

RESEARCH ARTICLE

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Cite this: *Inorg. Chem. Front.*, 2023, **10**, 4109**C₂O₄^{2−}-templated cage-shaped Ln₂₈ (Ln = Gd, Eu) nanoclusters with magnetocaloric effect and luminescence†**Qin Wang,^a Sheng-Hui Lu,^a Ling-Xi Xu,^b Ji-Lei Wang,^{id} ^a Ya-Ting Yu,^a Xu Bai,^a Hua Mei^a and Yan Xu ^{id} ^{*a}

The assembly of high-nuclearity lanthanide nanoclusters with favourable magnetocaloric effects suffers from a significant challenge. Herein, two outstanding examples of cage-shaped nanoclusters, namely, [Ln₂₈(IN)₂₅(C₂O₄)₆(HCOO)(μ₃-OH)₃₆(μ₂-OH)₂(H₂O)₃₆]·8Br·xH₂O (Ln = Gd and Eu; x = 21, abbreviated as **Gd**₂₈; x = 17, abbreviated as **Eu**₂₈, HIN = isonicotinic acid; H₂C₂O₄ = oxalic acid) have been triumphantly designed and constructed under hydrothermal conditions. The crystallographic study revealed that the aesthetically pleasing triangle-shaped **Gd**₁₂ subunit and **Gd**₁₆ subunit built separately from four **Gd**₃ units and four **Gd**₄ units, respectively, are shaped into an unprecedented cage-shaped configuration. Prominently, six small and simple C₂O₄^{2−} anions generated *via* the *in situ* reaction of HIN are faultlessly anchored in the cage-shaped framework. Furthermore, the existence of abundant Gd^{III} ions impart **Gd**₂₈ with a captivating magnetic entropy change (−ΔS_m^{max} = 37.5 J kg^{−1} K^{−1}) at 2.0 K for ΔH = 7.0 T.

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Introduction

Owing to severe pollution of the environment and deficiencies from energy shortages, research on lanthanide nanoclusters with beneficial magnetocaloric effects (MCEs) has been heralded in materials chemistry and magnetochemistry.^{1–7} The MCE, which explains the phenomenon of heat absorption or heat release of a magnetic material in a changing magnetic field, was first discovered in 1881 by Warburg.^{8,9} In particular, magnetic cooling materials at ultra-low temperatures play an indispensable role in the development of quantum computers.^{7,10–12} As a unique class of energy-efficient and environmentally friendly refrigerants at ultra-low temperatures, lanthanide nanoclusters, especially high-nuclearity Gd^{III} oxide/hydroxide clusters, are prospective materials featuring decent MCEs.^{13–15} At the same time, aesthetically captivating configurations with various conformations and shapes have been designed, such as chair, boat, cage, disk, wheel, nanocapsule, *etc.*^{16–21}

However, due to practical obstacles in their sizeable ionic radius and high coordination numbers, as well as the mutual

repulsion between lanthanide ions, the assembly of high-nuclearity lanthanide nanoclusters is a great challenge, especially when the number of the lanthanide ions is greater than 20.^{15,22,23} It is well known that *in situ* reactions can benefit the formation of anionic templates through decomposition, rearrangement and other unpredictable side reactions of solvents or ligands.²⁴ Once an *in situ* reaction occurs, the decomposition of ligands can effectively realize the slow release of anions. The decomposition process is pretty slow, thus avoiding the formation of precipitation caused by the direct introduction of raw materials, which makes the sophisticated coordination mode possible.^{25,26} For example, the synthesis of classical cage-like **Ln**₆₀ is through the *in situ* reaction of 2,2'-bipyridine-4,4'-dicarboxylic acid, where the small and simple carbonate anion is resoundingly encapsulated in the nanocluster. The synthesis of stable and compact inorganic-organic hybrid **Gd**₄ with twisted cubic [Gd₄O₄] units is bridged by *in situ* generated oxalate and sulfate.^{27,28} So far, it has been observed that ligands containing carboxylic acid, an N-donor or sulfur tend to react *in situ*.^{29,30} Indeed, pyridinecarboxylate acids, such as isonicotinic acid, may be converted into some small ligands *via* an *in situ* reaction to form into exquisite frameworks with large MCEs. As a result, the first mixed-ligand (oxalate and isonicotinic acid) coordination polymer [Zn₂(IN)₂(oxa)] was afforded under hydrothermal conditions from the *in situ* reaction of HIN to oxalate. Subsequently, a 3D compound of [La₂(C₂O₄)₂] was reported under hydrothermal conditions from the *in situ* reaction of HIN.^{31,32} Although HIN can be chemically rearranged to oxalate under appropriate con-

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ditions, it has never been observed in high-nuclearity lanthanide nanoclusters.

Based on the high-nuclearity lanthanide nanoclusters of **Ln**₂₆ (Ln = Ho and Er) and **Ho**₄₈ by employing isonicotinic acid as the ligand, we elaborately designed and isolated two unprecedented cage-shaped nanoclusters under hydrothermal conditions with the formulas of [Gd₂₈(IN)₂₅(C₂O₄)₆(HCOO)(μ₃-OH)₃₆(μ₂-OH)₂(H₂O)₃₆]·8Br·21H₂O and [Eu₂₈(IN)₂₅(C₂O₄)₆(HCOO)(μ₃-OH)₃₆(μ₂-OH)₂(H₂O)₃₆]·8Br·17H₂O.^{20,33} Structural analysis showed that the aesthetically elegant cage-shaped **Gd**₂₈ can be divided into the charming triangle-shaped **Gd**₁₂ subunit and the triangle-shaped **Gd**₁₆ subunit that are constructed from four **Gd**₃ units and four **Gd**₄ units, respectively. Remarkably, the small and simple C₂O₄²⁻ anion generated *via* the *in situ* reaction of HIN is splendidly anchored in the cage-shaped framework, which is the first case in the family of high-nuclearity lanthanide nanoclusters. Besides, magnetocaloric analysis showed that **Gd**₂₈ exhibited a considerable value of $-\Delta S_{\text{m}}^{\text{max}} = 37.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at 2.0 K for $\Delta H = 7.0 \text{ T}$.

