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Highly stable and differentially arranged hexanuclear lanthanide clusters: structure, assembly mechanism, and magnetic resonance imaging†

Wen-Wen Qin,^a Yun-Lan Li,^a Zhong-Hong Zhu, *\overline{100}* *\overline{100}* Fu-Pei Liang,^a Qiong Hu* *\overline{100}* and Hua-Hong Zou *\overline{100}* *\overline{100}* and

The directed and controllable synthesis of lanthanide clusters with precise structures has received considerable research attention, however, progress in such remains sluggish. The steps performed in a reaction system under "black-box" conditions are unpredictable and have very low controllability. The precise customization of lanthanide clusters with the same number of cores but different arrangements is particularly difficult. Using bis-acylhydrazone-derived multidentate chelating ligands with different substituents, differentially arranged hexanuclear lanthanide clusters (Dy6 and HNP-Dy6) with identical core connections but different template-motif arrangements were constructed herein for the first time using a multidentate chelating coordination method. Specifically, $\mathbf{Dy_6}$ with face-to-face and dislocation-arrangement template motifs was obtained using -N(Et)₂-substituted bis-acylhydrazone ligands with a strong steric hindrance effect. Changing $-N(Et)_2$ to a benzene ring with a strong $\pi-\pi$ interaction yielded HNP-Dy₆ with inverted and coplanar arrangements of template motifs. The controllable construction of these two hexanuclear dysprosium clusters represented great progress in the precise synthesis of lanthanide clusters. High-resolution electrospray ionization-mass spectrometry (HRESI-MS) with different ionsource energies demonstrated the high stabilities of Dy₆ and HNP-Dy₆ in solutions. Time-dependent HRESI-MS tracked the formation processes of Dy₆ and HNP-Dy₆ and led to the following possible selfassembly mechanisms: $L^1 + 2Dy \rightarrow Dy_2L^1 \rightarrow Dy_3L^1 \rightarrow Dy_6(L^1)_2$ and $L^2 + 2Dy \rightarrow Dy_2L^2 \rightarrow Dy_3L^2 \rightarrow Dy_5(L^2)_2/Dy_6(L^1)_2$ $Dy_6(L^2)_2 \rightarrow Dy_6(L^2)_2$. At 1-T magnetic field, the longitudinal and transverse relaxation rates of **Gd₆** were 12.06 and 24.10 mM⁻¹ s⁻¹, respectively. **Gd₆** with highly aggregated Gd(III) exhibited high relaxation rates, indicating its great potential as a T_1 -weighted magnetic resonance imaging contrast agent. This work provides an example of the design and synthesis of lanthanide clusters with high stabilities and relaxation rates, taking a big step toward the precise and controllable synthesis of lanthanide clusters.

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Introduction

Lanthanide clusters with a precise structure, a uniform nanoscale size, and rich functions have attracted widespread attention and have shown great application prospects in the fields of molecular magnetism, magnetocaloric effect, bio-imaging, solid-state luminescence, etc. 1-11 In particular, gadolinium(III) clusters with a nanometer size and highly concentrated metal centers break through the limitations of conventional magnetic resonance imaging (MRI) contrast agents (CAs) and exhibit a high imaging contrast. 12,13 According to the Solomon-Bloembergen Morgan (SBM) paramagnetic relaxation theory, it can be known that CAs with high relaxation, high resolution and high contrast can be obtained by connecting multiple single-nuclear or low-nuclear gadolinium complexes through multi-component integration. High-nuclear gadolinium clusters with highly aggregated Gd(III) undoubtedly show attractive application prospects in the field of MRI. In 2020, Sun et al. used 2,6-pyridine bistetrazolium-derived ligands with different bending angles to construct a watersoluble molecular cage Ln_{2n}L_{3n}, which showed high relaxation rates and excellent in vivo MRI imaging effects in mice. 13 In

^aSchool of Chemistry and Pharmaceutical Sciences, State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, Guangxi Normal University, Guilin 541004, P. R. China. E-mail: 18317725515@163.com, gxnuchem@foxmail.com

^bGuangxi Key Laboratory of Agricultural Resources Chemistry and Biotechnology, College of Chemistry and Food Science, Yulin Normal University, Yulin 537000, P. R. China. E-mail: huqiongscut@163.com

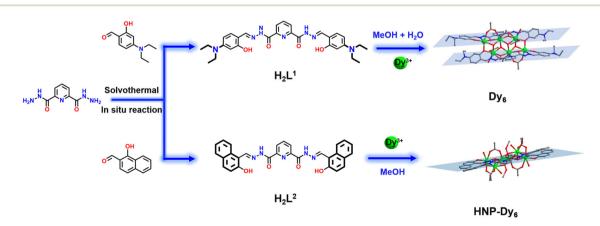
[†]Electronic supplementary information (ESI) available. CCDC 2283643 and 2283644. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d3qi01490h

Research Article

2023, Tong et al. used solvothermal synthesis technology to construct spherical nanoclusters Gd₃₂ with high stability, low toxicity and excellent water solubility. The highly aggregated Gd(III) in the structure leads to its excellent MRI imaging contrast both in vivo and in vitro. 12 Although substantial progress has been made in the application and expansion of lanthanide clusters, progress with regard to their controllable and precise synthesis remains unsatisfactory. 14 Previously, lanthanide clusters primarily relied on hydrolysis and the anion template method to guide their structural synthesis. Various lanthanide clusters with beautiful shapes and diverse topologies, such as wheel-shaped Gd₁₄₀, caged Gd₆₀, hamburger-shaped Dy₇₆, and tubular Dy72, have been constructed based on the abovementioned methods. 15-19 In 2018, Bu et al. induced the synthesis of a rare hamburger-shaped dysprosium cluster Dy₇₆ using a mixed-anion template that can be regarded as an assembly of two Dy48 clusters. In 2016, Zheng et al. synthesized a tubular dysprosium cluster Dy72 by controlling the hydrolysis of Dy(III) ions with N-methyldiethanolamine. 19 In 2022, Zheng et al. synthesized multinuclear lanthanide hydroxide clusters under the guidance of combined I⁻ and CO₃²⁻ as mixed templates.²⁰ The complex reaction and the extremely low controllability of the reaction system that lead to directional construction of lanthanide clusters remain to be very vague.

