Electronic Supplementary Information for

Unique (3,12)-connected coordination polymers displaying high stability, large magnetocaloric effect and slow magnetic relaxation

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Experimental Section:

Materials. All reactants were purchased without further purification except that the $Ln(ClO_4)_3·6H_2O$ (Ln = Gd and Dy) was prepared by $HClO_4$ and corresponding rare-earth oxide.

Measurement techniques. Powder X-ray diffraction measurements were carried out on a D/Max-2500 X-ray diffractometer using Cu Kα radiation. The Fourier transform infrared (FT-IR) spectra were performed with a Bruker Tensor 27 spectrophotometer on KBr disks. Thermogravimetric analyses (TGA) were measured on a Netzsch TG 209 TG-DTA analyzer from room temperature to 800 °C under nitrogen atmosphere with heating rate of 10 °C min^{-1}. Inductively coupled plasma (ICP) tests were measured on ICP-9000(N+M). Magnetic properties were studied on a Quantum Design MPMS-XL7 and PPMS-9 ACMS magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

Systhesis. Putting a mixture of isonicotinic acid (0.06 mmol, 0.0074 g), $Ln(ClO_4)_3·6H_2O$ (Ln = Gd (**1**), 0.1 mmol, 0.0564 g and Ln = Dy (**2**), 0.1 mmol, 0.0569 g), $LiOH·H_2O$ (0.08 mmol, 0.0033 g), 8 mL H_2O and 2 mL C_2H_5OH into a Teflon-lined stainless steel container, heated to 160 °C into 3 h and kept for 3 days, then cooled to room temperature by programmed cooling. Colorless rhomb crystals were obtained and the yields are 35% (calculated based on $Gd(ClO_4)_3·6H_2O$) and 41% (calculated based on $Dy(ClO_4)_3·6H_2O$) for **1** and **2**, respectively. Although isonicotinic acid ligand dose not appear in the compounds, it plays a vital role in the formation of the 3D coordination polymers. Since we have tried our best to construct the frameworks without isonicotinic acid, and we failed. IR (KBr disk, υ cm^{-1}): For **1**, 3128(br), 1122(m), 1086(m), 1040(w), 982(w), 858(w), 677(w), 617(w), 545(m). For **2**, 3123(br), 1132(m), 1089(m), 1042(w), 984(w), 857(w), 684(m), 614(w), 542(m). The IR spectra of **1** and **2** are very similar, and only **1** is analyzed as representation. The broad peak around 3123 cm^{-1} belongs to the O-H bonding of the aqua ligands. Characteristic peaks of ClO_4^- are in the range of 1122-858 cm^{-1}.[1] The 677-545 cm^{-1} region is attributed to Gd-O vibration.

Crystallographic Study

Appropriate single crystals of coordination polymers **1** and **2** were mounted on an Oxford iffractometer SuperNova TM at 122(2) K with a graphite-monochromatic Mo-Kα 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 and refined by full-matrix least-squares techniques based on F^2 using the SHELXS-97 and SHELXL-97 programs.[3] All the non-hydrogen atoms were refined with anisotropic parameters while hydrogen atoms were placed in calculated positions and refined using a riding model. In consideration of the charge balance and the reaction materials, there should be free OH^- in the lattice, but the free OH^- were not completely determined, which is frequently observed in reported coordination polymers. In compound **1**, the disordered O16 was split into two sites: O16A and O16B, and the hydrogen atoms of O16 were not placed.