Experimental section

Materials and physical measurements

Chemical raw solvents and reagents from commercial sources were available for use without further purification. A PerkinElmer 2400 analyzer (USA) was used for the elemental analyses of C, H, and N. A Bruker D8 diffractometer (Germany) was used to collect powder X-ray diffraction (PXRD) data using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) in the 2θ range of 3–50° at a scanning rate of 3° min^{−1} at room temperature. IR spectra of the two compounds in KBr pellets were recorded using a Nicolet Impact 410 spectrometer (Thermo Fisher, USA) in the region of 4000–400 cm^{−1}. In order to conduct a thermogravimetric analysis (TGA), a Q50 Thermogravimetric Analyzer (TA Instruments, USA) was used in flowing nitrogen air to record thermogravimetric curves of the two compounds from ambient temperature to 1000 °C at a rate of 10 °C min^{−1}. The energy dispersive spectrometry (EDS) data were acquired with a Hitachi S-4800 (Japan) emission scanning electron microscope with a 20 kV accelerating voltage. Magnetization measurements were performed using an MPMS-XL7 SQUID magnetometer (Quantum Design, USA) at 1.8–300 K and in fields of 0–7 T. The solid-state luminescence properties of **Eu**₂₈ were measured using an FLS1000 spectrophotometer (Edinburgh Instruments, UK) at room temperature.

X-ray crystallography

Under an optical microscope, single crystals of **Gd**₂₈ with good crystal quality were selected and coated quickly with epoxy glue in air, and placed on a thin glass fiber for data collection; the crystal data of **Eu**₂₈ were not good enough to be reported in detail. Single crystal X-ray diffraction (SCXRD) data of **Gd**₂₈ were collected by employing a Bruker Apex II CCD (Germany) with a sealed-tube X-ray source in the ω – 2θ scanning method at room temperature. The SHELX software package was used to

resolve the crystal structures with direct methods and refine the crystal structures *via* full-matrix least-squares approaches. Besides, all the non-hydrogen atoms were refined by using anisotropic thermal parameters according to experience. The H atoms of water were not located. The SQUEEZE command was used to remove the H₂O molecules. Table 1 provides the relevant crystal data. Table S5† shows the selected bond lengths and angles.

Synthesis of **Gd**₂₈

The reactants of HIN (0.25 g, 2.00 mmol), Gd₂O₃ (0.20 g, 0.55 mmol), Al₂O₃ (0.04 g, 0.39 mmol) and KBr (0.01 g, 0.08 mmol) were placed in a 25 mL Teflon-lined autoclave, to which were added HCOOH (0.04 g, 0.87 mmol) and 8 mL of distilled water. Immediately after, the mixture was magnetically stirred at room temperature for 12 hours, and then the pH was adjusted from 4.8 to 2.0 with HNO₃ (50%) under stirring conditions. Subsequently, the mixture was maintained at 170 °C for 7 days. After cooling to about room temperature, light-yellow quadrilateral crystals were harvested (as shown in Fig. S1†), which were washed with distilled water (37.0% yield based on Gd). Anal. calcd (%) for C₁₆₃H₂₅₃Gd₂₈N₂₅O₁₇₁Br₈ (formula weight = 10 341): C, 18.93; H, 2.45; N, 3.39. Found: C, 18.90; H, 2.41; N, 3.40.

Synthesis of **Eu**₂₈

The synthesis method is the same as the method used for **Gd**₂₈ except for Gd₂O₃ being replaced with Eu₂O₃. The light-yellow quadrilateral crystals were obtained (as shown in Fig. S1†) (35% yield based on Eu). Anal. calcd (%) for

Table 1 Crystal data and structure refinements for **Gd**₂₈

Compound	Gd ₂₈
Formula	C ₁₆₃ H ₂₅₃ Gd ₂₈ N ₂₅ O ₁₇₁ Br ₈
Formula weight	10 341
<i>T</i> (K)	296(2)
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	21.465(5)
<i>b</i> (Å)	24.112(5)
<i>c</i> (Å)	30.492(6)
α (°)	87.190(3)
β (°)	79.559(3)
γ (°)	88.080(3)
<i>V</i> (Å ³)	15 496(6)
<i>Z</i>	2
<i>D</i> _c (mg m ^{−3})	2.216
μ (mm ^{−1})	7.027
<i>F</i> (000)	9692
θ range (°)	0.680–27.322
Limiting indices	$-26 \leq h \leq 27$, $-30 \leq k \leq 29$, $-38 \leq l \leq 36$
Reflections collected	123 261
<i>R</i> (int)	0.0611
Data/restraints/parameters	61 613/852/3297
GOF	1.013
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0496, <i>wR</i> ₂ = 0.1353
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	<i>R</i> ₁ = 0.1085, <i>wR</i> ₂ = 0.1586

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}.$$

$C_{163}H_{245}Eu_{28}N_{25}O_{167}Br_8$ (formula weight = 10 269): C, 19.07; H, 2.40; N, 3.41. Found: C, 19.09; H, 2.37; N, 3.40.

Results and discussion

Synthetic description

The nearly light-yellow quadrilateral crystals of Gd_{28} were synthesized using the hydrothermal reaction of Gd_2O_3 , Al_2O_3 , HIN and KBr in the presence of $HCOOH$ at 170 °C for seven days. Notably, the reagent isonicotinic acid with both an O-donor and an N-donor on opposite sides is exceptionally significant in the self-assembly of the Gd_{28} nanocluster. Furthermore, the target product could not be captured when we tried to add oxalic acid directly to the reaction. Due to the slow production of $C_2O_4^{2-}$ anions in the *in situ* reaction of isonicotinic acid, the environment can self-adjust to realize the balance between the Gd^{III} ions, $C_2O_4^{2-}$ anions and HIN ligands, resulting in the assembly of the Gd_{28} nanocluster in the method of slow crystallization.¹⁵ According to the literature, formic acid ($HCOOH$), as the smallest carboxylate ligand, has been favourably used to prepare lanthanide clusters with great MCEs. Gd_2O_3 is a reactant which not only can slowly release Gd^{III} ions but also regulates the pH of the reaction system. Although Al^{III} ions are not involved in the final construction, we cannot obtain the target product without them. We replaced Al_2O_3 with other metallic oxides, such as Fe_2O_3 or Cr_2O_3 , but we did not get the target crystal. At the same time, we tried using Eu_2O_3 , Tb_2O_3 or Dy_2O_3 instead of Gd_2O_3 ; only from the environment of Eu_2O_3 were light-yellow quadrilateral crystals of Eu_{28} isolated, but unfortunately, the crystal data were not good enough to be reported in detail. On the other hand, the synthetic process of high-nuclearity Ln-exclusive nanoclusters is problematic and heavily relies on certain reaction factors, such as reaction conditions (duration, temperature, pH, cooling rate) and reactants (solvents, ligands, and the kinds of anions). For Gd_{28} , a temperature of 170 °C plays a remarkable role in the formation of the framework; no crystals can be obtained at 160 °C or 140 °C. Most importantly, an absolutely acidic environment (pH = 2) is quite prominent in the self-assembly of the structure, where no crystals can be obtained at pH = 3, pH = 4 or pH = 5. The high temperature and acidic conditions make it possible for the slow release or production of $C_2O_4^{2-}$ ions from HIN.