The tracking of the self-assembly process and the study of the self-assembly mechanism have accelerated the pace of the directional and rational construction of lanthanide clusters. 21-23 Since 2018, we have been using crystallography combined with high-resolution electrospray ionization-mass spectrometry (HRESI-MS) to explore and analyze the formation process and the self-assembly mechanism of several lanthanide clusters. We also proposed the out-to-in, linear, and annular growth mechanisms to guide the directional synthesis of lanthanide clusters. 24-28 In 2020, our research group successfully constructed a double-cage dysprosium cluster Dy₆₀ using a multidentate chelating coordination method, tracked the Dy₆₀ formation process using HRESI-MS, and proposed the possible self-assembly mechanism of Dy₆₀. ²⁹ In 2021, we first proposed that the out-to-in growth mechanism guides the directional construction of 16 nuclear discotic lanthanide clusters. 25,26,30 In 2022, also for the first time, we guided the directional construction of chiral lanthanide clusters with different connection modes and shapes by manipulating the annular growth mechanism.²⁷ We then successfully constructed the largest planar disk-shaped lanthanide cluster Dv₁₉ under solvothermal conditions and proposed its possible assembly mechanism (i.e., the planar epitaxial or planar internal growth mechanism).31 The bulky bis-acylhydrazone and Schiff base-derived ligands with multidentate chelation coordination sites can quickly capture the lanthanide metal ions in solutions to form template units, thereby further assembling to obtain the target lanthanide clusters. 24,32,33 These template units formed by linking lanthanide ions with bulky chelating ligands have a higher stability in solution than hydrolyzed products and anion templates, making the selfassembly process of lanthanide clusters more regular and promoting their designability.14 Based on the abovementioned foundations, we focus herein on the precise construction of lanthanide clusters with the same core connections but different template-motif arrangements, which has been difficult to achieve until now.

In this work, we use the -N(Et)2-substituted bis-acylhydrazone-derived ligand H₂L₁ (N'²,N'⁶-bis(4-(diethylamino)-2hydroxybenzylidene)pyridine-2,6-dicarbohydrazide) Dy(OAc)3.4H2O to perform a reaction under solvothermal conditions and acquire a Dv₆ sample, which has face-to-face and dislocation-arrangement template motifs (Scheme 1). Changing $-N(Et)_2$ to a benzene ring with a strong π - π interaction yields HNP-Dy6 with an inverted and coplanar arrangement of template motifs (Scheme 1). We employ HRESI-MS to evaluate the stabilities of the two hexanuclear clusters prepared in this study in a solution. Under the condition of an increasing ion-source energy from 0 to 100 eV, the molecularion peaks of Dy₆ and HNP-Dy₆ in the solution are found to be related to their structural skeletons, indicating that they both maintain a high stability in the solution. We implement timedependent HRESI-MS to track the species changes during the Dy₆ and HNP-Dy₆ formations under solvothermal "black-box"



Scheme 1 Schematic of the Dy₆ and HNP-Dy₆ synthesis.

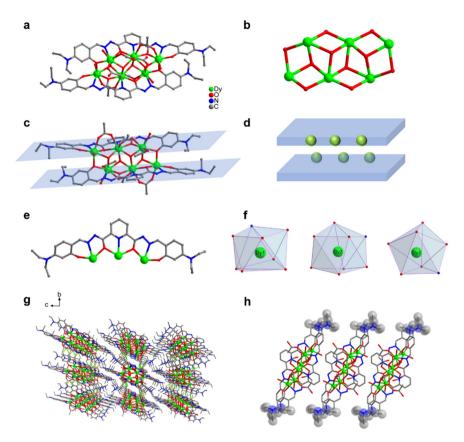


Fig. 1 (a) Dy₆ structure, (b) cluster core connection, (c) face-to-face and up-and-down dislocation arrangements of the Dy₃(L¹) template units, (d) schematic of the template-unit arrangement in Dy_6 , (e) coordination mode of ligand (L^1)²⁻, (f) coordination configurations of the metal-centered ions $Dy_1 - Dy_3$ (g) three-dimensional Dy_6 accumulation, and (h) arrangement among the three independent units of Dy_6 .

reaction conditions. The intermediates of various reactions are identified. Their possible self-assembly mechanisms are proposed as follows: $L^1 + 2Dy \rightarrow Dy_2L^1 \rightarrow Dy_3L^1 \rightarrow Dy_6(L^1)_2$ and L^2 $+ 2Dy \rightarrow Dy_2L^2 \rightarrow Dy_3L^2 \rightarrow Dy_5(L^2)_2/Dy_6(L^2)_2 \rightarrow Dy_6(L^2)_2$. To the best of our knowledge, this is the first time that multidentate chelation coordination is manipulated through substitution effects to construct heterogeneous hexanuclear lanthanide clusters with the same cluster core connections but different template-motif arrangements. The high cluster stability in the solution promotes the expansion of its application in the solution. Notably, low Gd₆ concentration exhibits high longitudinal and transverse relaxation rates $(r_1 \text{ and } r_2, \text{ respectively})$ at 1-T magnetic field, indicating its great potential as a T_1 -weighted MRI CA. This work paves a way for the directed and controllable synthesis of lanthanide clusters with precise structures and promotes the progress of lanthanide-cluster crystal engineering.

Results and discussion

Synthesis and structural analysis of Ln₆ clusters (Ln = Dy and Gd)

Approximately 0.4 mmol of Dy(OAc)3·4H2O and 0.05 mmol of the organic ligand H₂L¹ (N'²,N'⁶-bis(4-(diethylamino)-2-hydroxybenzylidene)pyridine-2,6-dicarbohydrazide) were accurately

