Article

The Assembly of Grid-type Lanthanide Cluster

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Abstract: A dicompartmental Schiff base ligand was synthesized and used for the assembly of a lanthanide grid-like complex. Dinuclear **Dy₂** and tetranuclear **Dy₄** complexes were isolated from the reaction of the ligand with different dysprosium salt. Single crystal X-ray diffractions show that the two Dy^{III} ions in **Dy₂** are adopted in the N_3O coordination pockets of the ligand and further coordinated by water molecules, whereas, for **Dy₄**, the four Dy^{III} ions are clamped by four ligands through their terminal N_3O coordination pockets, forming a grid-type assembly. Magnetic studies reveal that complex **Dy₂** shows field-induced single-molecule magnetic behavior under 1000 Oe dc field, complex **Dy₄** shows fast relaxation under zero field and field-induced single-molecule magnet (SMM) behavior under 500 Oe. The difference in the magnetic relaxation is related to the various deprotonation of the ligand and distinct topology of the assemblies.

Keywords: lanthanide complex; grid topology; field-induced SMM; QTM

1. Introduction

Lanthanides single-molecule magnets (Ln-SMMs) have attracted much attention since the first discovery of $(Bu_4N)[Tb(Pc)_2]$ [1], which shows record energy barriers and different relaxation mechanisms from that of the transition-metal-cluster SMMs. Since then, lanthanide has become the best candidate for the design and synthesis of high-performance SMMs [2–5] due to its potential applications in high-density information storage, quantum information processing [6], and molecular spintronic materials [7–12]. During the last two decades, thousands of Ln-SMM have been reported, and the record energy barrier (U_{eff}) and blocking temperature (T_B) were refreshed up to 1541 cm^{-1} and 80 K,[13] respectively, pushing the potential application of SMMs into reality. However, due to the presence of fast quantum tunneling of magnetization (QTM), the relaxations of magnetizations in most of the reported SMMs are short cut, resulting in a relatively low blocking temperature [14–16].

One efficient way for suppressing QTM in Ln-SMM is restricting the lanthanide ions in an axial ligand field, such as $C_{\infty v}$ [17,18], D_{4d} [19–22], D_{5h} [23–25], and D_{6d} coordination geometries for Dy^{III} ions. Due to the inherent high coordination number and flexible coordination nature of lanthanide ions, it is very difficult and challenging to fix the lanthanide ions in a perfect due coordination geometry. Alternatively, introducing magnetic interaction between lanthanide ions can suppress the QTM efficiently [26], especially in polynuclear SMMs. For instance, the reported single-electron Ln–Ln coupling in dimetallofullerenes shows very strong exchange interactions between 4f moments that result in a gigantic coercivity of 8.2 teslas at 5 K and blocking temperature up to 25.2 K [27–29]. Long and co-workers reported a mixed-valence dilanthanide complexes $(CpiPr_5)2Dy_2I_3$ that gives rise to an enormous coercive magnetic field with a lower bound of 14 tesla up to 60 K [30]. Additionally, high-performance polynuclear SMMs are also found in radical [31–33] and μ_2-OH$^-$ bridged [34–36] dinuclear lanthanide complexes, in which the spin centers are in axial ligand field and strongly coupled, suppressing the QTM efficiently. For Ln-SMMs with higher nuclearity, the poor axial ligand field, as well as the complicated topology of

the molecule, make it difficult to manipulate the relaxation processes and suppress the QTM [37–39].