Crystal structure

Counterions were confirmed *via* EDS analyses and charge balance studies, while the guest molecules were determined by elemental analysis, and TG and IR measurements. Data from SCXRD analysis revealed that Gd_{28} crystallized in a triclinic crystal system, with $P\bar{1}$ space group. As shown in Fig. 1a, the isolated nanocluster with formula $[Gd_{28}(IN)_{25}(C_2O_4)_6(HCOO)(\mu_3-OH)_{36}(\mu_2-OH)_2(H_2O)_{36}]$ can be viewed as being constructed from a 28-metal nanocage of $[Gd_{28}(C_2O_4)_6(\mu_3-OH)_{36}(\mu_2-OH)_2]^{34+}$ protected and stabilized by 25 IN^- groups, one $HCOO^-$ group and about 36 guest water molecules. Broadly, six small and



Fig. 1 (a) Plot of the whole molecular structure and (b) the $C_2O_4^{2-}$ anion template in the metal skeleton of Gd_{28} . Purple, Ln; blue, N; red, O; and black, C.

simple $C_2O_4^{2-}$ anions generated *via* the *in situ* reaction of HIN are splendidly anchored in the cage-shaped metal-organic framework to balance the high positive charges and stabilize its construction (Fig. 1b).

For the sake of facilitating the description and understanding of the structural skeleton, the cage-like cationic core of Gd_{28} can be subdivided into two different types of primary units, *i.e.*, a triangular Gd_3 unit formulated as $[Gd_3(\mu_3-OH)_2]^{7+}$ and a cubane-like Gd_4 unit formulated as $[Gd_4(\mu_3-OH)_4]^{8+}$. A Gd_3 -type unit, as shown in Fig. 2a, can be considered a triangular construction connected by two μ_3-OH groups and four Gd_3 units are linked by six $C_2O_4^{2-}$ anions and formed into a $[Gd_{12}(\mu_3-OH)_8(C_2O_4)_6]^{16+}$ (Gd_{12}) subunit. For clarity, each of the Gd_3 units, with a shell-shaped construction, is combined with six $C_2O_4^{2-}$ anions, and formed into a delicate triangle-like structure (Fig. 2d). A Gd_4 -type unit is a cubane-like configuration formed by the banding of four μ_3-OH groups, which is extremely common in other lanthanide clusters (Fig. 2c). Four Gd_4 units are combined with the same six $C_2O_4^{2-}$ anions forming a $[Gd_{16}(\mu_3-OH)_{16}(C_2O_4)_6]^{20+}$ (Gd_{16}) subunit. For clarity, each tetrahedron is connected by six $C_2O_4^{2-}$ anions forming a fancy triangle-shaped framework (Fig. 2e). As shown in Fig. 2f,

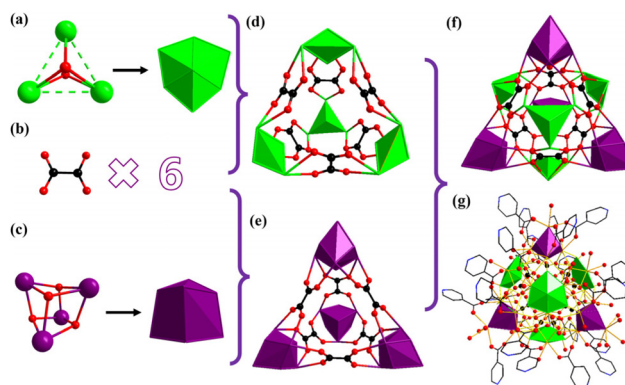


Fig. 2 Ball-and-stick views of (a) the triangular $[Gd_3(\mu_3-OH)_2]^{7+}$ unit; (b) the $C_2O_4^{2-}$ anion; (c) the cubane-like $[Gd_4(\mu_3-OH)_4]^{8+}$ unit; (d) the $[Gd_{12}(\mu_3-OH)_8(C_2O_4)_6]^{16+}$ subunit; (e) the $[Gd_{16}(\mu_3-OH)_{16}(C_2O_4)_6]^{20+}$ subunit; (f) the $[Gd_{28}(C_2O_4)_6(\mu_3-OH)_{36}(\mu_2-OH)_2]^{34+}$ nanocluster; and (g) the subunits representing Gd_{28} .

the frog-shaped Gd_{12} subunit and the frog-shaped Gd_{16} subunit are bonded together into an individual cage-shaped framework templated by six $\text{C}_2\text{O}_4^{2-}$ anions. The cage-like nanocluster is further stabilized by the 25 IN^- groups and one HCOO^- group. Additionally, the IN^- ligands in Gd_{28} display three different types of coordination modes, $\mu_2\text{-}\eta^1\text{:}\eta^0\text{:}\eta^1$, $\mu_1\text{-}\eta^0\text{:}\eta^1$ and $\mu_1\text{-}\eta^1\text{:}\eta^0\text{:}\eta^1$ (Fig. 3a), and the six $\text{C}_2\text{O}_4^{2-}$ anions exhibit only one coordination mode, $\mu_6\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{:}\eta^2$ (Fig. 3b).