weighed and dissolved in a mixed solvent of MeOH: H2O (1.0 mL:0.3 mL) and added with 100 µL of triethylamine. After an even mixing, the reaction was derived under solvothermal conditions at 80 °C for 48 h to obtain an orange blocky crystal of Dy₆ (Fig. 1). The results of single-crystal X-ray diffraction (SCXRD) showed that Dy_6 crystallized in the $P\bar{1}$ space group of the triclinic system (Tables S1-S4†). Dy₆ comprised six Dy(III) ions, two multidentate chelating ligands $(L^{1})^{2-}$, four μ_{3} - O^{2-} , six OAc⁻, and four terminally coordinated H₂O molecules and had the following molecular formula: $[Dy_6(L^1)_2(\mu_3-O)_4(OAc)_6(H_2O)_4]$ (Fig. 1a). The six metal-centered Dy(III) ions of Dy_6 were distributed on the equatorial plane and connected by oxygen atoms in the ligands and μ_3 -O²⁻ bridges to form the {Dy/O} cluster nucleus (Fig. 1b). The multidentate chelating ligand (L1)2- chelated three Dy(III) ions to form the $Dy_3(L^1)$ template motif. Notably, in the Dy_6 structure, two Dy₃(L¹) were arranged in face-to-face and up-and-down dislocation arrangements (Fig. 1c and d, respectively). The two ligands at the cluster core periphery tightly wrapped the cluster core to resist the attack of foreign solvent molecules, further ensuring the Dy6 stability. Each ligand chelated three Dy(III) ions and had the following coordination modes: $\mu_3 - \eta^1 : \eta^1 : \eta^2 : \eta^1 : \eta^2 : \eta^1 : \eta^1$ (Fig. 1e). The six metal-centered Dy(III) ions in the Dy6 structure had three coordination environments. The metal-centered Dy1 had an O7N coordination

environment provided by the $(L^1)^{2-}$ ligand, μ_3 - O^{2-} , OAc^- , and H₂O molecule (Fig. 1f). The SHAPE calculations showed that the coordination configuration was a Johnson biaugmented trigonal prism (J50) with a C_{2v} symmetric environment (Table S4†). The metal-centered Dy2 had an O7N coordination environment provided by the $(L^1)^{2-}$ ligand, μ_3 -O²⁻, and OAc⁻ (Fig. 1f). The SHAPE calculations demonstrated that the coordination configuration was a biaugmented trigonal prism (J50) with a C_{2v} symmetric environment (Table S4†). Meanwhile, the metal-centered Dy3 had an O₆N₂ coordination environment provided by the $(L^1)^{2-}$ ligand, μ_3 - O^{2-} , OAc^- , and H₂O molecule (Fig. 1f). The SHAPE calculations for this indicated that the coordination configuration was a Johnson pentagonal bipyramid (J13) with a D_{5h} symmetric environment (Table S4†). According to further weak interaction analysis and stacking diagrams, the strong steric hindrance of -N(Et)2 caused the template units in the Dy6 structure to form face-toface and dislocation arrangements (Fig. 1g and f). The structural analysis demonstrated that all the Dy-O/N bond lengths were within the normal range (Table S2†). We changed the metal salt to Gd(OAc)3·H2O and obtained the Gd6 homologue of Dy₆ under the same conditions.

We changed 4-(diethylamino)salicylaldehyde to 2-hydroxy-1naphthaldehyde to construct a diacylhydrazone-derived ligand, $(N'^2, N'^6$ -bis((2-hydroxynaphthalen-1-yl)methylene)pyridine-2,6-dicarbohydrazide). The yellow blocky crystals of HNP-Dy6 in Scheme 1 were obtained when the abovementioned solvothermal reaction was realized using H₂L² and the solvent was changed to 2.0 mL of anhydrous methanol. The SCXRD results showed that HNP-Dy₆ crystallized in the P1 space group of the triclinic system (Tables S1-S4†). HNP-Dy₆ comprised six Dy(III) ions, two multidentate chelating ligands $(L^2)^{2-}$, four μ_3 -O²⁻, four OAc⁻, four CH₃O⁻, and four terminally coordinated H2O molecules with the following molecular $[Dy_6(L^2)_2(\mu_3-O)_4(OAc)_4(CH_3O)_4(H_2O)_4] \cdot 3CH_3OH$ (Fig. 2a). Similarly, the six metal-centered Dy(III) ions in the HNP-Dy₆ structure were also distributed on the equatorial plane and connected by oxygen atoms in the ligands and μ_3 -O²⁻ bridges to form the {Dy/O} cluster nucleus (Fig. 2b). The HNP-Dy₆ structure comprised a multidentate chelating ligand that chelated three Dy(III) ions to form the Dy₃(L²) template unit. Surprisingly, the two Dy₃(L²) template units were found in the same plane and arranged in face-to-face and parallel arrangements, which was considerably different from Dy₆ (Fig. 2c and d). The coordination mode of the multidentate chelating ligand $(L^2)^{2-}$ was $\mu_3 - \eta^1 : \eta^1 : \eta^2 : \eta^1 : \eta^2 : \eta^1 : \eta$ The six metal-centered Dy(III) ions in the HNP-Dy₆ structure all had an O₇N coordination environment. Their coordination configurations were Johnson biaugmented trigonal prism (J50) (Dy1), biaugmented trigonal prism (Dy2), and triangular dodecahedron (Dy3) (Fig. 1f and Table S5†). An obvious π - π stacking (3.820 Å) was observed in the HNP-Dy₆ structure. The strong π - π interaction led to the reverse and planar arrangement of the template units (Fig. 2g and h). The structural analysis demonstrated that all the Dy-O/N bond lengths were within the normal range (Table S3†).

The controllable construction of the two distinct hexanuclear dysprosium clusters marked a great progress in the precise lanthanide-cluster synthesis. We initially proposed the multidentate chelating coordination (MCC) method for the rational construction of lanthanide clusters. For the first time, we selected herein a diacylhydrazone-derived ligand with multiple coordination sites and manipulated the MCC method to realize the precise synthesis of planar and dislocation-parallel differential hexanuclear dysprosium clusters. Specifically, when the substituent -N(Et)2 with a large steric hindrance was selected, Dy₆ was obtained with template units having face-toface and upper and lower dislocation arrangements. Further increasing the conjugated ring on the ligand yielded HNP-Dy₆ with template units located in the same plane and arranged face-to-face. To the best of our knowledge, most of the reported hexanuclear lanthanide clusters tend to be in the second arrangement. Precisely controlling and obtaining lanthanide clusters with the same cluster nuclei but different arrangements is difficult. Adjusting the multidentate chelating-ligand substituents enabled us to realize the directional assembly of heterogeneous hexanuclear lanthanide clusters with different arrangements. We were also able to reveal the controllability of the structural design of the hypernuclear lanthanide clusters, which is a big step toward a precise synthesis.

