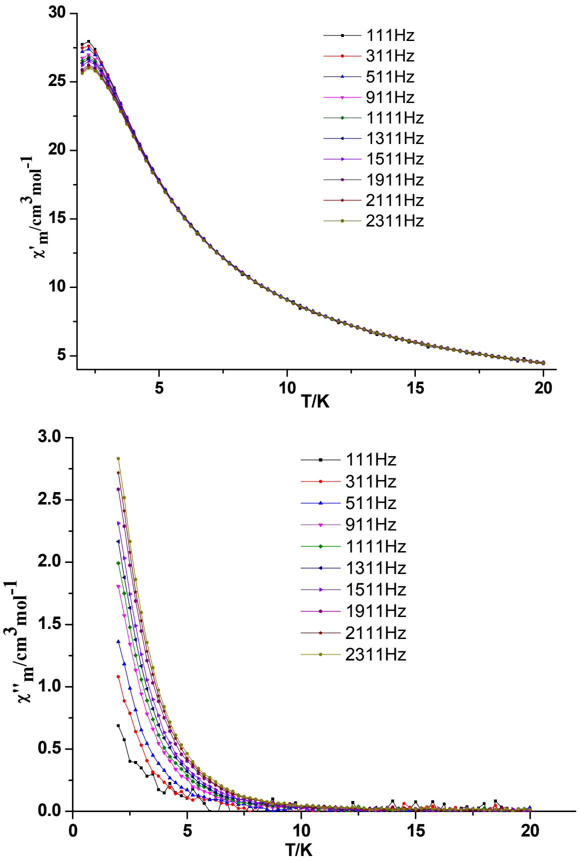


Figure S10. Temperature-dependent of the in-phase (χ') (left) and out of phase (χ'') (right) ac susceptibility components at different frequencies for **2** under 2000 Oe dc field.

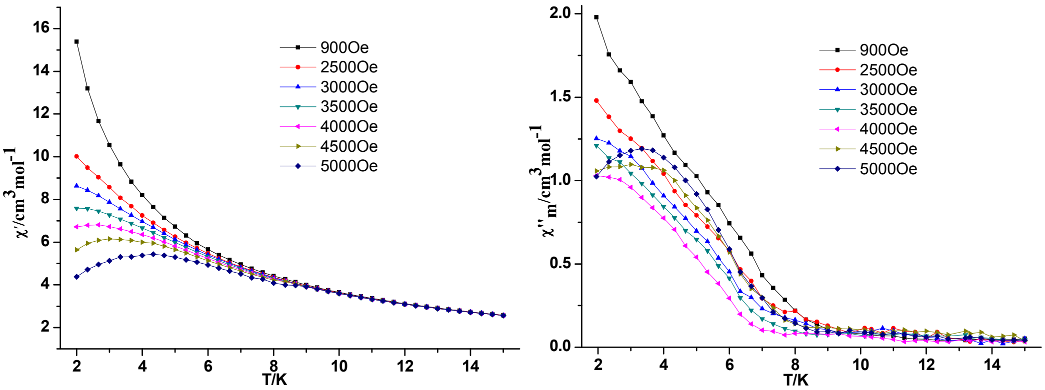


Figure S11. Temperature-dependent of in-phase (χ′) (Left) and the out-of-phase (χ″) (Right) ac susceptibility components for **2** measured at 500 Hz with different dc fields and an oscillation of 3 Oe.