Our research interests are focused on the unique magnetic behavior [40] in grid-type lanthanide assemblies, in which the QTM could be suppressed by the magnetic interaction between lanthanide ions [41]. For this, we have designed several types of ditopic and tritopic hydrazone ligands with suitable coordination pockets to accommodate lanthanide ions and arrange them in a grid [42–44] or hexagonal [45–47] topology. Herein, the linkers in the ligands are very important for the transmission of intermolecular magnetic interactions. As was reported in the literature, pyrimidine is a good linker to arrange transition metal ions into grid-type topologies [48–52]. However, the assembly of lanthanide grids based on pyrimidine ligands is rare [53]. Herein, we designed a pyrimidine-based dicompartmental Schiff base ligand with a pyrimidine linker, by using which a dinuclear **Dy₂** was isolated (Scheme 1). After optimizing the reaction conditions, tetranuclear **Dy₄** featuring a [2 × 2] grid topology was also obtained. The magnetic study revealed that complex **Dy₂** shows field-induced single-molecule magnetic behavior under a 1000 Oe dc field. **Dy₄** shows fast relaxation under zero field, which was slowed down by the application of 500 Oe, resulting in the field-induced single-molecule magnet.

Scheme 1. Schematic drawing of the assemblies of complexes **Dy₂** and **Dy₄** from the dicompartmental Schiff base ligand.

2. Materials and Methods

2.1. Synthesis of Ligand H₂L

A 100-mL flask was charged with a magnetic stirrer bar and 4,6-dihydrazineylpyrimidine [54] (1.4 g, 10 mmol, 1 eq) in 50 mL methanol. 6-(hydroxymethyl)-2-carbaldehydepyridine [55] (2.74 g, 20 mmol, 2 eq) was then added. The reaction was stirred and refluxed overnight. Upon cooling, the precipitate was filtered, washed with ether, and dried under vacuum, giving the pure product **H₂L** (((pyrimidine-4,6-diylbis(hydrazin-2-yl-1-ylidene))bis(methaneylylidene))bis(pyridine-6,2- diyl))dimethanol) as a pale yellow powder. Yield: 3.1 g (82%). Elemental analysis (%) calcd for $C_{18}H_{18}N_8O_2$, MW = 378.16: C, 57.14, H, 4.79, N, 29.61; found C, 57.28, H, 4.81, N, 29.65. ^{1}H NMR (500 MHz, DMSO-d_6) δ = 11.43 (2 H, s), 8.24 (1 H, d, J 0.9), 8.14 (2 H, s), 7.93–7.85 (4 H, m), 7.46 (2 H, d, J 7.3), 6.94 (1 H, s), 5.47 (2 H, d, J 6.0), 4.62–4.58 (4 H, m). IR (KBr disks) $\tilde{v}$ [cm^{-1}] = 3394 (w), 3190 (m), 3047 (w), 1608 (s), 1585 (s), 1562 (s), 1504 (m), 1462 (m), 1421 (m), 1375 (m), 1323 (m), 1255 (m), 1198 (m), 1134 (s), 1084 (m), 993 (m), 916 (w), 833 (s), 746 (s), 719 (m), 651 (m), 624 (w), 561 (w), 501 (w) 463 (w).

2.2. Synthesis of Dy₂

DyBr₃·9H₂O (0.6 mmol) and ligand **H₂L** (0.2 mmol) in a mixture of 10 mL methanol and 5 ml DCM was stirred at room temperature for 10 min. The reaction was stirred at room temperature overnight. The solution was filtered and exposed to air to allow the slow evaporation of the solvent. Yellow crystals of **Dy₂** suitable for X-ray diffraction were

obtained after 4 days. Yield: 90 mg, (32%, based on metal salt). Elemental analysis (%) calcd for $[Dy_2(H_2L)(H_2O)_{10}]\cdot Br_6\cdot 3H_2O$ ($C_{18}H_{44}Br_6Dy_2N_8O_{15}$, MW = 1417.07): C, 15.26, H, 3.14, N, 7.91; found C, 15.28, H, 3.11, N, 7.85. IR (KBr disks) $\tilde{\upsilon}$ [cm^{-1}] = 3336 (br, w), 3207 (br, w), 3060 (br, w), 1635 (s), 1610 (s), 1568 (m), 1531 (w), 1514 (w), 1487 (m), 1456 (m), 1410 (w), 1290 (m), 1221 (w), 1188 (s), 1146 (m), 1101 (w), 1049 (w), 1012 (w), 827 (w), 740 (w), 696 (w), 655 (w), 605 (w), 567 (w), 544 (m), 501 (w), 476 (m), 459 (w), 447 (w).