The metal framework of Gd_{28} is shown in Fig. 1b; four tetrahedra (16 Gd^{III}) and four triangles (12 Gd^{III}) were joined together to complete the nano-caged framework. All Gd^{III} ions are located in eight-coordinated or nine-coordinated environments with different geometries (Fig. S5†). Gd_3 , Gd_5 , Gd_6 , Gd_8 , Gd_{11} , Gd_{12} , Gd_{14} , Gd_{16} , Gd_{25} , Gd_{26} , Gd_{27} and Gd_{28} represent eight coordination modes in the $[\text{GdO}_8]$ polyhedra; Gd_1 , Gd_2 , Gd_4 , Gd_7 , Gd_9 , Gd_{10} , Gd_{13} , Gd_{15} , Gd_{17} , Gd_{18} , Gd_{19} , Gd_{20} , Gd_{21} , Gd_{22} , Gd_{23} and Gd_{24} display nine coordination modes in the $[\text{GdO}_9]$ polyhedra. As shown in Fig. S5,† 28 Gd^{III} ions have different coordination environments. For example, Gd_1 is coordinated with one HIN, one $\text{C}_2\text{O}_4^{2-}$ anion, four $\mu_3\text{-OH}$ groups and two coordinated water molecules. According to the continuous shape measurement (CShM) analysis, the 28 Gd^{III} ions have seven different configurations. For instance, Gd_{28} exhibits a twisted octa-coordinated square antiprism, while Gd_{10} shows a distorted nine-coordinated spherical capped square antiprism (Tables S1 and 2†). The bond

lengths between two neighboring ions ($\text{Gd-O} = 2.3\text{--}2.9 \text{ \AA}$) and the bond angles between the neighboring ions ($\text{O-Gd-O} = 58.8\text{--}155.3^\circ$) are equivalent to the previously reported Gd-based nanocluster (Table S5†).

Remarkably, cage-shaped high-nuclearity Gd-based nano-scale clusters, where the number of lanthanide ions is more than 20, are still underdeveloped. To date, only cage-shaped Gd_{20} , Gd_{26} , Gd_{27} , Gd_{32} , Gd_{38} , Gd_{50} , Gd_{60} and Gd_{104} nanoclusters have been reported.^{18,34–37} The Gd_{28} nanocluster reported in this work is extraordinarily different from other reported cage-shaped nanoclusters. For example, the spherical Gd_{26} nanocluster consists of five cubane-like Gd_4 units and two triangular Gd_3 units templated by nine CO_3^{2-} anions. Nicotinic acid is the organic linker and the protective ligand in the formation of Gd_{26} .³⁵ Other cage-shaped Gd_{27} nanoclusters

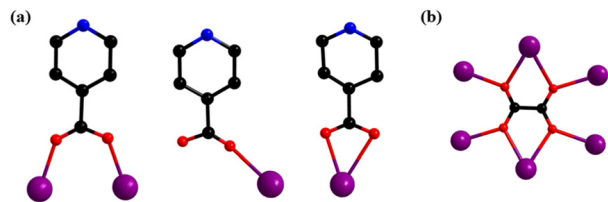


Fig. 3 Coordination modes of (a) IN^- ligands and (b) $\text{C}_2\text{O}_4^{2-}$ in Gd_{28} .

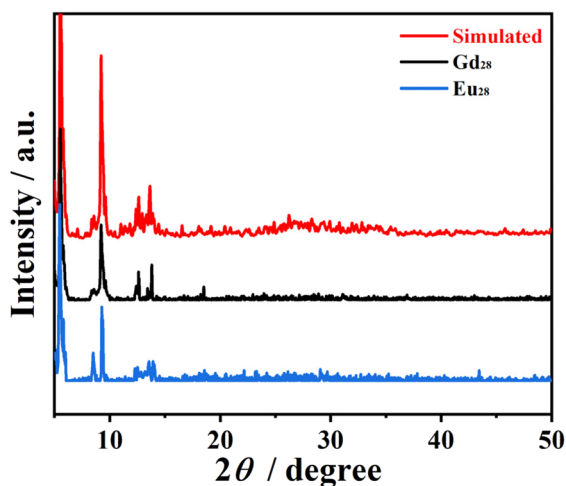


Fig. 4 PXRD patterns of Gd_{28} and Eu_{28} .

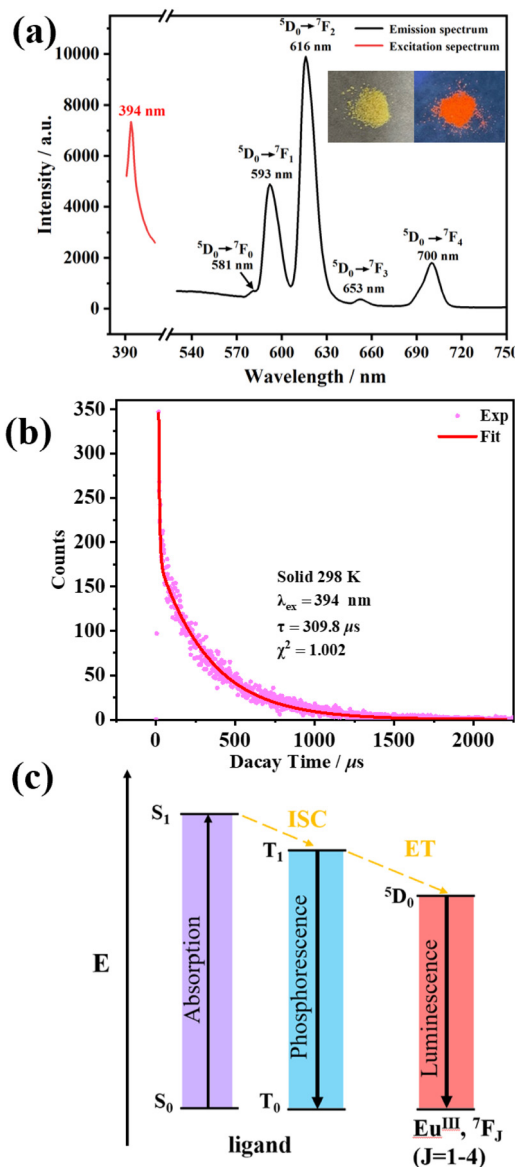


Fig. 5 (a) Excitation and emission spectra; (b) luminescence lifetime; and (c) Jablonsky level diagrams of Eu_{28} .

have been isolated by employing sodium propionate as the ligand. The metal skeleton of **Gd**₂₇ is achieved by five tetrahedral **Gd**₄ units and one crown-shaped **Gd**₇ unit templated by eight CO₃²⁻ anions.¹⁸ Explicitly, the **Gd**₂₈ nanocluster exhibits an unprecedented configuration in the family of high-nuclearity cage-shaped nanoclusters.

