Electronic Supplementary Information

A series of [2×2] square grid Ln^{III}_4 clusters: large magnetocaloric effect and single-molecule-magnet behavior

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Experimental Section

Synthesis of $Ln(acac)_3 \cdot 2H_2O$

A solution of $Ln(NO_3)_3 \cdot 6H_2O$ (Ln^{III} = Gd, Tb, Dy and Ho, 10 mmol) in distilled water (10 mL) was stirred for 20 min at room temperature, to which then 30 mmol acetylacetone was added and adjust the pH to 7 by using ammonia-water solution. The mixture was stirred for another 4 h. A precipitate formed was collected through filtration and washed with distilled water, vacuum drying for 24 h, obtaining the $Ln(acac)_3 \cdot 2H_2O$ crude product.

Synthesis of H_3L

Methyl 6-(Hydroxymethyl) Picolinate

65 mmol $NaBH_4$ was added in small portions over a period of 1 h to a stirred suspension of dimethylpyridine-2,6-dicarboxylate (40 mmol) in 200 mL MeOH at 0 °C. This mixture was stirred at room temperature for another 3 h and then MeOH was removed in a rotary evaporator. A saturated $NaHCO_3$ aqueous solution (200 mL) was added to the residue and the resulting aqueous solution was extracted with $CHCl_3$ (5×100 mL). The combined organic layers were dried by anhydrous Na_2SO_4, filtered, and concentrated in vacuo to dryness. The resulting crude residue was purified by column chromatography (n-hexane/EtOAc; 1:1, then 1:2) giving the desired product as a white solid. Anal. Calcd (%) for $C_8H_9NO_3$: C, 57.5; H, 5.4; N, 8.4. Found: C, 57.9; H, 5.2; N, 8.5.

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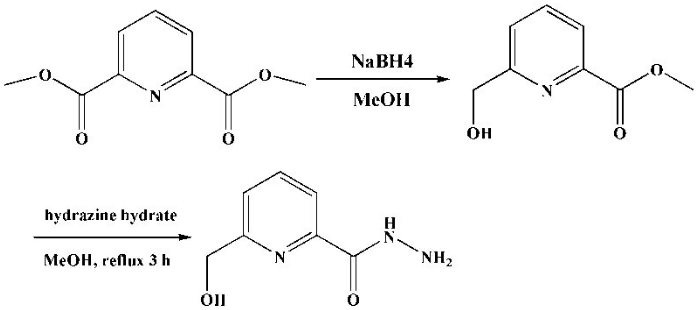
6-(Hydroxymethyl) Picolinohydrazide

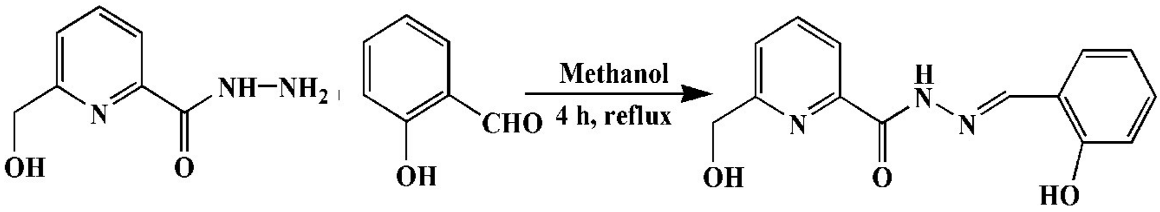
A methanolic solution of methyl 6-(hydroxymethyl) picolinate (10 mmol) was added dropwise to a stirred solution of hydrazine hydrate (50 mmol) in 30 mL methanol at room temperature. After the addition was over, the reaction mixture was heated under reflux for 3 h and subsequently allowed to come to room temperature before being kept in a refrigerator at 5 °C. A needle-shaped crystalline product was isolated which was suction-filtered, washed with a small amount of cold methanol, and air-dried. Anal. Calcd (%) for $C_7H_9N_3O_2$: C, 50.29; H, 5.43; N, 25.14. Found: C, 50.02; H, 5.16; N 24.86.