2.3. Synthesis of **Dy₄**

A mixture of $Dy(ClO_4)_3\cdot 6H_2O$ (0.3 mmol) and ligand **H₂L** (0.2 mmol) in a mixture of 10 mL methanol and 5 ml DCM was stirred at room temperature for 10 min, triethylamine (0.2 mmol) was then added dropwise. The reaction was stirred at room temperature overnight. The solution was filtered and exposed to air to allow the slow evaporation of the solvent. Yellow crystals of **Dy₄** suitable for X-ray diffraction were obtained after 5 days. Yield: 97 mg (65%, based on metal salt). Elemental analysis (%) calcd for $[Dy_4L_4]\cdot(ClO_4)_4\cdot 12MeOH\cdot 4H_2O$ ($C_{84}H_{120}Cl_4Dy_4N_{32}O_{40}$, MW = 3009.91): C, 33.52, H, 4.02, N, 14.89; found C, 33.49, H, 4.03, N, 14.78. IR (KBr disks) $\tilde{\upsilon}$ [cm^{-1}] = 3456 (br, w), 3343 (br, w), 3016 (br, w), 2981 (br, w), 1635 (s), 1606 (s), 1558 (m), 1533 (m), 1477 (s), 1417 (m), 1375 (w), 1297 (m), 1223 (w), 1193 (s), 1145 (w), 1101 (s), 1036 (w), 1006 (w), 898 (w), 771 (w), 654 (w), 625 (m), 597 (w), 578 (w), 525 (w), 501 (w), 469 (w).

2.4. Crystallography

Single-crystal X-ray diffraction data were collected by the Bruker Apex II CCD diffractometer (Bruker AXS GMBH, Germany), using graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). In the Olex2 package [56], the structures were solved by using SHELXT [57] (direct methods), and all non-hydrogen atoms were refined by using SHELXL [58] (full-matrix least-squares techniques) on $F2$ with anisotropic thermal parameters). All hydrogen atoms were introduced in calculated positions and refined with fixed geometry relative to their carrier atoms. The solvent voids (164.1 Å^3 and 14.1 e$^-$ peer cell) in **Dy₄** were refined using a solvent masking routine in the Olex2 package. Due to the poor diffraction of **Dy₄**, it is difficult to introduce hydrogen atoms on some of the solvent molecules in the lattice. Crystallographic data of **Dy₂** and **Dy₄** are listed in Table S1. CCDC 2220302 and 2220303 contain supplementary crystallographic data for this paper.
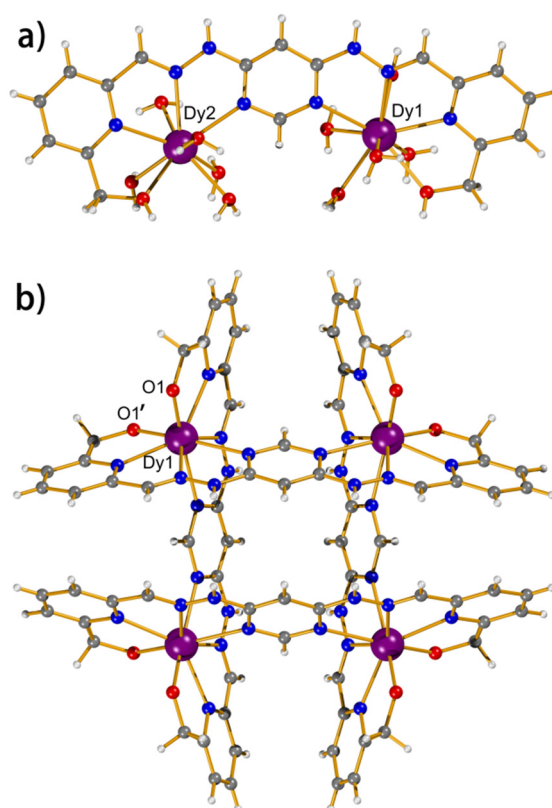
2.5. Magnetic Measurements