The thermal stability analysis of Dy₆ and HNP-Dy₆ was performed under a flowing N2 atmosphere. The temperature was slowly increased from 35 °C to 1000 °C at a 5 °C min⁻¹ rate (Fig. S2†). As the temperature was gradually increased from 35 °C to 140 °C, we obtained a Dy₆ weight loss rate of 5.18% that corresponded to the loss of four terminally coordinated water molecules and one OAc-. The theoretical value for this was 5.13%. The Dy₆ weight loss rate was 11.60% when the temperature was increased from 310 °C to 405 °C. This process corresponded to the loss of five OAc-. The theoretical value for this was 11.55%. Finally, Dy6 was rapidly decomposed at a temperature above 480 °C (Fig. S2a†). Similarly, the HNP-Dy₆ weight loss rate was 6.53% when the temperature was gradually increased from 35 °C to 115 °C. This corresponded to the loss of four terminally coordinated water molecules and three methanol molecules. The theoretical value for this was 6.78%. The HNP-Dy₆ weight loss rate was 11.14% when the temperature was gradually increased from 32 °C to 390 °C. This rate corresponded to the loss of four terminally coordinated CH₃O⁻ and three OAc⁻. The theoretical value for this was 11.70%. Finally, the HNP-Dy₆ structure was rapidly decomposed at a temperature of >500 °C (Fig. S2b†). The powder X-ray diffraction experimental and simulated values for Dy₆, Gd₆, and HNP-Dy₆ were compared at 35 °C. The results showed their pure phases (Fig. S3†).

Stabilities of Dy₆ and HNP-Dy₆

In recent years, HRESI-MS had been extensively used to evaluate the stability, solubility, and ionization degree of the lanthanide clusters in solutions. 6,12,29,34 In this work, to further explore the stabilities of Dy₆ and HNP-Dy₆ in solution, we used HRESI-MS with different ion-source energies to monitor the

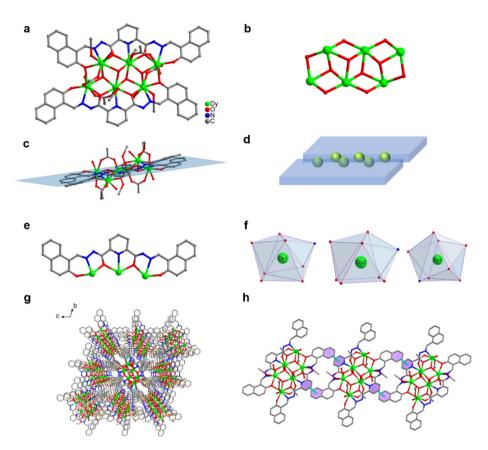


Fig. 2 (a) HNP-Dy₆ structure, (b) cluster core connection, (c) face-to-face arrangement of the Dy₃(L²) template units in the same plane, (d) schematic of the template-unit arrangement in HNP-Dy₆, (e) ligand coordination mode, (f) metal-centered coordination configuration, (g) three-dimensional HNP-Dy₆ accumulation, and (h) π - π stacking of the three independent units of HNP-Dy₆.

molecular-ion peak fragments of Dy₆ and HNP-Dy₆. We specifically dissolved small amounts of pure Dy6 and HNP-Dy6 in chromatographic N,N-dimethylformamide (DMF) and performed HRESI-MS testing after extensive dilution using chromatographic methanol. The yielded data were collected within the m/z = 400-4000 range (Fig. 3a and 4a and Tables S6 and S7†). The results showed that Dy₆ can maintain a high stability under the HRESI-MS conditions. The captured molecular-ion peaks of different m/z were related to the structural framework that can be assigned to $[Dy_6(L^1)_2(O)_4(CH_3COO)_x(OH)(solv.)]$ $(x \le 5; \text{ solv.} = \text{DMF, CH}_3\text{OH, and H}_2\text{O}; +1, +2 \text{ valence})$. The abovementioned molecular-ion peak fragments were specifically resolved as $[Dy_6(L^1)_2(O)_4(OH)_4(CH_3OH)_3(H_2O)_2]^{2+}$ (calc. 1163.59, 1163.54), $[Dy_6(L^1)_2(O)_4(CH_3COO)_2(OH)_2$ exp. $(CH_3OH)_2]^{2+}$ (calc. 1172.58, exp. 1172.55), $[Dy_6(L^1)_2(O)_4(CH_3COO)_2]$ $(OH)_2(CH_3OH)_2(H_2O)]^{2+}$ (calc. 1181.09, exp. $[Dy_6(L^1)_2(O)_4(OH)_4(DMF)_2(CH_3OH)]^{2+}$ (calc. 1188.10, exp. 1188.08), $[Dy_6(L^1)_2(O)_4(CH_3COO)_4(OH)(H_2O)_3]^+$ (calc. 2435.17, exp. 2435.16), $[Dy_6(L^1)_2(O)_4(CH_3COO)_5(DMF)(H_2O)]^+$ (calc. 2513.20, exp. 2513.18), and $[Dy_6(L^1)_2(O)_4(CH_3COO)_4(OH)(DMF)(CH_3OH)_2$ $(H_2O)_3^{\dagger}$ (calc. 2572.26, exp. 2572.22) (Fig. S4 and Table S6†). Similarly, HNP-Dy₆ presented a +1 valent molecular-ion peak fragment related to the structural framework in the m/z = 2000-3000range, which can be attributed to $[Dy_6(L^2)_2(O)_4(CH_3COO)_x(CH_3O)_y$

(solv.)] $(x \le 4; y \le 4; \text{ solv.} = \text{DMF, CH}_3\text{OH, and H}_2\text{O})$. The molepeak cular-ion fragments were assigned $[Dy_6(L^2)_2(O)_4(CH_3COO)_2(CH_3O)(OH)_2(H_2O)_2]^{\dagger}$ (calc. 2261.91, exp. 2261.87), $[Dy_6(L^2)_2(O)_4(CH_3COO)_2(CH_3O)_3(CH_3OH)(H_2O)]^{\dagger}$ (calc. 2302.96, exp. 2302.89), $[Dy_6(L^2)_2(O)_4(CH_3COO)_2(CH_3O)_3]$ $(CH_3OH)(H_2O)_2$ ⁺ (calc. 2321.97, exp. 2321.89), $[Dy_6(L^2)_2(O)_4]$ $(CH_3COO)_4(CH_3O)(CH_3OH)(H_2O)_2$ (calc. 2375.96, exp. 2375.94), $[Dy_6(L^2)_2(O)_4(CH_3COO)_4(CH_3O)(CH_3OH)_5(H_2O)_5]^+$ (calc. 2560.09, exp. 2560.02), and $[Dy_6(L^2)_2(O)_4(CH_3COO)_4(CH_3O)(CH_3OH)_5]$ $(H_2O)_6$ [†] (calc. 2576.10, exp. 2576.04) (Fig. S5 and Table S7†).