Scheme. S1. Detailed outline of the synthesis of 6-(Hydroxymethyl) Picolinohydrazide.

N′-(2-hydroxybenzylidene)-6-(hydroxymethyl)picolinohydrazide (H_3L).

A 10 mL methanolic solution of salicylic aldehyde (5 mmol) was added dropwise to a stirred suspension of 6-(hydroxymethyl) picolinohydrazide (5 mmol) in methanol (5 mL) at room temperature. The reaction mixture was heated under reflux overnight, then cooled to room temperature and kept for 8 h without stirring. A precipitate formed was collected through filtration and washed with MeOH. Yield: 1.06 g (78.3%). Anal. Calcd (%) for $C_{14}H_{13}N_3O_3$: C, 61.99; H, 4.80; N, 15.50. Found: C, 61.82; H, 4.93; N, 15.68.



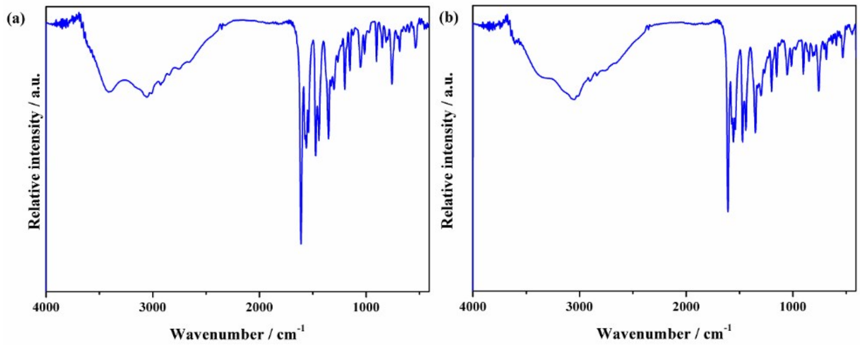
Scheme. S2. Detailed outline of the synthesis of the ligand (H_3L).

Table S1 The Dy^{III} geometry analysis by SHAPE 2.0 for cluster **3**.

	D_{4d}SAPR	**D_{2d}TDD**	**C_{2v}JBTPR**	**C_{2v}BTPR**	**D_{2d}JSD**
$Dy1^{III}$	5.193	5.128	4.448	4.516	4.851
$Dy2^{III}$	4.914	4.973	4.332	4.360	4.743

Table S2 Relaxation fitting parameters from Least-Squares Fitting of $\chi(\omega)$ data for **3** under 0 dc filed.

T (K)	χ_1 ($cm^3\ mol^{-1}$)	χ_2 ($cm^3\ mol^{-1}$)	α
2.0	0.38305	4.60936	0.355
3.0	0.31575	4.59341	0.324
4.0	0.30279	3.93743	0.263
5.0	0.26449	3.63018	0.265
6.0	0.26195	3.1146	0.215
7.0	0.22448	2.5685	0.216
8.0	0.25829	2.75276	0.184
9.0	0.23362	2.31709	0.199
10.0	0.31854	1.96088	0.177
11.0	0.26665	2.1331	0.186
12.0	0.40678	1.71136	0.1731
13.0	0.50885	1.60046	0.134
14.0	0.51376	1.53432	0.083