Magnetic measurements were performed by using a Quantum Design MPMS-XL-7 SQUID magnetometer (Quantum Design, United States) equipped with a 7 T magnet. Susceptibility measurements were carried out on the polycrystalline sample of the two complexes. In the temperature range of 2–300 K, the direct-current (dc) susceptibility measurements were obtained under an applied field of 1000 Oe. Diamagnetic corrections were made with Pascal's constants [59] for all the constituent atoms and the contributions of the sample holder. The field-dependent magnetizations were obtained in the field range of 0−7 T. In the frequency range of 1–1488 Hz, the alternating-current (ac) susceptibility measurements were obtained in a 3 Oe ac oscillating field under various dc fields.

3. Results and Discussions

3.1. Structures of **Dy₂** and **Dy₄**

The ligand H₂L ((((pyrimidine-4,6-diylbis(hydrazin-2-yl-1-ylidene)) bis(methaneylylidene))bis(pyridine-6,2-diyl))dimethanol) was synthesized from the condensation of 4,6-dihydrazineylpyrimidine and 6-(hydroxymethyl)-2- carbaldehyde-pyridine in good yield (Figure S1). As shown in Scheme 1, two four-membered O-N-N-N pockets reside at both sides of the ligand, which can capture two Dy^{III} ions in a planar arrangement. Indeed, a dinuclear **Dy₂**, with formula of $[Dy_2(H_2L)(H_2O)_{10}]\cdot Br_6\cdot 3H_2O$, was obtained from the reaction of DyBr₃·9H₂O (0.6 mmol) and ligand H₂L. Yellow crystals of **Dy₂** suitable for X-ray diffraction were obtained after the workup. Single-crystal X-ray diffraction revealed

that complex **Dy₂** crystallizes in the triclinic space group *P*-1 with *Z* = 2 (Table S1). The asymmetric unit contains one ligand, two Dy^{III} ions, ten coordinated water, six free Br^-, and three water molecules in the lattice. The ligand is not deprotonated and coordinates with the Dy^{III} ions by its coordination pockets on both sides (Figure 1a). **Dy₁** and **Dy₂** reside in the four-membered O-N-N-N pocket, with each further coordinated with five H_2O molecules, forming a nine-coordination environment (O_6N_3). The Dy-O bonds are in the range of 2.37–2.46 Å, which is much shorter than the Dy-N bond (2.50–2.57 Å, Table S1), probably because of the hard-base behavior of the coordinated O atoms. The Dy^{III} ions in the molecule are separated by the pyrimidine group with a distance of 6.67 Å. The Br^- anions reside in the lattice to balance the positive charge of the molecule and form hydrogen bondings with the coordinated and free H_2O, bridging the molecules into three-dimensional frameworks (Figure S6).

Figure 1. Structures of complexes **Dy₂** (**a**) and **Dy₄** (**b**). The cations and solvents have been omitted for clarity.