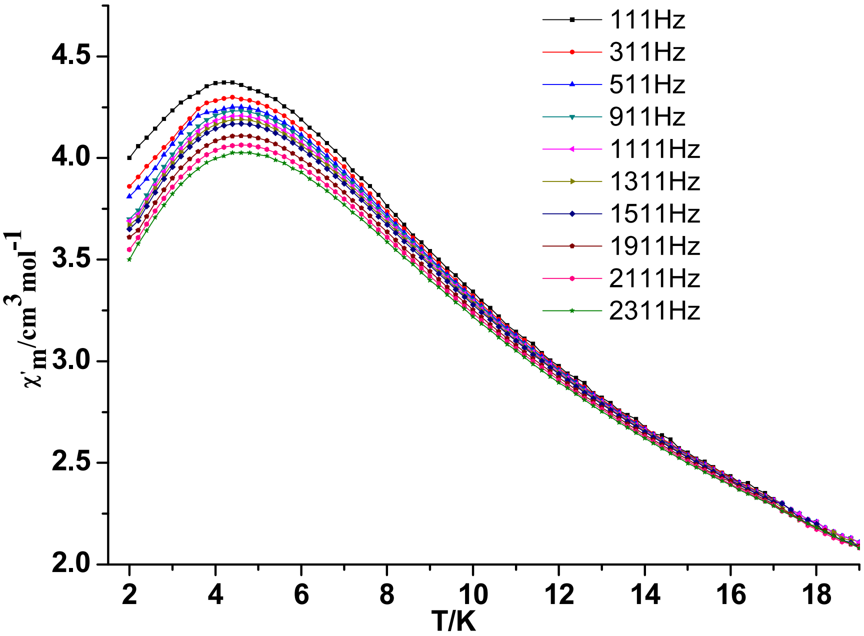
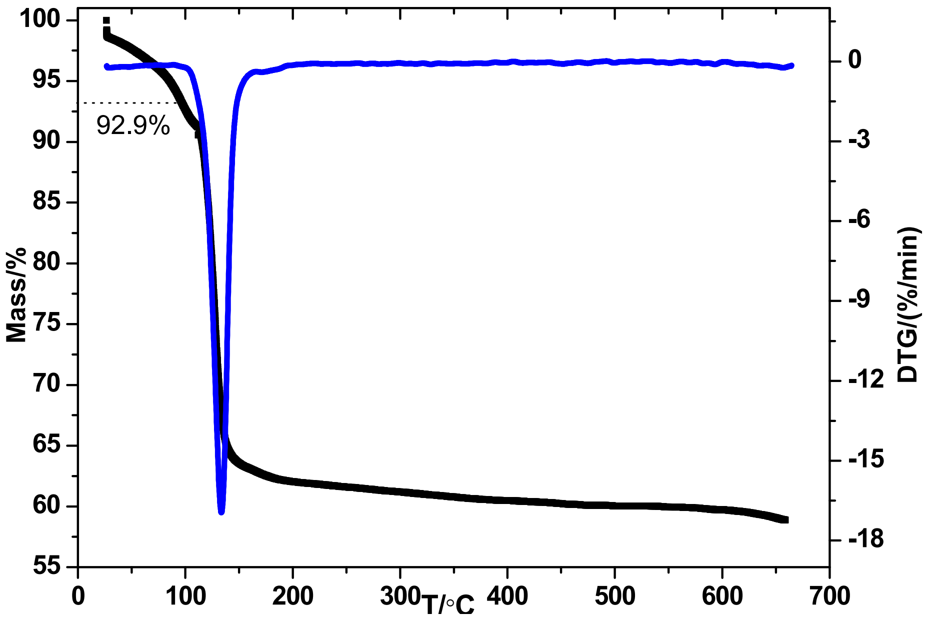


Figure S12. Temperature-dependent of the in-phase (χ') ac susceptibility components at different frequencies for **2** under 5000 dc field.

Table S2. -ΔS_m of reported Cu-Gd clusters.