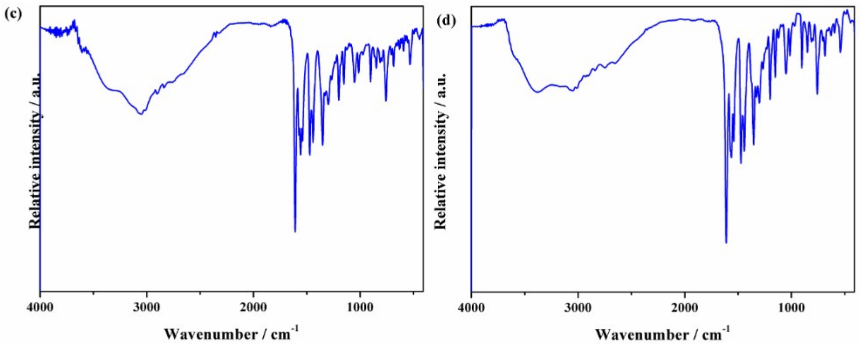


Fig. S1 The IR spectra of clusters **1**(a), **2**(b), **3**(c) and **4**(d).

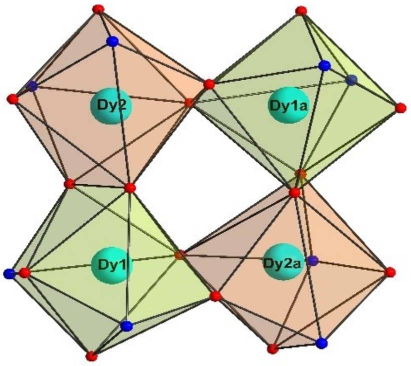


Fig. S2 Coordination polyhedra observed in cluster **3** showing distorted triangular dodecahedron geometry for Dy1 and Dy2. (Symmetry codes: A, -x+1, y, -z+1/2).

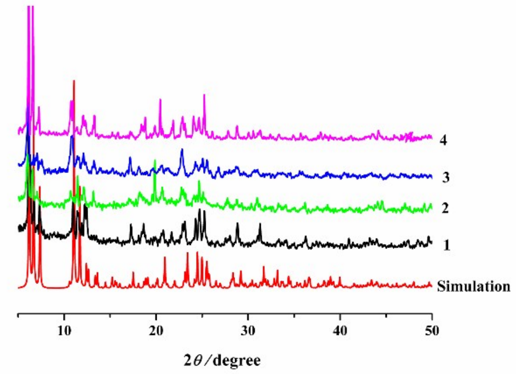


Fig. S3 The PXRD patterns for **1**-**4** and the corresponding simulated ones.

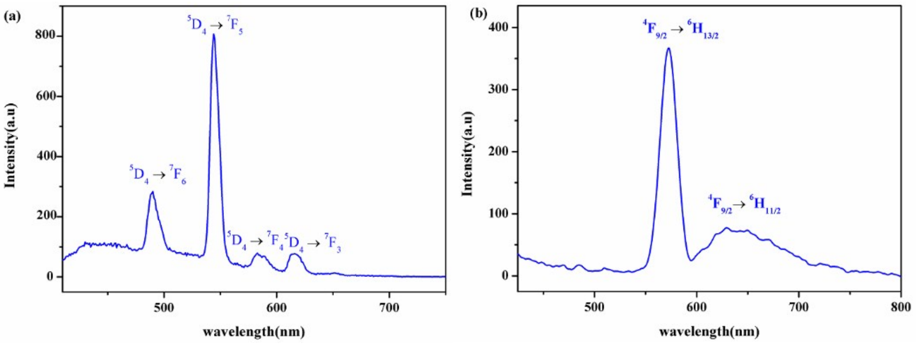


Fig. S4 The solid-state luminescence spectra of **2** (a) and **3** (b) at room temperature.

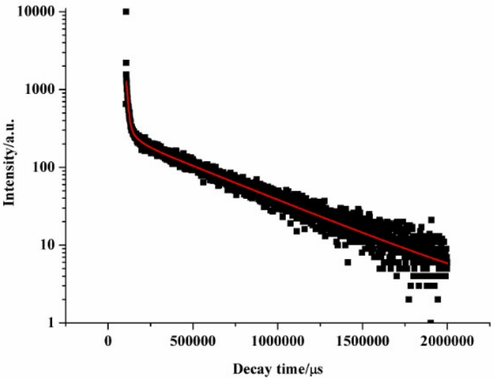


Fig. S5 Luminescence decay curve of cluster **2**.