After adjusting the ligand–metal ratio and reaction conditions, fortunately, a tetranuclear grid-like complex **Dy₄** ([Dy₄L₄]·(ClO₄)₄·12MeOH·4H₂O) was isolated. Single crystal X-ray diffraction shows that complex **Dy₄** crystallizes in the tetragonal space group *P4₂/nmc* with *Z* = 2. The molecule contains four double deprotonated ligands, four Dy^{III} ions, four perchloride, and some solvent molecules (MeOH and H_2O) in the lattice. The molecule features a [2 × 2] grid topology with the four ligands as the edges and four Dy^{III} ions bending in the corners (Figure 1b). Due to the high symmetry of the molecule, all the Dy^{III} ions and ligands are identical, with each Dy^{III} ion clamped by two N₃O coordination pockets from two crossed ligands, forming an eight-coordination environment. The ligands are deprotonated on both hydroxymethyl group sites, resulting in relatively short Dy-O bonds (2.27 Å), which is also much shorter than that of in complex **Dy₂** (Dy-O > 2.39 Å). The shortest intramolecular Dy···Dy distance is 6.9 Å longer than that of **Dy₂** (6.67 Å). This can be ascribed to the deprotonation of the hydroxymethyl groups that drag the Dy^{III} ions close to the terminal sites of the ligand. The long Dy···Dy distance suggests the
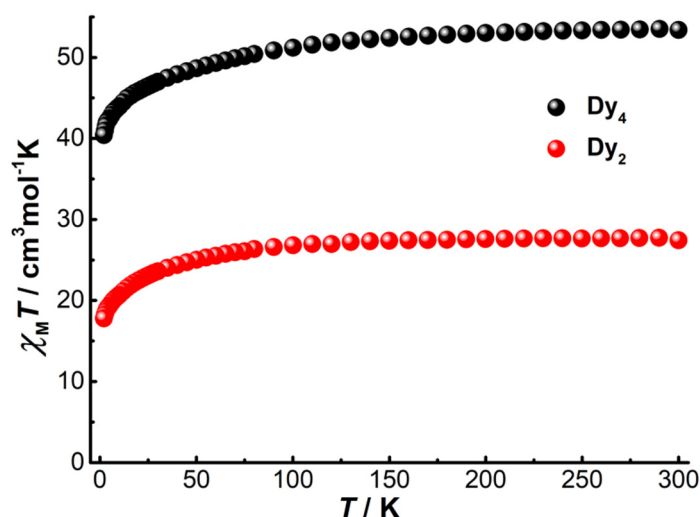
weak or negligible magnetic exchange interaction within the complex. The molecules pack along the crystallographic *C* axis and are separated by the ClO_4^- and solvent molecules in the lattice.

To gain more insight into the coordination difference of Dy^{III} ions in the two complexes, the coordination geometries of the Dy^{III} centers were quantified by the SHAPE analyses [60,61]. As shown in Figure S8, the Dy^{III} ions in **Dy₂** are both nine coordinated, and the coordination geometry of Dy1 and Dy2 in **Dy₂** are close to Muffin (C_s) with CShM value of 1.369 and capped square antiprism (C_{4v}) with CShM value of 0.743 (Table S4), respectively. In **Dy₄**, the four Dy^{III} ions are identical, and eight are coordinated in an N_6O_2 coordination environment, the coordination geometry for Dy1 in a large distorted augmented trigonal prism (C_{2v}) with a CShM value of 3.284. The difference in the coordinate geometry of the Dy^{III} ions in **Dy₂** and **Dy₄** will influence the magnetic relaxation significantly (see below).