Only the molecular-ion peaks $[Dy_6(L^1)_2(O)_4(OH)_4(CH_3OH)_3]$ $(H_2O)_2$ ²⁺ (calc. 1163.59, exp. 1163.56) and $[Dy_6(L^1)_2(O)_4(CH_3COO)_4]$ $(OH)(H_2O)_3$ ⁺ (calc. 2435.16, exp. 2435.17), which were related to the complete structural skeleton, were detected in the Dy₆ solution as the ion-source voltage was gradually increased from 0 to 100 eV (Fig. S6 and Table S8†). HNP-Dy₆ also only depicted the molecular-ion peak fragment of [Dy₆(L²)₂(O)₄(CH₃COO)₄(CH₃O) $(CH_3OH)_5(H_2O)_5^{\dagger}$ (calc. 2560.09, exp. 2560.04), which was consistent with the structural skeleton (Fig. S7 and Table S9†). These results indicate that both Dy₆ and HNP-Dy₆ exhibited high stabilities in solution (Fig. 3b and 4b). Based on the structural analysis results of Dy₆ and HNP-Dy₆, their stabilities can be attributed to the two large-volume chelating ligands on the cluster core periphery tightly wrapping around the cluster core, effectively resisting

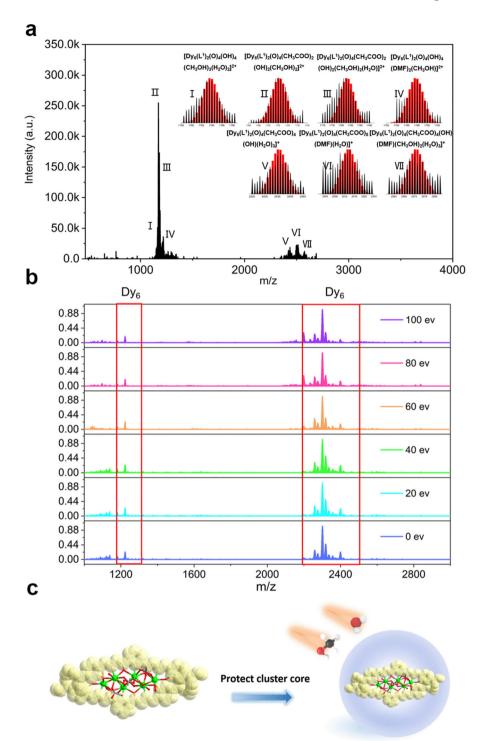


Fig. 3 (a) HRESI-MS spectrum of Dy₆ dissolved in DMF in the positive-ion mode, (b) HRESI-MS spectrum of Dy₆ dissolved in DMF under different ion-source voltages (in-source CID), and (c) schematic of the chelating ligands effectively protecting the cluster core.

the attack of foreign solvent molecules on the cluster core (Fig. 3c and 4c).

Assembly mechanism of Dy₆ and HNP-Dy₆

We further explored the self-assembly mechanism of Dy₆ and HNP-Dy₆ by performing time-dependent HRESI-MS to track

the species changes separately during their formation (Fig. 5a and 6a and Tables S10 and S11†). The HRESI-MS data suggested that Dy6 was formed through a step-by-step assembly. Fig. 5b depicts the time-dependent change trend of the species in the solution during the self-assembly process of Dy₆. First, the reaction system was stirred at room temperature

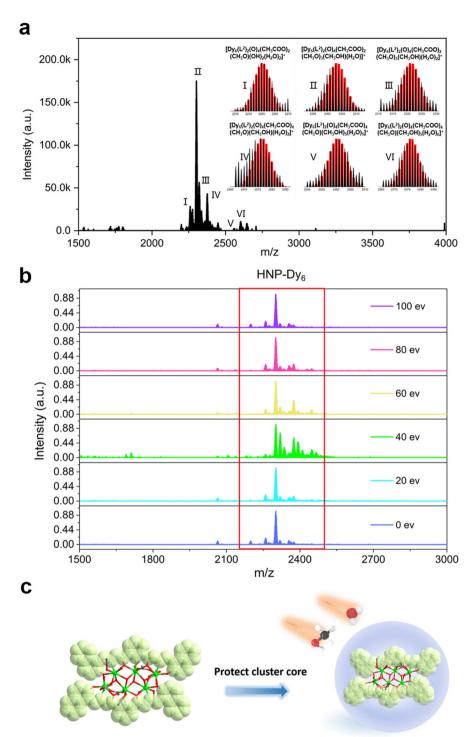


Fig. 4 (a) HRESI-MS spectrum of HNP-Dy₆ dissolved in DMF in the positive-ion mode, (b) HRESI-MS spectrum of HNP-Dy₆ dissolved in DMF under different ion-source voltages (in-source CID), and (c) schematic of the chelating ligands effectively protecting the cluster core.

for 5 min (0 min), during which the ligand H_2L immediately reacted with the metal Dy(III) ions to generate multiple $[Dy_2L^1]$ fragments. The ligand fragment with the highest intensity appeared in the m/z=877.49 position, which can be assigned to $[Dy_2(L^1)(OH)_2(DMF)_8(CH_3OH)_6(H_2O)_4]^{2+}$ (Fig. 5a and S8†). The other molecular-ion peak fragments related to $[Dy_2L^1]$

appeared at positions m/z=878.48 and 891.50. By fitting, the molecular formulas of these fragments were found as $[Dy_2(L^1)(OH)_2(DMF)_8(CH_3OH)_5(H_2O)_6]^{2+}$ (calc. 878.37, exp. 878.48) and $[Dy_2(L^1)(OH)_2(DMF)_8(CH_3OH)_8(H_2O)_2]^{2+}$ (calc. 891.40, exp. 891.50) (Fig. 5a and S8†). The experimental results showed that the H_2L^1 ligand removed two protons and pre-