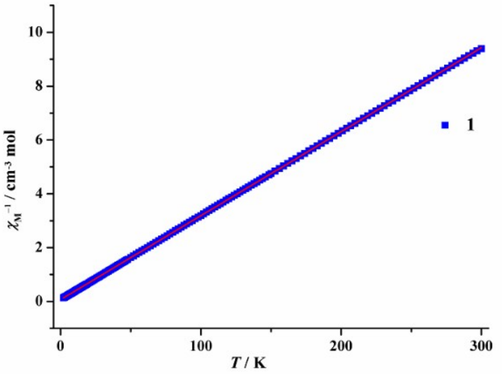


Fig. S6 Temperature dependence of the magnetic susceptibility in the form of χ_M^{-1} vs *T* for **1** at an applied field of 1000 Oe between 2.0 and 300 K. The red solid line was generated from the best fit by the Curie-Weiss expression.

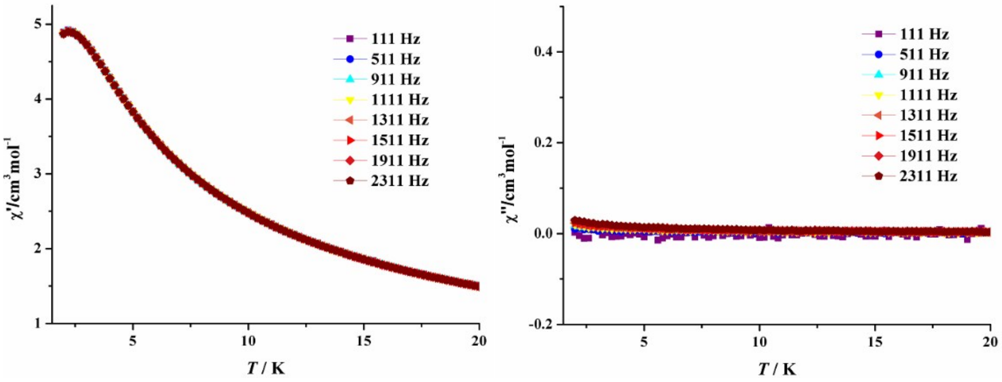


Fig. S7 Temperature dependence of in-phase (χ′) and out-of-phase (χ″) components of the *ac* magnetic susceptibility under zero *dc* field for **2**.

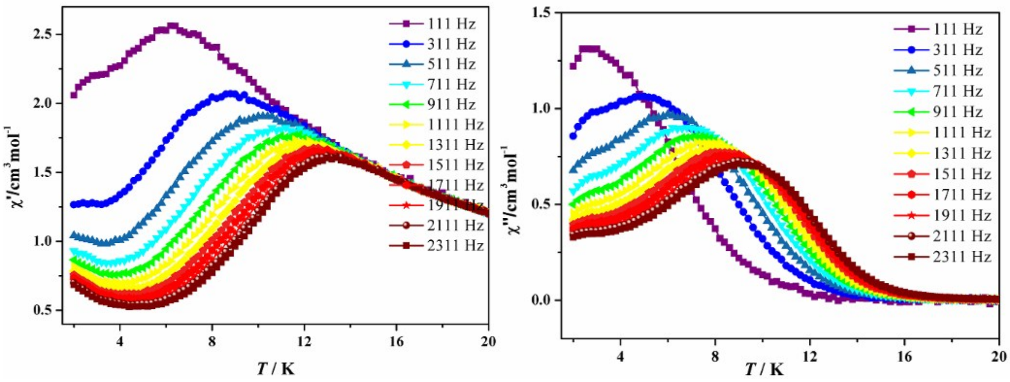


Fig. S8 Temperature dependence of in-phase (χ') and out-of-phase (χ'') components of the *ac* magnetic susceptibility under zero *dc* field for **3**.