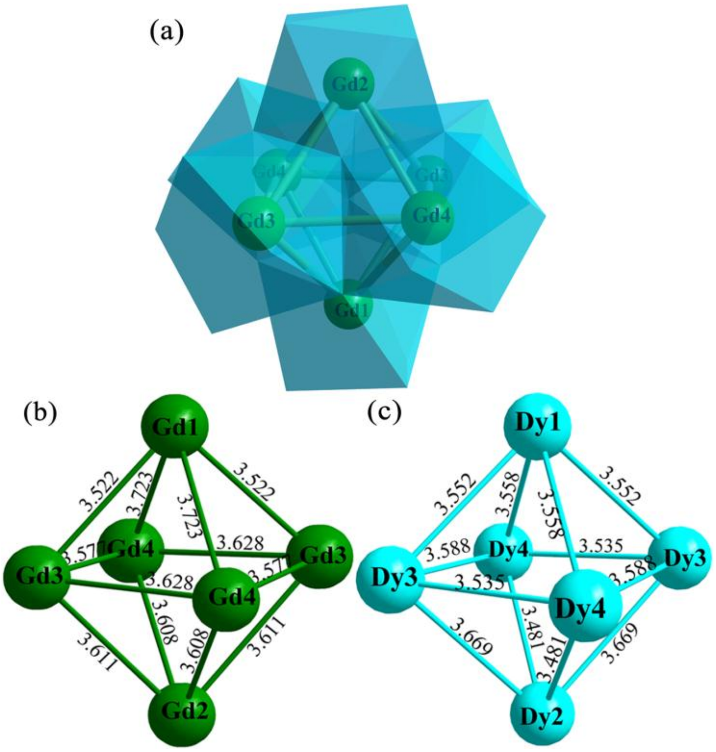


Fig. S1 (a) The distorted octahedron of [Gd_6] and the mono-capped square antiprism geometry of Gd^{3+}, (b) Distances between Gd···Gd (Å), and (c) Distances between Dy···Dy (Å).

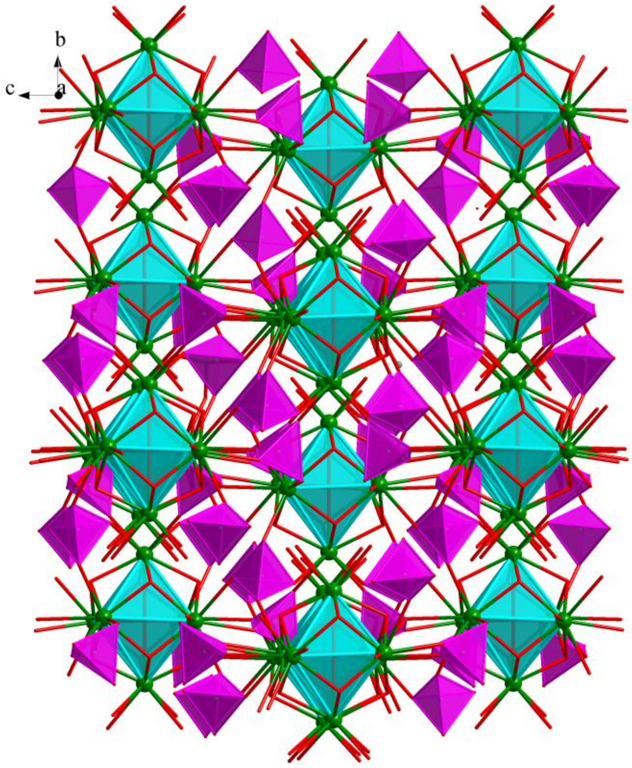


Fig. S2 The 3D framework of **1** viewed along the *a* direction. Purple and blue polyhedrons stand for ClO_4^- and [Gd_6] clusters, respectively.

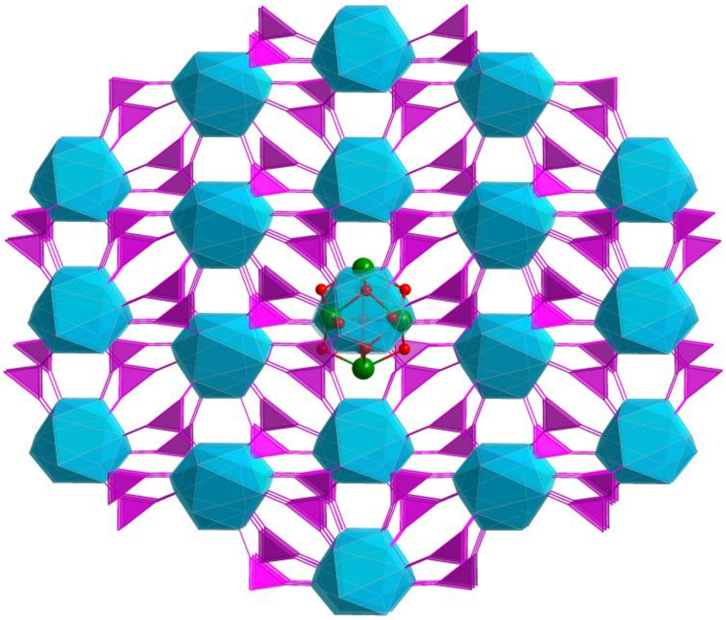


Fig. S3 The binodal (3,12)-connected topological structures of **1**, viewed along the *a* direction. Purple triangles and blue polyhedrons represent 3-connected ClO_4^- and 12-connected [Gd_6] clusters, respectively.