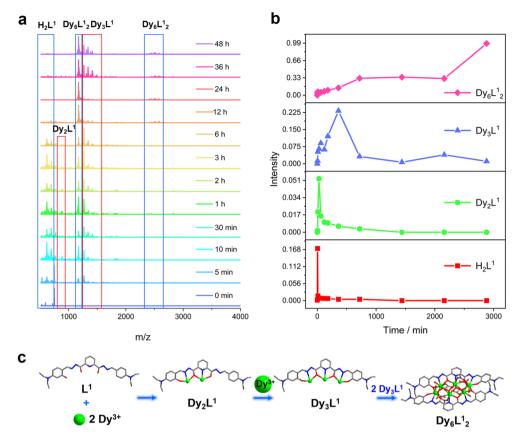


Fig. 5 (a) Time-dependent HRESI-MS tracking of the Dy_6 formation process, (b) intensity—time curves of the molecular-ion peaks of different species during the reaction, and (c) schematic of the possible formation process and the self-assembly mechanism of Dy_6 .

sented -2 valence under triethylamine regulation, while the (L¹)²⁻ ligand removed two protons combined with two metalcentered Dy(III) ions to form the [Dy₂L¹] fragments. The intensity of the [Dy₂L¹] fragments gradually decreased with increasing reaction time. These fragments disappeared after heating for 12 h and were transformed into a small amount of [Dy₃L¹] fragments with the increasing heating time. They began to appear at 5 min, formed in large quantities at 1 h, reached the maximum intensity at 6 h, and weakened after 12 h. Their molecular-ion peak appeared in the m/z = 1242.03-1416.14range, and the molecular formulas obtained by fitting were $[Dy_3(L^1)(OH)_6(DMF)(H_2O)_2]^+$ (calc. 1242.13, exp. 1242.03), $[Dy_3(L^1)(OH)_6(CH_3OH)_2(H_2O)_2]^+$ (calc. 1265.16, exp. 1265.08), $[Dy_3(L^1)(OH)_6(DMF)_2(CH_3OH)_2]^+$ (calc. 1345.07, exp. 1345.23), and $[Dy_3(L^1)(OH)_6(DMF)_2(CH_3OH)_2(H_2O)_4]^+$ (calc. 1416.26, exp. 1416.14) (Fig. 5a and S8†). The $[Dy_6L_2^1]$ fragments also began to appear at 5 min from the beginning of the reaction, formed in large quantities at 6 h, and showed a gradually increasing intensity. The molecular-ion peaks related to $[Dy_6L_2^1]$ were observed in the m/z = 1151.53-2572.22 range. The molecular formulas of these fragments obtained by fitting were $[Dy_6(L^1)_2(O)_4(CH_3COO)(OH)_3(CH_3OH)_2]^{2+}$ (calc. 1151.58, exp. 1151.53), $[Dy_6(L^1)_2(O)_4(OH)_4(CH_3OH)_3(H_2O)_2]^{2+}$ (calc. $[Dy_6(L^1)_2(O)_4(CH_3COO)_2(OH)_2$ 1163.59, exp. 1163.54), $(CH_3OH)_2$ ²⁺ (calc. 1172.58, exp. 1172.55), $[Dy_6(L^1)_2(O)_4]$

 $(CH_3COO)_2(OH)_2(CH_3OH)_2(H_2O)]^{2+}$ (calc. 1181.09, 1181.08), $[Dy_6(L^1)_2(O)_4(OH)_4(DMF)_2(CH_3OH)]^{2+}$ (calc. 1188.10, exp. 1188.08), $[Dy_6(L^1)_2(O)_4(CH_3COO)_5(DMF)]^+$ (calc. 2496.21, exp. 2496.20), $[Dy_6(L^1)_2(O)_4(CH_3COO)_5(DMF)(H_2O)]^+$ (calc. 2513.20, exp. 2513.18), and $[Dy_6(L^1)_2(O)_4(CH_3COO)_4(OH)(DMF)$ $(CH_3OH)_2(H_2O)_3$ (calc. 2572.26, exp. 2572.22) (Fig. 5a and S8). Surprisingly, the $[Dy_6L^{1}_{2}]$ fragments also began appearing at the same time as the [Dy₃L¹] fragments were detected at 5 min from the start of the reaction. The results indicate that the trinuclear fragment [Dy₃L¹] was quickly used as a template motif after its formation to rapidly react to form the [Dy₆L¹₂] fragment. Therefore, the formation process of Dy₆ underwent a stepwise assembly and had the possible assembly mechanism of $L^1 + 2Dy \rightarrow Dy_2L^1 \rightarrow Dy_3L^1 \rightarrow 2Dy_3L^1 \rightarrow Dy_6L^1_2$ (Fig. 5c).

Similarly, we tracked the **HNP-Dy**₆ formation using time-dependent HRESI-MS and proposed its possible self-assembly mechanism. First, the reaction system was stirred at room temperature for 5 min (the label in the figure is 0 min), during which the ligand H_2L immediately reacted with the metal-centered Dy(III) ions to generate multiple $[Dy_2L^2]$ fragments. The ligand fragment with the highest intensity appeared in the m/z = 925.03 position that can be assigned to $[Dy_2(L^2)(CH_3O)_2(OH)(H_2O)]^+$ (Fig. 6a and S9†). The other molecular-ion peak fragments related to $[Dy_2L^2]$ appeared at positions 1008.93 and 1070.96. The molecular formulas of these fragments obtained

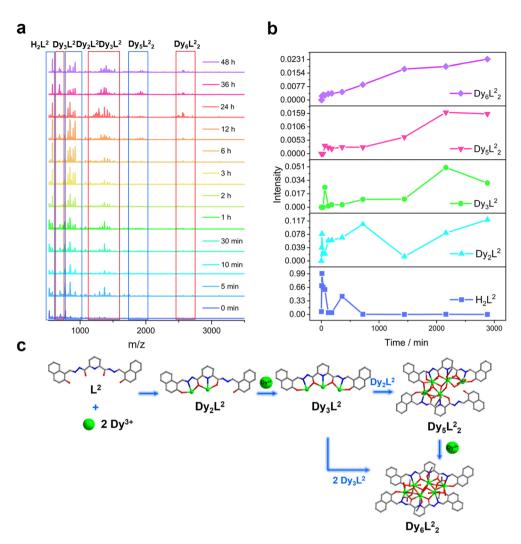


Fig. 6 (a) Time-dependent HRESI-MS tracking of the HNP-Dy₆ formation process, (b) HRESI-MS spectra intensity-time profiles of the species, and (c) schematic of the possible assembly mechanism of HNP-Dy₆.