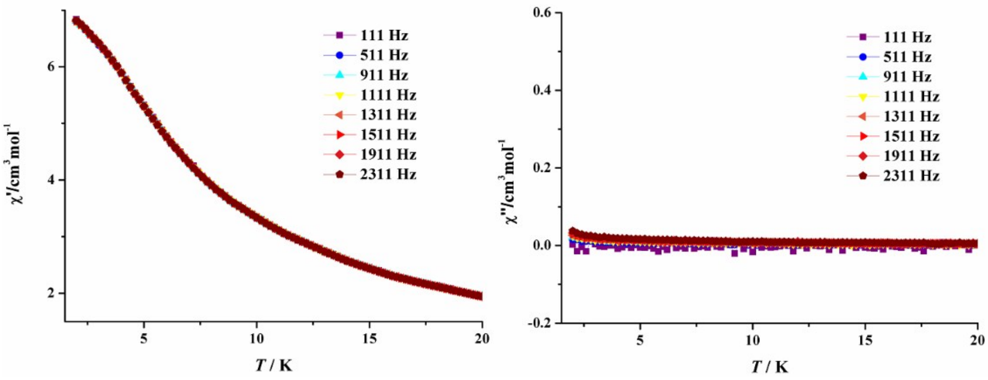


Fig. S9 Temperature dependence of in-phase (χ') and out-of-phase (χ'') components of the *ac* magnetic susceptibility under zero *dc* field for **4**.

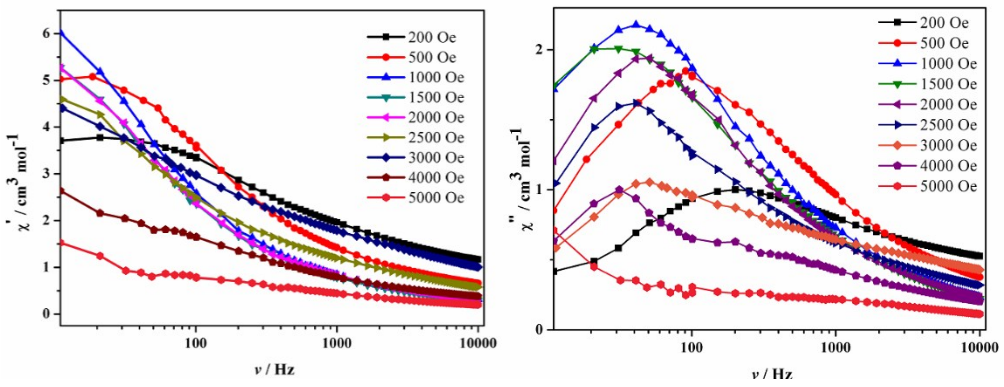


Fig. S10 Frequency dependency of the ac susceptibility was measured on cluster **3** under the applied field from 200 to 5000 Oe at 2.0 K.

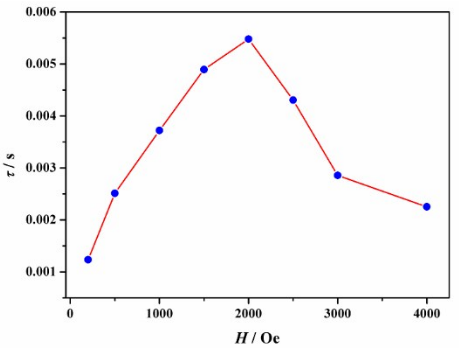


Fig. S11 The τ versus H plots for cluster **3** under different applied dc field.