Thermal and solvent stabilities

To investigate their thermal stability, the Thermo-gravimetric analyses (TGA) of compounds **1** and **2** were implemented. As shown in Fig. S4, there are almost no weight loss from room temperature to about 160 ℃, corresponding to no free guest molecules are in the compounds. Then from 160 ℃ to about 300 ℃, the weight loss correspond to the six coordinated water molecules (for **1**, calcd 6.48%, found 5.65%; for **2**, calcd 6.36%, found 5.71%.). Above 400 ℃, the mass lost quickly, indicating the frameworks start to collapse. Supposed that the final residues of the thermal decomposition of the two compounds are pure Ln_2O_3 (Ln = Gd (**1**) and Dy (**2**)), then the percentages of the final decomposed compounds are 65.14 and 65.78% for **1** and **2**, respectively. While the final residues of the thermal decomposition of the two compounds are pure $LnCl_3$ (Ln = Gd (**1**) and Dy (**2**)), then the percentages of the final decomposed compounds are 94.74 and 94.84% for **1** and **2**, respectively. The percentages of the final products of the experiments are 89.83 and 89.46% for **1** and **2**, respectively, which are between the pure Ln_2O_3 and pure $LnCl_3$, so the final products are the mixture of Ln_2O_3 and $LnCl_3$ (Ln = Gd (**1**) and Dy (**2**)).

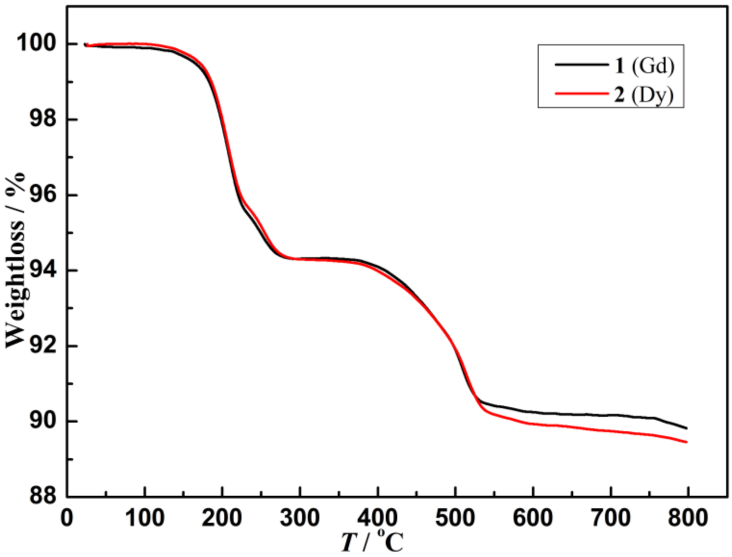


Fig. S4 TGA plots of coordination polymers **1** and **2**.

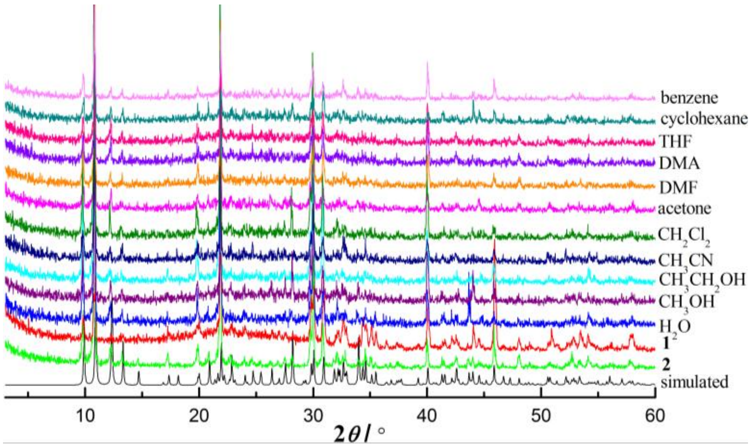


Fig. S5 The simulated and experimental PXRD patterns of compounds **1**, **2**, and **1** in different solvents.