by fitting were $[Dy_2(L^2)(CH_3O)_2(OH)(CH_3OH)(H_2O)_4]^+$ (calc. 1009.10, exp. 1008.93) and $[Dy_2(L^2)(OH)_3(DMF)_2(CH_3OH)]$ $(H_2O)^{-1}$ (calc. 1071.14, exp. 1070.96). We also observed that a small amount of [Dy₂L²] fragments chelated with the metalcentered Dy(III) ions to form the [Dy₃L²] fragments, which began appearing at 5 min. Their molecular-ion peaks appeared at the m/z = 1342.08-1524.10 position. The molecular formulas of these fragments obtained by fitting were [Dy₃(L²) $(OH)_6(DMF)_3(CH_3OH)^{-1}$ (calc. 1342.13, exp. 1342.08), $[Dy_3(L^2)]$ $(OH)_6(DMF)(CH_3OH)_3(H_2O)_6$ ⁺ (calc. 1370.16, exp. 1370.07), $[Dy_3(L^2)(OH)_6(DMF)(CH_3OH)_{4}(H_2O)_2]^{+}$ (calc. exp. 1448.08), and $[Dy_3(L^2)(OH)_6(DMF)_2(CH_3OH)_5(H_2O)_7]^+$ (calc. 1524.26, exp. 1524.10) (Fig. 6a and S9†). With the continuous increase of the heating time, the [Dy₅L²₂] fragments started to appear at 1 h and formed by chelating a [Dy₂L²] fragment with a [Dy₃L²] fragment. The molecular-ion peak of the $[Dy_5L_2^2]$ fragment was observed at the m/z = 1919.98-1967.96position. The molecular formulas of these fragments acquired $[Dy_5(L^2)_2(O)_4(OH)_2]^+$ fitting were (calc.

exp. 1919.98), $[Dy_5(L^2)_2(O)_4(OH)_2(CH_3OH)]^+$ (calc. 1946.94, exp. 1946.96), and $[Dy_5(L^2)_2(O)_4(OH)_2(CH_3OH)(H_2O)]^+$ (calc. 1967.98, exp. 1967.96). The $[Dy_3L^2]$ and $[Dy_5L^2]$ fragments gradually disappeared with up 48 h of heating time. The [Dy₆L²₂] fragments also began to appear at 5 min from the beginning of the reaction, formed in large quantities at 6 h, and showed a gradually increasing intensity. The molecularion peaks related to the $[Dy_6L^2_2]$ fragments appeared in the m/z = 2261.87-2576.04 range. The molecular formulas of these fragments obtained by fitting were $[Dy_6(L^2)_2(O)_4(CH_3COO)_2]$ $(CH_3O)(OH)_2(H_2O)_2$ (calc. 2261.91, exp. 2261.87), $[Dy_6(L^2)_2]$ $(O)_4(CH_3COO)_2(CH_3O)_3(CH_3OH)(H_2O)]^+$ (calc. 2302.96, exp. 2302.87), $[Dy_6(L^2)_2(O)_4(CH_3COO)_2(CH_3O)_3(CH_3OH)(H_2O)_2]^{+}$ (calc. 2321.97, exp. 2321.89), $[Dy_6(L^2)_2(O)_4(CH_3COO)_4(CH_3O)]$ $(CH_3OH)(H_2O)_2$ ⁺ (calc. 2375.96, exp. 2375.94), $[Dy_6(L^2)_2(O)_4]$ $(CH_3COO)_4(CH_3O)(CH_3OH)_5(H_2O)_5^{\dagger}$ (calc. 2560.09, exp. 2560.04), and $[Dy_6(L^2)_2(O)_4(CH_3COO)_4(CH_3O)(CH_3OH)_5(H_2O)_6]^{\dagger}$ (calc. 2576.10, exp. 2576.04) (Fig. 6a and S9†). Therefore, the formation process of HNP-Dy₆ was a combination of the stepwise

and template assemblies with two possible self-assembly mechanisms: $L^2 + 2Dy \rightarrow Dy_2L^2 \rightarrow Dy_3L^2 \rightarrow Dy_5L^2 \rightarrow Dy_6L^2$ or $L^2 + 2Dy$ \rightarrow Dy₂L² \rightarrow Dy₃L² \rightarrow 2Dy₃L² \rightarrow Dy₆L²₂ (Fig. 6c).

MRI performance of Gd₆

As one of the most mature medical imaging techniques available, MRI has been extensively used in clinical medical diagnosis in the recent years. However, CAs are usually required to improve the imaging contrast and clarity of MRI. 12,13,35-38 Therefore, CAs with high resolution and clear imaging effects must be designed and developed. Gadolinium-based chelates are currently extensively used as a T₁-weighted MRI CA for clinical diagnosis, and they usually require higher doses to achieve excellent imaging results. 39-41 To explore the feasibility of Gd_6 as a T_1 -weighted MRI CA, we tested the relaxation time with the Gd(III) concentration changes at 1-T magnetic field strength and obtained the longitudinal and transverse relaxation rates (r_1 and r_2 , respectively). The results showed the Gd_6 r_1 and r_2 values of 12.06 and 24.10 mM⁻¹ s⁻¹, respectively, at 1-T magnetic field strength (Fig. 7a). Gd₆ with a highly aggregated Gd(III) exhibited higher relaxation rates compared to the conventional Gd chelates. $r_2/r_1 = 1.99 (r_2/r_1 < 2)$ indicated that $\mathbf{Gd_6}$ is a potential T_1 -weighted MRI CA candidate. ^{12,42,43} Under the same magnetic field, the r_1 and r_2 of gadopentetate dimeglumine injection (Gd-DTPA), a currently used clinical MRI contrast agent, are 4.55 and 5.77 mM⁻¹ s⁻¹, respectively. 12 In comparison, Gd₆ shows higher relaxation values. With the gradual increase of the Gd(III) concentration of Gd₆ in the aqueous solution, the T_1 -weighted image gradually became brighter under 1-T magnetic field. By contrast, the T_2 -weighted image gradually turned darker from bright, indicating that Gd_6 exhibited a good T_1 imaging effect in the solution. The T_1 mapping images displayed by different Gd₆ concentrations at 1-T magnetic field also depicted its great potential as an MRI CA in biomedical diagnosis (Fig. 7b). In addition, we dissolved Gd₆ crystals in DMSO and dispersed them in H₂O and phosphate buffered saline (PBS), respectively, and recorded the Gd₆

dispersed in the above solutions in 1-5 days by UV-visible absorption spectroscopy, which was the absorbance (OD) change at 422 nm. We found that there was no significant change in the absorbance of Gd₆ at 422 nm from the 1-5 days. The results show that Gd_6 has excellent stability (Fig. S10†).^{5,12}