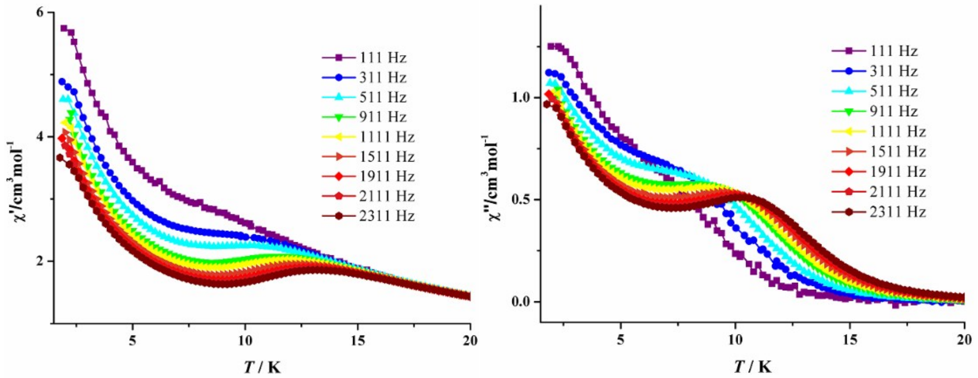


Fig. S12 Temperature dependence of in-phase (χ') and out-of-phase (χ'') components of the *ac* magnetic susceptibility under 2000 *dc* field for **3**.

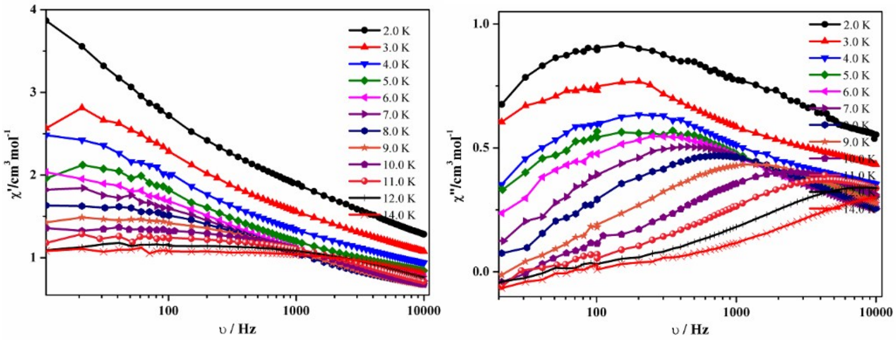


Fig. S13 Frequency dependence of in-phase (χ') and out-of-phase (χ'') components of the *ac* magnetic susceptibility under 2000 *dc* field for **3**.

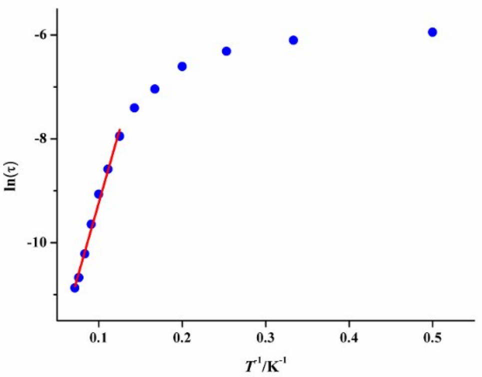


Fig. S14 ln ($1/\tau$) vs $1/T$ plots for **3** under 2000 *dc* field (the red line represents the best fit of the Arrhenius relationship).

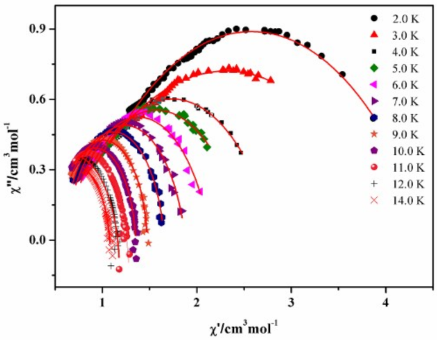


Fig. S15 Cole–Cole plots between 2.0 and 14.0 K for **3** under 2000 *dc* field. The red solid lines indicate the best fits to the experiments with the generalized Debye model.