3.2. Magnetic Properties of **Dy₂** and **Dy₄**

3.2.1. Static Magnetic Properties of **Dy₂** and **Dy₄**

Direct current (dc) magnetic susceptibility measurements were carried out on polycrystalline samples under an applied field of 1000 Oe in the temperature range of 2–300 K. As shown in Figure 2, the temperature-dependent $\chi_M T$ product (χ_M = molar magnetic susceptibility) of the two complexes show similar profiles. The $\chi_M T$ at 300 K are 27.44 and 53.39 cm³·K·mol⁻¹ for **Dy₂** and **Dy₄**, respectively, which are close to the expected value for two (28.34 cm³·K·mol⁻¹) and four (56.68 cm³·K·mol⁻¹) free-ion approximation of Dy^{III} ions ($S = 5/2$, $L = 5$, $^6H_{15/2}$, $g = 4/3$). Upon cooling, the $\chi_M T$ products decrease gradually before a quick drop below 10 K and reach the value of 17.78 cm³·K·mol⁻¹ (**Dy₂**) and 40.41 cm³·K·mol⁻¹ (**Dy₄**) at 2 K. The quick drop of the $\chi_M T$ products at low temperatures can be ascribed to the thermal depopulation of the Stark sublevels as well as the possibility of dominated weak antiferromagnetic interaction between the Dy^{III} ions.
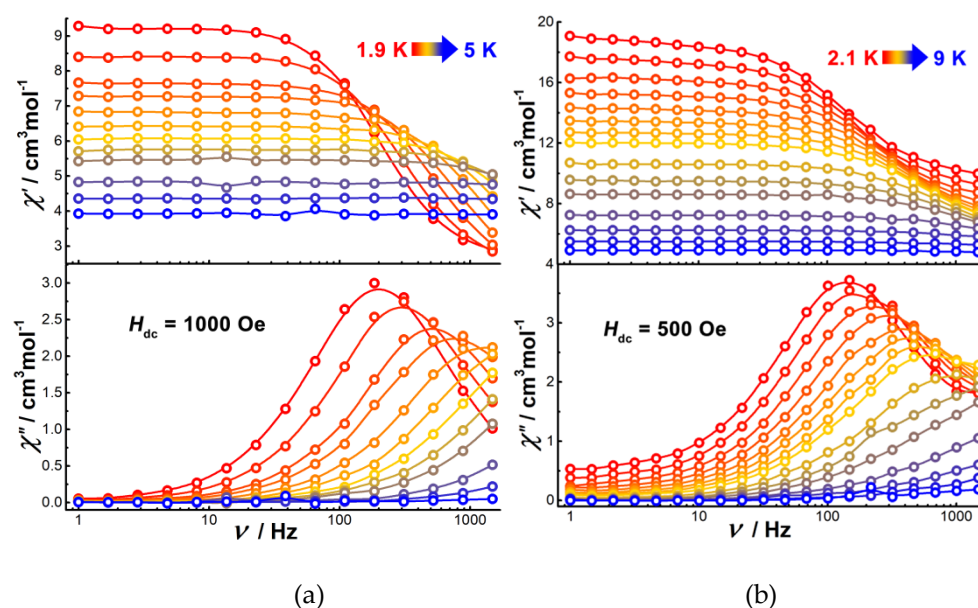

Figure 2. Temperature-dependent $\chi_M T$ products at 1 kOe between 2 and 300 K for **Dy₂** and **Dy₄**.

The field-dependent molar magnetizations (*M*) *vs. H* plot for **Dy₂** and **Dy₄** at 1.9 K (Figures S10 and S11) shows a sharp increase at low fields and then linear increases at high fields, reaching the values of 10.68 μ_B (**Dy₂**) and 19.85 μ_B (**Dy₄**) at 7 T, which are close to the expected value for two (10 μ_B) and four Dy^{III} ions (20 μ_B) in a pure $m_J = |\pm15/2>$ ground state. The *M* versus *H* curves at 3 and 5 K also show similar increasing tendencies but do not overlap on the curve at 1.9 k, which can be attributed to significant magnetic anisotropy and/or the existence of low-lying excited states.