It is worth noting that the structure of the **Eu**₂₈ nanocluster is roughly the same as that of **Gd**₂₈, according to the main characteristic diffraction peaks of the PXRD (Fig. 4). Meanwhile, the free H₂O molecules of the two nanoclusters were determined by TG analysis, as shown in Fig. S9 and 10.† In the temperature range of 25–265 °C, the weight loss of 3.67% (calcd 3.66%) was attributed to the loss of 21 free water molecules for **Gd**₂₈, while the weight loss of 2.96% (calcd 2.98%) was attributed to the loss of 17 free water molecules for **Eu**₂₈.

Luminescence of **Eu**₂₈

One of the most meaningful characteristics of lanthanide ions is their picturesque photoluminescence properties derived from f-f intraconfigurational transitions.¹³ Additionally, Eu^{III} is most commonly used in sensing applications due to its strong visible light emission in the red region.³⁸ Accordingly, the luminescence properties of **Eu**₂₈ with 28 Eu^{III} ions were measured at room temperature, as shown in Fig. 5. Under UV lamp irradiation, we observed the solid-state luminescence of **Eu**₂₈. Besides, under maximum excitation at 394 nm, the elec-

tronic transitions of Eu^{III} from ⁵D₀ → ⁷F_J (*J* = 0, 1, 2, 3 and 4) were observed. The relatively weak emission bands at 581, 653 and 700 nm are attributed to the electronic transitions of ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄, respectively. In comparison, the two sharp lines at 593 and 616 nm are assigned to the dominant electronic transitions of ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂, respectively. Notably, the absence of a strong and broad peak from the IN⁻ ligand indicates the high energy transfer efficiency to the Eu^{III} center emission, known as the “antenna effect”.³⁹ Furthermore, under the maximum excitation at 394 nm, the luminescence lifetime and the solid-state photoluminescence quantum yield (PLQY) of **Eu**₂₈ were 309.8 μs and 4.18%, respectively (Fig. 5b). To further learn about the solid-state luminescence of **Eu**₂₈, we drew a simple Jablonsky level diagram to explain the luminescence properties (Fig. 5c).^{40–43} These findings are of significant value for understanding the optical properties of the lanthanide clusters and their applications in optoelectronic devices, among others.⁴⁴

Magnetic properties of **Gd**₂₈

At an applied direct current (dc) magnetic field of 1.0 kOe from 1.8 K to 300 K, temperature-dependent magnetic susceptibilities of **Gd**₂₈ were characterized. The observed $\chi_M T$ value (225.0 cm³ K mol⁻¹) at 300 K is slightly larger than the expected value (220.5 cm³ K mol⁻¹) based on 28 independent Gd^{III} ions (*S* = 7/2, *g* = 2) with the Lande formula.⁶ As shown in Fig. 6a, as the temperature drops from 300 K to 1.8 K, the $\chi_M T$



Fig. 6 (a) Plot of experimental magnetic susceptibility ($\chi_M T$) versus T ; (b) χ_M^{-1} versus T plot; (c) plot of $M-H$ under different temperatures; and (d) plot of experimental magnetic entropy change ($-\Delta S_m$) versus T for **Gd**₂₈.

value gradually decreases to a minimum of $94.4 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K.⁴⁵ The overall trend of $\chi_M T$ vs. T data indicated that **Gd**₂₈ exhibited antiferromagnetic interaction between these metal cations. At the same time, fitting the χ_M^{-1} vs. T data with the Curie–Weiss law from 1.8 K to 300 K resulted in the Weiss constant $\theta = -5.7 \text{ K}$ and Curie constant $C = 226.5 \text{ cm}^3 \text{ K mol}^{-1}$. All the above discussions demonstrate the existence of weak antiferromagnetic interactions among metal ions (Fig. 6b).^{46–49}

A large number of **Gd**^{III} ions and fairly weak magnetic interactions between **Gd**^{III} ions make **Gd**₂₈ nanoclusters a valid class of materials for magnetic cooling applications. Hence, it encouraged us to conduct research of the magnetocaloric effect of **Gd**₂₈. Here, the magnetization (M) and magnetic field (H) at low temperature (1.8 K–10 K) was measured (Fig. 6c). With the increase of magnetic field (H), the magnetization (M) also increased steadily to the maximum of $180.3N\beta$ under 1.8 K and 7 T; the discrepancy between the two magnetization values (calculated value is $196.0N\beta$ based on 28 uncorrelated metal ions) resulted from the weak antiferromagnetic interaction in the nanocluster. Subsequently, we investigated the magnetocaloric effects of **Gd**₂₈ by employing the Maxwell equation of $\Delta S_m(T)_{\Delta H} = \int [\partial M(T, H) / \partial T]_H dH$ (Fig. 6d).⁵⁰ With an increased H and a reduced T , the experimental entropy changes gradually increased, and the $-\Delta S_m^{\max}$ is $37.5 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\Delta H = 7 \text{ T}$ at 2 K. By using the equation of $-\Delta S_m = nR \ln(2S + 1)$, the 28 uncorrelated **Gd**^{III} ions were calculated and resulted in a theoretical value of $46.8 \text{ J kg}^{-1} \text{ K}^{-1}$; the discrepancy between the two ΔS_m values might be due to the existence of antiferromagnetic exchanges among the metal centers.⁵¹ As far as we know, the **Gd**₂₈ nanocluster exhibits a decent magnetocaloric effect value, comparable to those of the reported high-nuclearity nanoscale clusters **Gd**₂₇ ($-\Delta S_m = 41.8 \text{ J kg}^{-1} \text{ K}^{-1}$), **Gd**₃₈ ($-\Delta S_m = 37.9 \text{ J kg}^{-1} \text{ K}^{-1}$) and **Gd**₃₆ ($-\Delta S_m = 39.7 \text{ J kg}^{-1} \text{ K}^{-1}$), validating its excellent potential application in magnetic cooling (Table S3†).^{18,36,52}

Conclusions

In summary, we triumphantly obtained two novel high-nuclearity lanthanide nanoclusters **Gd**₂₈ and **Eu**₂₈ in the presence of HIN under hydrothermal conditions. Subsequently, through structural characterization studies, we observed that the charming triangle-shaped **Gd**₁₂ subunit and **Gd**₁₆ subunit assembled by four **Gd**₃ units and four **Gd**₄ units, respectively, were arranged into an unprecedented cage-shaped structure featuring six $\text{C}_2\text{O}_4^{2-}$ anions. Notably, this is the first case of an *in situ* hydrolysis of isonicotinic acid to $\text{C}_2\text{O}_4^{2-}$ ions in constructing high-nuclearity lanthanide nanoclusters. Magnetization analysis revealed that **Gd**₂₈ exhibits a decent magnetocaloric effect of $37.5 \text{ J kg}^{-1} \text{ K}^{-1}$ at 2.0 K for $\Delta H = 7.0 \text{ T}$. This paper has given a new idea for introducing $\text{C}_2\text{O}_4^{2-}$ from the *in situ* reaction of HIN to assemble high-nuclearity lanthanide clusters with large magnetic entropy changes. Next, we will continue to isolate molecular magnetocaloric materials

based on **Gd** nanoclusters through the *in situ* hydrolysis of HIN and probe more excellent properties and potential applications for high-nuclearity lanthanide clusters.