Compound	-ΔS_m(J kg^{-1} K^{-1})	Δ*H*(T)	Reference
Cu_5Gd_4	31	9	4
Cu_6Gd_6	23.5	7	5
$Cu_{24}Gd_6$	21.2	7	This work
$Cu_{36}Gd_{24}$	21	7	6
Cu_8Gd_4	14.6	7	7



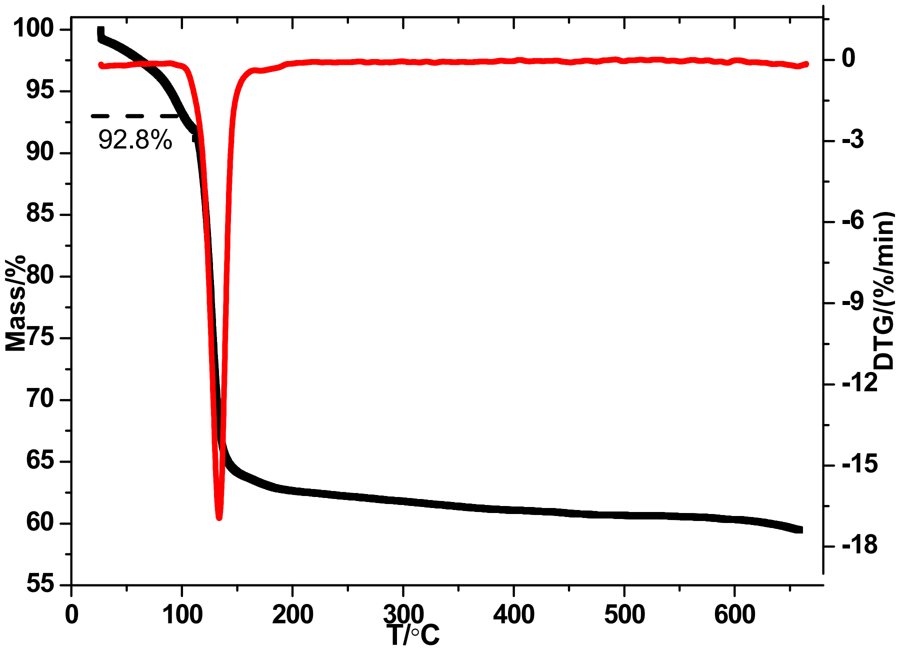


Figure S13. TG Curves for **1** (Top) and **2** (Down).

The thermogravimetric analyses of **1** and **2** were performed under N_2 atmosphere by the heating rate of 10 °C /min, as shown in Figure. S13. The TG curves of **1** and **2** were similar because of they are isomorphic. From room temperature to about 97 °C, the weight loss of **1** and **2** is 7.1% and 7.2%, respectviely, close to the theoretical value of removal 22 lattice H_2O (**1**, 6.5 % and **2**, 6.4%). Further heating, the coordination water molecules lose. When the temperature reached to about 130 °C, both of clusters decomposed.

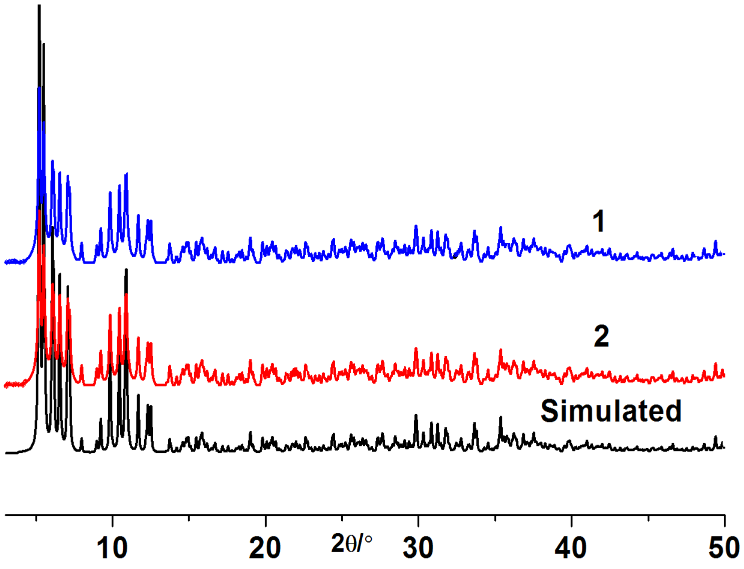


Figure S14. PXRD patterns of **1**, **2** and simulated.

References

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