3.2.2. Dynamic Magnetic Properties of **Dy₂** and **Dy₄**

To investigate the dynamics of magnetization, alternating current (AC) susceptibility measurements were carried out with an oscillating field of 3.0 Oe. However, complex **Dy₂** does not show any relaxation under zero dc field. It seems the magnetic interactions between the two Dy^{III} ions are very weak and cannot suppress the fast relaxation of the complex. Field-dependent ac susceptibility measurements were carried out at 1.9 K with a frequency of 1000 Hz. As shown in Figure S12, the out-of-phase ac susceptibility (χ'') peak is detected around 1000 Oe, which should be the optimized dc field that can slow down the magnetic relaxation. Thus, we performed the ac susceptibility measurements under 1000 Oe dc field, and the temperature-dependent χ'' showed frequency-dependent peaks at low temperatures (Figure S13), indicating the slow relaxation of the magnetization. The frequency-dependent χ'' peaks shift to a higher frequency when raising the temperature, suggesting the thermal relaxation behaviors. For complex **Dy₄**, the χ'' signals are observed under zero dc field but without peaks (Figure S14). This is probably related to the fast relaxation of QTM that shortcuts the relaxation of the magnetization.[62,63] This kind of relaxation can usually be suppressed by the application of dc field.[64,65] The optimized dc field was determined through the field-dependent ac susceptibility measurements (Figure S15), giving the optimized dc field of 500 Oe. After applying this dc field, frequency- and temperature-dependent χ'' peaks were observed in the ac measurements (Figures 3 and S16), indicative of the field-induced single-molecule magnetic property.
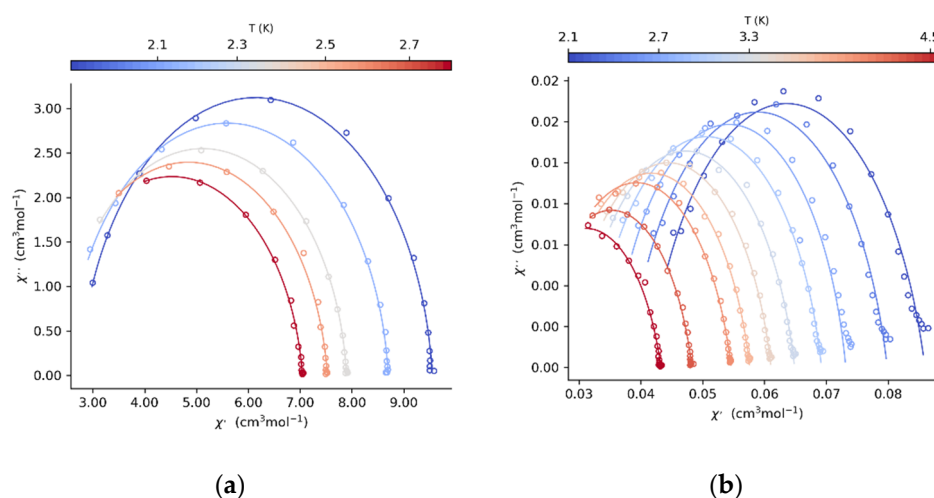

Figure 3. Frequency-dependent ac susceptibility of **Dy₂** (**a**) and **Dy₄** (**b**) under indicated dc field and temperature. The dots and solid lines are the data from ac measurements.

To explore the magnetic relaxation mechanics, Cole–Cole plots were represented as χ'' versus χ' (Figure 4). For complexes **Dy₂** and **Dy₄**, the Cole–Cole plots show semi-circular profiles (Figure 4), suggesting the presence of a homogeneous relaxation process. Fitting the Cole–Cole plots with the *CC-FIT2* program [66] using the Debye model [67] gives the temperature-dependent relaxation time. The relevant parameters of the fitting results are listed in Tables S5 and S6. Thereafter, we fit temperature-dependent relaxation by the following equation [68] to investigate the mechanics of the relaxation process:
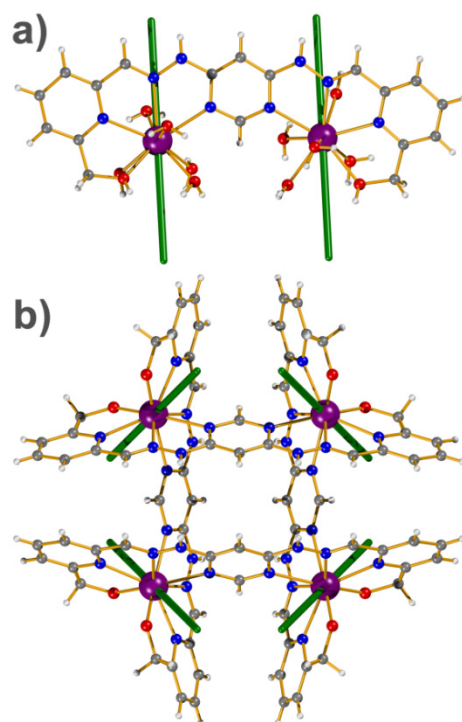
$$\frac{1}{\tau_{\text{obs}}} = \frac{1}{\tau_{QTM}} + AH^4 T + CT^n + \tau_0^{-1}\exp\left(-U_{eff}\big/T\right) \qquad (1)$$