Magnetic properties

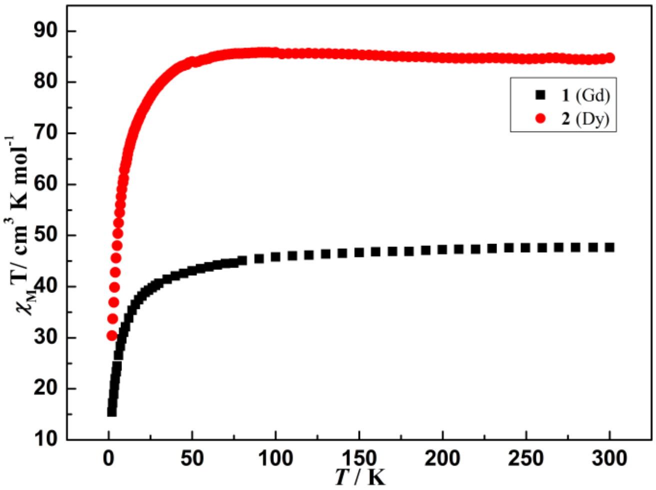


Fig. S6 Temperature dependence magnetic susceptibilities of compounds **1** and **2**.

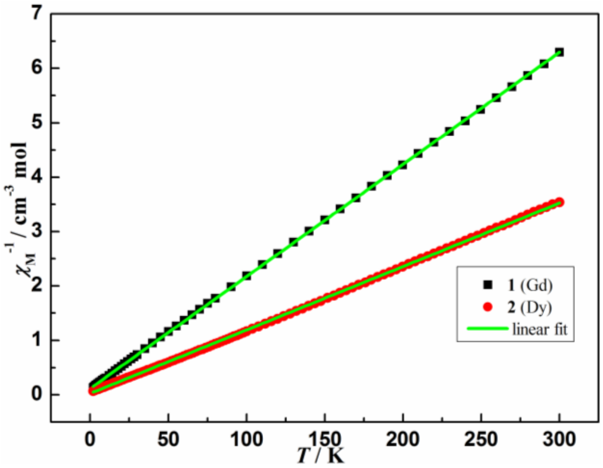


Fig. S7 The χ_M^{-1} versus *T* and the Curie-Weiss linear fit for **1** and **2**.

The data over the temperature range of 2-300 K of **1** fit well the Curie-Weiss law: $\chi_M = C/(T\text{-}\theta)$ (Fig. S7), with Curie constant C = 48.52 $cm^3 \cdot K \cdot mol^{-1}$ and Weiss constant θ = -5.50 K for **1**. The negative θ value for **1** supports the presence of antiferromagnetic coupling between Gd^{3+}.

For compound **2** (Dy), the data over the temperature range of 2-300 K fit well the Curie-Weiss law: $\chi_M = C/(T\text{-}\theta)$ (Fig. S7), with Curie constant C = 85.69 $cm^3 \cdot K \cdot mol^{-1}$ and Weiss constant θ = -2.10 K. However, small negative θ value will not imply the antiferromagnetic coupling between Dy^{3+} due to the large orbital angular momentum and strong spin-orbit coupling for Dy^{3+}, and this case is similar with those of the Co^{2+}-based compounds. Theoretically, the thermally depopulation of the Stark sublevels of Dy^{3+} with decreasing temperature will directly cause $\chi_M T$ to decline, and the experimental $\chi_M T$ value keep unchanged from 300 to 50 K. Therefore, we may clear deduce the ferromagnetic interaction must operate between adjacent Dy^{3+}, which can compensate the descent of $\chi_M T$ caused by the thermal depopulation of Stark sublevels.