Conflicts of interest

The authors declare no competing financial interest.

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References

- W. P. Chen, P. Q. Liao, Y. Yu, Z. Zheng, X. M. Chen and Y. Z. Zheng, A Mixed-Ligand Approach for a Gigantic and Hollow Heterometallic Cage $\{\text{Ni}_{64}\text{RE}_{96}\}$ for Gas Separation and Magnetic Cooling Applications, *Angew. Chem., Int. Ed.*, 2016, **55**, 9375–9379.
- N. F. Li, Q. F. Lin, Y. M. Han, Z. Y. Du and Y. Xu, The chain-shaped coordination polymers based on the bowl-like $\text{Ln}_{18}\text{Ni}_{24(23.5)}$ clusters exhibiting favorable low-field magnetocaloric effect, *Chin. Chem. Lett.*, 2021, **32**, 3803–3806.
- N. F. Li, Q. F. Lin, X. M. Luo, J. P. Cao and Y. Xu, Cl^- -Templated Assembly of Novel Peanut-like $\text{Ln}_{40}\text{Ni}_{44}$ Heterometallic Clusters Exhibiting a Large Magnetocaloric Effect, *Inorg. Chem.*, 2019, **58**, 10883–10889.
- E. Moreno Pineda, F. Tuna, R. G. Pritchard, A. C. Regan, R. E. Winpenny, E. J. McInnes and Y. Z. Zheng, Molecular amino-phosphonate cobalt-lanthanide clusters, *Chem. Commun.*, 2013, **49**, 3522–3524.
- J. B. Peng, Q. C. Zhang, X. J. Kong, Y. Z. Zheng, Y. P. Ren, L. S. Long, R. B. Huang, L. S. Zheng and Z. Zheng, High-nuclearity 3d-4f clusters as enhanced magnetic coolers and molecular magnets, *J. Am. Chem. Soc.*, 2012, **134**, 3314–3317.
- Z. X. Lu, Z. Zhuo, W. Wang, Y. G. Huang and M. C. Hong, $\{\text{Gd}_{44}\text{Ni}_{22}\}$: a gigantic 3d-4f wheel-like nanoscale cluster with a large magnetocaloric effect, *Inorg. Chem. Front.*, 2023, **10**, 979–983.
- J. L. Wang, M. X. Yang, N. F. Li, X. M. Liu, J. N. Li, Q. D. Ping and Y. Xu, Two Ni-Substituted Trilacunary Keggin-Type Polyoxometalates: Syntheses, Crystal Structures, NLO Studies, and Magnetic Properties, *Inorg. Chem.*, 2021, **60**, 13748–13755.
- E. Warburg, Magnetische Untersuchungen, *Ann. Phys.*, 1881, **249**, 141–164.
- N. F. Li, Q. Wang, J. N. Li, Y. T. Yu and Y. Xu, Two SiO_4^{4-} -Templated $\text{Ln}_{23}\text{Ni}_{20}$ Clusters with Magnetic Cooling and Stability, *Inorg. Chem.*, 2022, **61**, 7180–7187.
- Y. Zheng, Q. C. Zhang, L. S. Long, R. B. Huang, A. Muller, J. Schnack, L. S. Zheng and Z. Zheng, Molybdate templated assembly of $\text{Ln}_{12}\text{Mo}_4$ -type clusters ($\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$) con-