Magnetic analysis of Ln₆

Lanthanide complexes have been extensively explored as candidate materials for single-molecule magnets (SMMs) and magnetic refrigerants. Especially the dysprosium complexes constructed by Dy(III) ions are mainly attributed to their significant magnetic anisotropy.³⁴ Therefore, we investigated the magnetic behavior of Dy₆ and HNP-Dy₆. The temperature-varying molar susceptibilities of the Dy₆ and HNP-Dy₆ pure phases were tested under an external DC magnetic field of 1000 Oe in the 2-300 K temperature range (Fig. S11a and 11c†). 44-49 The $\chi_{\rm m}T$ values of Dy₆ and HNP-Dy₆ at 300 K were 83.65 and 82.13 cm³ K mol⁻¹, respectively (${}^{6}H_{15/2}$, S = 5/2, g = 4/3, J = 15/2, and L =5). The $\chi_{\rm m}T$ values of both Dy₆ and HNP-Dy₆ were slightly lower than the theoretical value (i.e., 85.02 cm³ K mol⁻¹) of the six Dy(III) ions. As the temperature decreased, the $\chi_{\rm m}T$ value of Dy₆ continued to decrease, and when the temperature reached 2 K, the $\chi_{\rm m}T$ of Dy₆ droped rapidly to 68.15 cm³ K mol⁻¹. However, when the temperature decreased from 300 K to 2 K, the $\chi_{\rm m}T$ value of HNP-Dy₆ first increased slowly and then decreased, and its $\chi_{\rm m}T$ value reached 82.13 cm³ K mol⁻¹ at 100 K, while its $\chi_{\rm m}T$ decreased rapidly to 63.18 cm³ K mol⁻¹ when the temperature reached 2 K.49,50 These findings showed that the temperature-decreasing $\chi_{\rm m}T$ value may be caused by a decrease in the Stark sublevel of the Dy(III) excited state and the induced crystal field effect. Subsequently, we tested the field-dependent magnetization of Dy6 and HNP-Dy6 at different temperatures (2-5 K) and applied fields of 0-7 T. The M vs. H/T curves were plotted in Fig. S11b and 11d.† Their measured magnetizations at 2 K rapidly increased in the lowfield region, but gradually became flat in the high-field region. Dy_6 reached a maximum value of 75.98N β , while HNP-Dy₆

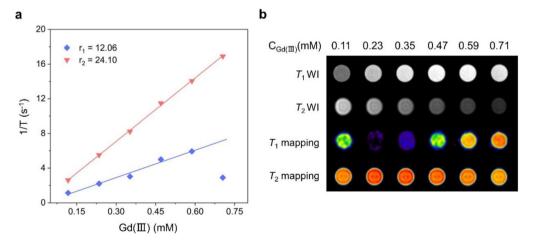


Fig. 7 (a) Comparison of the r_1 and r_2 of Gd₆ under 1-T magnetic field and (b) comparison of the solution imaging of different Gd₆ concentrations under 1-T magnetic field.

reached 36.90N β at a 13 kOe static field. The M vs. H/T curves of Dy_6 and $HNP-Dy_6$ at different temperatures did not significantly overlap. The test results indicated that the Dy(III) ions may have low excited states and/or a large magnetic anisotropy. The hysteresis loops of Dy₆ and HNP-Dy₆ in Fig. S12† were not obvious at 2 K, which may be due to the existence of the crystal field and strong quantum tunneling effects. We further tested the alternating-current susceptibility of Dy6 and HNP-Dy₆ to explore their dynamic magnetic behavior. We found that neither of the Dy₆ nor HNP-Dy₆ out-of-phase (χ'') signals showed an obvious frequency-dependent behavior under the zero DC field (Fig. S13†). Generally speaking, multinuclear gadolinium clusters have better MCE properties and can be used as an excellent magnetocaloric material.^{51,52} We tested the magnetocaloric effect of Gd₆ at 2-8 K and 0-7 T. As shown in Fig. S14,† when T = 2 K and $\Delta H = 7$ T, the maximum experimental entropy change value of Gd₆ is 25.76 J kg⁻¹ K⁻¹, which is smaller than the theoretical $-\Delta S_{\rm m}$ value (40.06 J kg⁻¹ K^{-1}), calculated based on the formula: $-\Delta S_{\rm m} = nR \ln(2S + 1) (R$ = 8.3145 J mol⁻¹ K⁻¹, S = 7/2). This can be attributed to the antiferromagnetic interaction between Gd(III) ions. 17 In addition, its $-\Delta S_{\rm m}$ value is higher than most of the reported hexanuclear gadolinium clusters, showing better MCE performance. 26,51 Therefore, magnetic studies show that **Gd**₆ is a potential magnetic refrigeration material.

Conclusions

In conclusion, diacylhydrazone-derived ligands are used to enable controllable construction of differentiated hexanuclear lanthanide clusters with identical cores but different templatemotif arrangements. Different substituents are used to regulate the template-motif arrangements formed by multidentate chelating ligands, taking a big step toward the controllable and precise synthesis of lanthanide clusters. HRESI-MS results prove that the two hexanuclear lanthanide clusters obtained herein exhibit high stabilities in solutions. Time-dependent HRESI-MS is employed to track the formation of these hexanuclear lanthanide clusters and propose their possible formation mechanisms. The findings reveal a novel strategy for the rational construction of lanthanide clusters with specific shapes and template-motif arrangements. Notably, the aggregation of Gd(III) ions leads to considerably enhanced relaxation rates of the Gd₆ clusters and an excellent MRI resolution. Magnetic studies show that Gd₆ exhibits remarkable MCE performance, which can be used as a potential magnetic refrigeration material. This work presents a new idea for the controllable synthesis of complex clusters and promotes progress in the crystal engineering of clusters with precise structures.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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