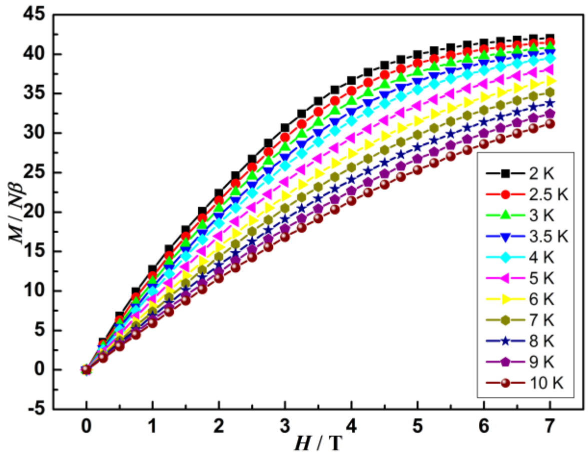
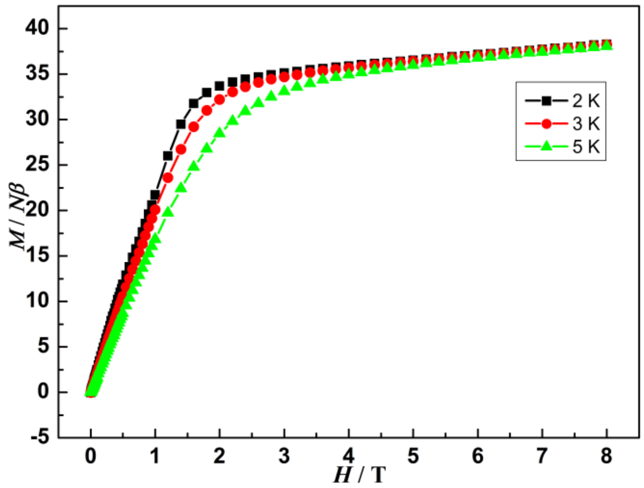


Fig. S8 Field dependence magnetization plots at indicated temperatures for **1**.



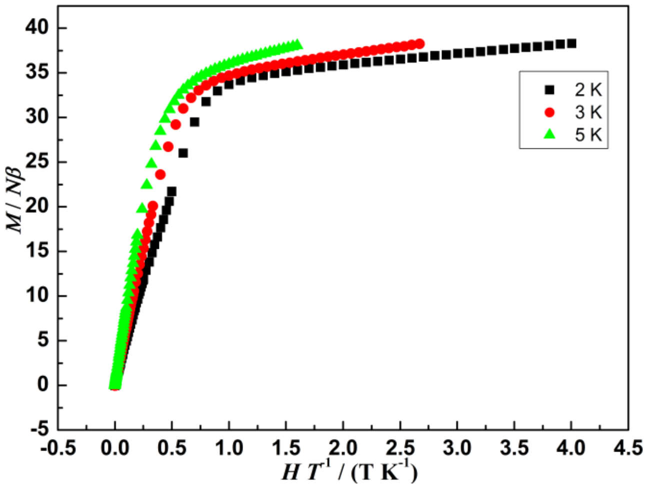


Fig. S9 Field dependence of the magnetization at different temperatures of **2** (Top: *M*-*H*, Bottom: *M*-*H*/*T*).

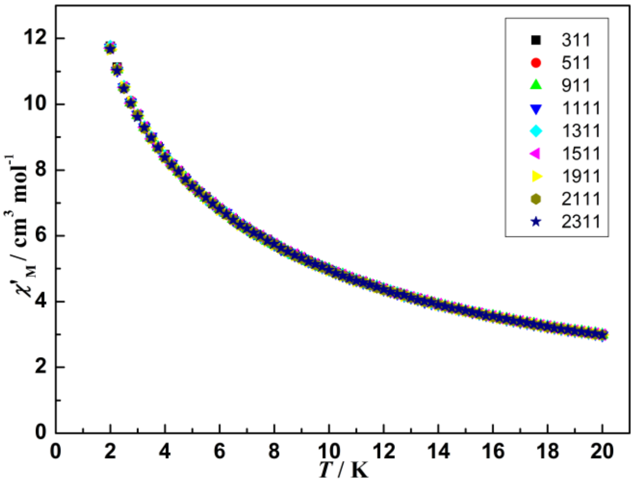


Fig. S10 Temperature dependence of the in-phase (χ') ac susceptibility components for **2** at the indicated frequencies and in zero dc field.

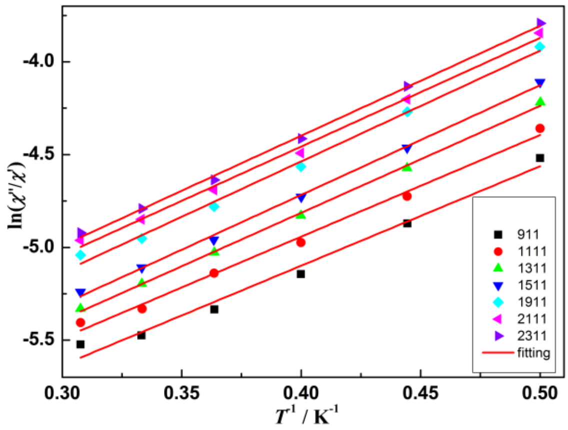


Fig. S11 Plots of natural logarithm of χ''/χ' versus T^{-1} for **2**, the solid lines represent the fitting in the range of 2.0-3.25 K.