where $1/\tau_{QTM}$, AH^4T, CT^n, and $\tau_0^{-1} \cdot \exp(-U_{eff}/T)$ represent quantum tunneling, direct, Raman, and Orbach relaxation processes, respectively. The relevant parameters obtained from the best fittings are listed in Table S7. Both complexes show Raman and Orbach relaxation processes with comparative Raman relaxation parameters (Table S7). The energy barriers of the two complexes are also comparative with $U_{eff} = 17(4)$ K, $\tau_0 = 4.3(3) \times 10^{-7}$ s, $C = 144(5)$ $s^{-1} \cdot K^{-n}$, and $n = 3(0.3)$ for **Dy$_2$**, and $U_{eff} = 16(2)$ K, $\tau_0 = 1.0(2) \times 10^{-3}$ s, $C = 98(9)$ $s^{-1} \cdot K^{-n}$, and $n = 3(0.8)$ for **Dy$_4$**.

Figure 4. Cole-Cole plots for **Dy$_2$** under 1000 Oe (**a**) and **Dy$_4$** under 500 Oe (**b**) at the indicated temperature range. The solid lines represent the best fit.

The low energy barriers for both complexes are probably related to the poor axial ligand field of the Dy^{III} ions. In complex **Dy$_2$**, the Dy^{III} ions reside in nine coordination environments with Dy-O bond length in the range of 2.37–2.46 Å and Dy-N bond of 2.50–2.57 Å, which indicate a relatively weak ligand field. For **Dy$_4$**, the deprotonated hydroxymethyl groups give two shortest Dy-O bonds of 2.27 Å, which probably provides an axial ligand field that dominates the anisotropy of the complex. In order to investigate the anisotropies differences in the two complexes, we use the Magellan program [69] to calculate the anisotropy axes of each Dy^{III} ion. The calculation is based on the X-ray structures and electrostatic model of the complexes, with the Dy^{III} ions containing three positive charges and the coordinated O$^-$ and free Br$^-$ possessing one negative charge. For complex **Dy$_2$**, the anisotropy axes of Dy1 and Dy2 are close to the cape-point of the capped square antiprism coordination polyhedron (Figure 5). For complex **Dy$_4$**, the anisotropy axis of the Dy1 is parallel to the O1···O1' direction (Figure 5), which is beneficial from the shortest Dy-O bonds (2.27 Å) that provides a relatively stronger axial ligand field. Therefore, complex **Dy$_4$** shows magnetic relaxation under zero field and a relatively slower relaxation time at low temperatures than that of **Dy$_2$**.

Figure 5. Orientations of the main magnetic axes of the ground state of **Dy2** (**a**) and **Dy4** (**b**) calculated based on the molecule structure.

4. Conclusions

In conclusion, we synthesized a novel dicompartmental Schiff base ligand based on pyrimidine, by using which a dinuclear **Dy2** and tetranuclear **Dy4** grid were constructed. Due to the distinct coordination environments and topology in the two complexes, the magnetic relaxation of these complexes is different. In **Dy2**, the Dy^{III} ions are in a relatively weak ligand field with relatively long coordination bonds; therefore, the complexes only show field-induced single-molecule magnet behavior. For complexes **Dy4**, the deprotonated ligand gives a pair of relatively short Dy-O bonds, resulting in the axial ligand field that slows down the relaxation. Therefore, complex **Dy4** shows relaxation under zero dc field and field-induced single-molecule magnetic behavior under 500 Oe dc field. Although the magnetic interactions in both complexes are weak and have no positive effect on the magnetic relaxation, the assembly of grid-type lanthanide clusters in the work provides an efficient strategy to regulate the topology of lanthanide ions. The next step will be focused on the enhancement of the magnetic coupling between lanthanide ions.

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