- taining a truncated tetrahedron core, *Chem. Commun.*, 2013, **49**, 36–38.
- 11 Y. Z. Zheng, E. M. Pineda, M. Helliwell and R. E. Winpenny, Mn^{II}-Gd^{III} phosphonate cages with a large magnetocaloric effect, *Chem. – Eur. J.*, 2012, **18**, 4161–4165.
 - 12 J. J. Hu, Y. Peng, S. J. Liu and H. R. Wen, Recent advances in lanthanide coordination polymers and clusters with magnetocaloric effect or single-molecule magnet behavior, *Dalton Trans.*, 2021, **50**, 15473–15487.
 - 13 Q. Wang, Y. T. Yu, J. L. Wang, J. N. Li, N. F. Li, X. Fan and Y. Xu, Two Windmill-Shaped Ln₁₈ Nanoclusters Exhibiting High Magnetocaloric Effect and Luminescence, *Inorg. Chem.*, 2023, **62**, 3162–3169.
 - 14 J.-L. Liu, Y.-C. Chen, F.-S. Guo and M.-L. Tong, Recent advances in the design of magnetic molecules for use as cryogenic magnetic coolants, *Coord. Chem. Rev.*, 2014, **281**, 26–49.
 - 15 X. Y. Zheng, X. J. Kong, Z. Zheng, L. S. Long and L. S. Zheng, High-Nuclearity Lanthanide-Containing Clusters as Potential Molecular Magnetic Coolers, *Acc. Chem. Res.*, 2018, **51**, 517–525.
 - 16 J. Hao, L. Geng, J. Zheng, J. Wei, L. Zhang, R. Feng, J. Zhao, Q. Li, J. Pang and X. H. Bu, Ligand Induced Double-Chair Conformation Ln₁₂ Nanoclusters Showing Multifunctional Magnetic and Proton Conductive Properties, *Inorg. Chem.*, 2022, **61**, 3690–3696.
 - 17 J. N. Li, N. F. Li, J. L. Wang, X. M. Liu, Q. D. Ping, T. T. Zang, H. Mei and Y. Xu, A new family of boat-shaped Ln₈ clusters exhibiting the magnetocaloric effect and slow magnetic relaxation, *Dalton Trans.*, 2021, **50**, 13925–13931.
 - 18 X. Y. Zheng, J. B. Peng, X. J. Kong, L. S. Long and L. S. Zheng, Mixed-anion templated cage-like lanthanide clusters: Gd₂₇ and Dy₂₇, *Inorg. Chem. Front.*, 2016, **3**, 320–325.
 - 19 J. M. Peng, H. L. Wang, Z. H. Zhu, J. Bai, F. P. Liang and H. H. Zou, Series of the Largest Dish-Shaped Dysprosium Nanoclusters Formed by In Situ Reactions, *Inorg. Chem.*, 2022, **61**, 6094–6100.
 - 20 L. Chen, J. Y. Guo, X. Xu, W. W. Ju, D. Zhang, D. R. Zhu and Y. Xu, A novel 2-D coordination polymer constructed from high-nuclearity waist drum-like pure Ho₄₈ clusters, *Chem. Commun.*, 2013, **49**, 9728–9730.
 - 21 L. X. Chang, G. Xiong, L. Wang, P. Cheng and B. Zhao, A 24-Gd nanocapsule with a large magnetocaloric effect, *Chem. Commun.*, 2013, **49**, 1055–1057.
 - 22 Z.-R. Luo, H. L. Wang, Z. H. Zhu, T. Liu, X. F. Ma, H. F. Wang, H. H. Zou and F. P. Liang, Assembly of Dy₆₀ and Dy₃₀ cage-shaped nanoclusters, *Commun. Chem.*, 2020, **3**, 30–36.
 - 23 W. Q. Lin, X. F. Liao, J. H. Jia, J. D. Leng, J. L. Liu, F. S. Guo and M. L. Tong, Lanthanide oxide clusters: from tetrahedral [Dy₄(μ₄-O)]¹⁰⁺ to supertetrahedral [Ln₂₀(μ₄-O)₁₁]³⁸⁺ (Ln = Tb, Dy, Ho, Er), *Chem. – Eur. J.*, 2013, **19**, 12254–12258.
 - 24 S. J. Liu, S. D. Han, J. P. Zhao, J. Xu and X. H. Bu, *In situ* synthesis of molecular magnetorefrigerant materials, *Coord. Chem. Rev.*, 2019, **394**, 39–52.
 - 25 J. Xu, W. Su and M. Hong, 3D lanthanide–transition-metal–organic frameworks constructed from tetranuclear {Ln₄} SBUs and Cu centres with fsc net, *CrystEngComm*, 2011, **13**, 3998–4004.
 - 26 X. Y. Zheng, S. Q. Wang, W. Tang, G. L. Zhuang, X. J. Kong, Y. P. Ren, L. S. Long and L. S. Zheng, Two nanosized 3d-4f clusters featuring four Ln₆ octahedra encapsulating a Zn₄ tetrahedron, *Chem. Commun.*, 2015, **51**, 10687–10690.
 - 27 X. M. Luo, Z. B. Hu, Q. F. Lin, W. Cheng, J. P. Cao, C. H. Cui, H. Mei, Y. Song and Y. Xu, Exploring the Performance Improvement of Magnetocaloric Effect Based Gd-Exclusive Cluster Gd₆₀, *J. Am. Chem. Soc.*, 2018, **140**, 11219–11222.
 - 28 S.-D. Han, X. H. Miao, S. J. Liu and X. H. Bu, Magnetocaloric effect and slow magnetic relaxation in two dense (3,12)-connected lanthanide complexes, *Inorg. Chem. Front.*, 2014, **1**, 549–552.
 - 29 P. F. Shi, Y. Z. Zheng, X. Q. Zhao, G. Xiong, B. Zhao, F. F. Wan and P. Cheng, 3 D MOFs containing trigonal bipyramidal Ln₅ clusters as nodes: large magnetocaloric effect and slow magnetic relaxation behavior, *Chem. – Eur. J.*, 2012, **18**, 15086–15091.
 - 30 S. Zhang, E. Duan and P. Cheng, An exceptionally stable 3D GdIII-organic framework for use as a magnetocaloric refrigerant, *J. Mater. Chem. A*, 2015, **3**, 7157–7162.
 - 31 L. Z. Zhang, W. Gu, B. Li, X. Liu and D. Z. Liao, {[Nd₄(ox)₄(NO₃)₂(OH)₂(H₂O)₂·5H₂O]_n}: A Porous 3D Lanthanide-Based Coordination Polymer with a Special Luminescent Property, *Inorg. Chem.*, 2007, **46**, 622–624.
 - 32 J. Y. Lu, J. Macias, J. Lu and J. E. Cmaidalka, An Unforeseen Chemical Rearrangement of Pyridine carboxylate to Oxalate under Hydrothermal Conditions Afforded the First Oxalato and Isonicotinato Mixed-Ligand Guest-Inclusion Coordination Polymer, *Cryst. Growth Des.*, 2002, **2**, 485–487.
 - 33 L. Chen, L. Huang, C. Wang, J. Fu, D. Zhang, D. Zhu and Y. Xu, Hydrothermal synthesis, structure, and properties of two new nanosized Ln₂₆ (Ln=Ho, Er) clusters, *J. Coord. Chem.*, 2012, **65**, 958–968.
 - 34 L. Qin, G. J. Zhou, Y. Z. Yu, H. Nojiri, C. Schroder, R. E. P. Winpenny and Y. Z. Zheng, Topological Self-Assembly of Highly Symmetric Lanthanide Clusters: A Magnetic Study of Exchange-Coupling “Fingerprints” in Giant Gadolinium(III) Cages, *J. Am. Chem. Soc.*, 2017, **139**, 16405–16411.
 - 35 R. Sen, D. K. Hazra, M. Mukherjee and S. Koner, Gd₂₆ Cluster Consisting of Distorted Cubane Cores: Synthesis, Structure and Heterogeneous Catalytic Epoxidation of Olefins, *Eur. J. Inorg. Chem.*, 2011, **2011**, 2826–2831.
 - 36 F. S. Guo, Y. C. Chen, L. L. Mao, W. Q. Lin, J. D. Leng, R. Tarasenko, M. Orendac, J. Prokleska, V. Sechovsky and M. L. Tong, Anion-templated assembly and magnetocaloric properties of a nanoscale {Gd₃₈} cage versus a {Gd₄₈} barrel, *Chem. – Eur. J.*, 2013, **19**, 14876–14885.
 - 37 J. B. Peng, X. J. Kong, Q. C. Zhang, M. Orendac, J. Prokleska, Y. P. Ren, L. S. Long, Z. Zheng and