Table S1. Crystallographic data for compounds **1** and **2**.

Compound	**1** (Gd)	**2** (Dy)
Empirical formula	$Cl_4Gd_6H_{24}O_{35}$	$Cl_4Dy_6H_{24}O_{35}$
Formula weight	1669.49	1700.99
Temperature	122(2) K	122(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, *C*2/*c*	Monoclinic, *C*2/*c*
Unit cell dimensions	a =12.3981(6) Å, α = 90.00° b = 13.3478(9) Å, β = 100.777(6)° c =14.7429(14) Å, γ = 90.00(4)°	a = 12.2429(6) Å ,α = 90.00°. b = 13.2583(5) Å, β= 100.697(5)° c = 14.6293(7) Å, γ = 90.00(4)°
Volume	2396.7(3) A^3	2333.38(19) A^3
Z, Calculated density	4, 4.438 Mg/m^3	4, 4.637 Mg/m^3
Absorption coefficient	16.967 mm^{-1}	19.565 mm^{-1}
F(000)	3024	3072
Crystal size	0.23 × 0.21 × 0.20 mm	0.22 × 0.20 × 0.19 mm
Theta range for data collection	2.83 to 25.01°	2.52 to 25.01°
Limiting indices	$-10 \leq h \leq 14$, $-15 \leq k \leq 14$, $-17 \leq l \leq 12$	$-14 \leq h \leq 13$, $-14 \leq k \leq 15$, $-17 \leq l \leq 11$
Reflections collected / unique	4355 / 2041[R(int) = 0.0280]	3864 / 2045 [R(int) = 0.0470]
Completeness to theta = 25.01	96.3%	99.0%
Data / restraints / parameters	2041 / 5 / 207	2045 / 8 / 199
Goodness-of-fit on F^2	1.065	1.062
Final R indices [I>2sigma(I)]	$R_1{}^a = 0.0367$, $wR_2{}^b = 0.0967$	R1 = 0.0418, wR2 = 0.0944
R indices (all data)	$R_1 = 0.0390$, $wR_2 = 0.1000$	R1 = 0.0630, wR2 = 0.1173

$^aR_1 = \Sigma \| F_o| - |F_c \| /\Sigma|F_o|$ and $^bwR_2 = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table S2. $-\Delta S_m$ of **1** compared with those of the reported compounds.

Compounds	Dimensionality	$-\Delta S_m$/J kg^{-1} K^{-1} (ΔH = 7 T)
$\{[Mn(H_2O)_6][MnGd(oda)_3]_2\cdot 6H_2O\}_n$[4]	3D	50.1
$[Gd_2(OAc)_3(H_2O)_{0.5}]_n$[5]	1D	47.7
Compound **1** in this work	3D	46.6
$[Gd_{24}(DMC)_{36}(\mu_4\text{-}CO_3)_{18}(\mu_3\text{-}H_2O)_2]\cdot 6H_2O$[6]	0D	46.1
$[Gd(HCOO)(OAc)_2(H_2O)_2]_n$[7]	2D	45.9
$[Gd_2(OAc)_3(MeOH)]_n$[5]	1D	45.0