- L. S. Zheng, Beauty, symmetry, and magnetocaloric effect-four-shell keplerates with 104 lanthanide atoms, *J. Am. Chem. Soc.*, 2014, **136**, 17938–17941.
- 38 T. Q. Lu, H. Xu, L. T. Cheng, X. T. Wang, C. Chen, L. Cao, G. L. Zhuang, J. Zheng and X. Y. Zheng, Family of Nanoclusters, Ln_{33} ($\text{Ln} = \text{Sm}/\text{Eu}$) and Gd_{32} , Exhibiting Magnetocaloric Effects and Fluorescence Sensing for MnO_4^- , *Inorg. Chem.*, 2022, **61**, 8861–8869.
- 39 Y. L. Li, H. L. Wang, Z. C. Chen, Z. H. Zhu, Y. C. Liu, R. Y. Yang, F. P. Liang and H. H. Zou, Lanthanoid hydrogen-bonded organic frameworks: Enhancement of luminescence by the coordination-promoted antenna effect and applications in heavy-metal ion sensing and sterilization, *Chem. Eng. J.*, 2023, **451**, 138880.
- 40 H. F. Wang, X. F. Ma, Z. H. Zhu, H. H. Zou and F. P. Liang, Regulation of the Metal Center and Coordinating Anion of Mononuclear $\text{Ln}(\text{III})$ Complexes to Promote an Efficient Luminescence Response to Various Organic Solvents, *Langmuir*, 2020, **36**, 1409–1417.
- 41 H. F. Wang, Z. H. Zhu, J. M. Peng, B. Yin, H. L. Wang, H. H. Zou and F. P. Liang, Multifunctional Binuclear $\text{Ln}(\text{III})$ Complexes Obtained via In Situ Tandem Reactions: Multiple Photoresponses to Volatile Organic Solvents and Anticounterfeiting and Magnetic Properties, *Inorg. Chem.*, 2020, **59**, 13774–13783.
- 42 J. Zhou, H. Li, H. Zhang, H. Li, W. Shi and P. Cheng, A Bimetallic Lanthanide Metal-Organic Material as a Self-Calibrating Color-Gradient Luminescent Sensor, *Adv. Mater.*, 2015, **27**, 7072–7077.
- 43 S. S. Sun, Z. Wang, X. W. Wu, J. H. Zhang, C. J. Li, S. Y. Yin, L. Chen, M. Pan and C. Y. Su, ESIPT-Modulated Emission of Lanthanide Complexes: Different Energy-Transfer Pathways and Multiple Responses, *Chem. – Eur. J.*, 2018, **24**, 10091–10098.
- 44 P.-Da Liu, Ao.-G. Liu, P.-M. Wang, Y. Chen and B. Li, Smart crystalline frameworks constructed with bisquinoxaline-based component for multi-stimulus luminescent sensing materials, *Chin. J. Struct. Chem.*, 2023, **42**, 100001.
- 45 W. P. Chen, P. Q. Liao, P. B. Jin, L. Zhang, B. K. Ling, S. C. Wang, Y. T. Chan, X. M. Chen and Y. Z. Zheng, The Gigantic $\{\text{Ni}_{36}\text{Gd}_{102}\}$ Hexagon: A Sulfate-Templated “Star-of-David” for Photocatalytic CO_2 Reduction and Magnetic Cooling, *J. Am. Chem. Soc.*, 2020, **142**, 4663–4670.
- 46 F. Shao, J. J. Zhuang, M. G. Chen, N. Wang, H. Y. Shi, J. P. Tong, G. Luo, J. Tao and L. S. Zheng, Facile and environmentally friendly synthesis of six heterometallic dumbbell-shaped MLn ($\text{M} = \text{Co}, \text{Ni}$; $\text{Ln} = \text{Eu}, \text{Gd}, \text{Dy}$) clusters as cryogenic magnetic coolants and molecular magnets, *Dalton Trans.*, 2018, **47**, 16850–16854.
- 47 M. H. Du, D. H. Wang, L. W. Wu, L. P. Jiang, J. P. Li, L. S. Long, L. S. Zheng and X. J. Kong, Hierarchical Assembly of Coordination Macromolecules with Atypical Geometries: $\text{Gd}_{44}\text{Co}_{28}$ Crown and $\text{Gd}_{95}\text{Co}_{60}$ Cage, *Angew. Chem., Int. Ed.*, 2022, **61**, e202200537.
- 48 N. F. Li, Y. M. Han, J. N. Li, Q. Chen and Y. Xu, Efficiently increasing low-field magnetic entropy by incorporating SO_3^{2-} into $\text{Gd}_{22}\text{Ni}_{21}$ clusters, *Dalton Trans.*, 2022, **51**, 2669–2673.
- 49 P. Hu, S. Li, L. Cao, A. Liu, G. L. Zhuang, L. Ji and B. Li, Construction of a High Nuclear Gadolinium Cluster with Enhanced Magnetocaloric Effect through Structural Transition, *ACS Omega*, 2022, **7**, 38782–38788.
- 50 N. F. Li, X. M. Luo, J. Wang, J. L. Wang, H. Mei, Y. Song and Y. Xu, Largest 3d-4f 196-nuclear $\text{Gd}_{158}\text{Co}_{38}$ clusters with excellent magnetic cooling, *Sci. China: Chem.*, 2022, **65**, 1577–1583.
- 51 R. Chen, C. L. Chen, M. H. Du, X. Wang, C. Wang, L. S. Long, X. J. Kong and L. S. Zheng, Soluble lanthanide-transition-metal clusters $\text{Ln}_{36}\text{Co}_{12}$ as effective molecular electrocatalysts for water oxidation, *Chem. Commun.*, 2021, **57**, 3611–3614.
- 52 M. Y. Wu, F. L. Jiang, X. J. Kong, D. Q. Yuan, L. S. Long, S. A. Al-Thabaiti and M. C. Hong, Two polymeric 36-metal pure lanthanide nanosize clusters, *Chem. Sci.*, 2013, **4**, 3104–3109.