$[Gd_2(OAc)_6(H_2O)_4]\cdot 4H_2O$[8]	0D	41.6
$[Co_{10}Gd_{42}]$[9]	1D	41.26
$[Ni_{10}Gd_{42}]$[9]	1D	38.2
$[Gd_4(OAc)_2(acac)_8(H_2O)_4]$[5]	0D	37.7
$[Ni_{12}Gd_{36}]$[10]	0D	36.3
$[Mo_4Gd_{12}]$[11]	0D	35.3
$[Mn_4Gd_6]$[12]	0D	33.7
$[ZnGd_5]$[13]	3D	30.7
$[Gd_2(N\text{-}BDC)_3(DMF)_4]$[14]	3D	29.0
$[Co_6Gd_8]$[15]	0D	28.6
$[Mn_9Gd_9]$[12]	0D	28.0
$[Fe_5Gd_8]$[16]	0D	26.7
$[Ni_6Gd_6P_6]$[17]	0D	26.5
$[Gd_2(OAc)_2(Ph_2acac)_4(MeOH)_2]$[5]	0D	23.7
$[Co_4Gd_6]$[15]	0D	23.6
$[Cu_6Gd_6]$[18]	0D	23.5
$[Gd_7]$[19]	0D	23.0
$[Co_8Gd_4]$[20]	0D	22.3
$[Ni_8Gd_4]$[21]	0D	22.0
$[Co_8Gd_8]$[15]	0D	21.4
$[Co_8Gd_4]$[15]	0D	21.1
$[Cu_{36}Gd_{24}]$[22]	0D	21.0
$[Zn_8Gd_4]$[21]	0D	20.8
$[Co_8Gd_8]$[20]	0D	20.4
$[Co_4Gd_2]$[15]	0D	20.0
$[Co_4Gd_6]$[20]	0D	19.9
$[Mn^{III}_4Gd_4]$[23]	0D	19.0
$[Zn_8Gd_4]$[21]	0D	18.0
$[Cu_8Gd_4]$[21]	0D	14.6
$[Co_8Gd_2]$[15]	0D	11.8
$[W_{10}Gd]$[24]	0D	4.7

$[W_{30}Gd]$[24]	0D	1.9
$[Mn^{III}_6Mn^{II}_8]$[25]	0D	25
$[Fe_{14}]$[26]	0D	20.3
$[Fe_{14}]$[27]	0D	17.6
$[Mn^{III}_6Mn^{II}_4]$[25]	0D	17.0
$[Dy_{24}]$[6]	0D	13.8
$[Mn^{III}_6Mn^{II}_4]$[25]	0D	13.0
$[Co_3Dy]$[28]	0D	12.58
$[Co_3Er]$[28]	0D	11.53
$[ZnDy_5]$[13]	3D	10.82
$[Co_3Tm]$[28]	0D	10.30
$[Co_3Yb]$[28]	0D	9.94
$[Co_3Ho]$[28]	0D	8.90
$[Mn^{III}_{12}Mn^{II}_7]$[29a]	0D	8.9
$[Fe_{17}]$[29b]	0D	8.9
$[Co_3Y]$[28]	0D	6.04
[prussian blue analogues][30]	3D	5.9~6.9
$[Cr_7Cd]$[31]	0D	5.1

Table S3. The summary of the (3,12)-connected compounds and corresponding Schläfli symbols.

Compounds	Schläfli symbol	Ref.
Compound **1** in this work	$(4^{20}\cdot6^{26}\cdot8^{20})(4^3)_4$	
$[Zn_8(\mu_3\text{-}OH)_4(oba)_6(bbi)(H_2O)_2]$	$(3^2\cdot4)_2(3^8\cdot4^{22}\cdot5^{16}\cdot6^{18}\cdot7^2)$	32
$[Na_{0.5}Zn_{4.75}(\mu_3\text{-}OH)_2(BTB)_2(HBTB)(H_2O)_{0.5}]\cdot5DMF\cdot1.5EtOH\cdot10H_2O$	$(4^3)_{12}(4^{12}\cdot6^{36}\cdot8^{18})_2(4^{12}\cdot6^{24}\cdot8^{30})$	33
$[Co_5(\mu_3\text{-}OH)_2(5\text{-}NH_2\text{-}bdc)_4(H_2O)_2]\cdot7.5H_2O$	$(4^{19}\cdot6^{27}\cdot8^{20})(4^3)_4$	34
$[Co_8(\mu_3\text{-}OH)_4(SO_4)_2(dcpbpy)_4(H_2O)_4]\cdot12DMF\cdot4EtOH\cdot24H_2O$	$(4^{12}\cdot6^{34}\cdot8^{20})(4^3)_4$	35
$[Ln_4(OH)_4(3\text{-}SBA)_4(H_2O)_4]\cdot nH_2O$ (Ln = Eu, Gd, Tb)	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	36
$[Ln(TTP)_2]\cdot(CF_3SO_3)_3\cdot C_3H_6O\cdot5H_2O$ (Ln = Eu, Gd)	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	37
$[Eu_6(\mu_6\text{-}O)(\mu_3\text{-}OH)_8(H_2O)_6(SO_4)_4]_n$	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	38
$Ln_4(OH)_4(SO_4)_4(H_2O)_3$ (Ln = Y, Er)	$(4^{20}\cdot6^{28}\cdot8^{18})(4^3)_4$	39

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