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Probing the magnetic relaxation and magnetic moments arrangement in a series of Dy₄ squares

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Three *u*-0 bridged Dy₄ squares, {[Dy₄(µ₄-O)(HL¹)₄(H₂O)₄]₂(NO₃)₃(OH)}·2H₂O·2CH₃OH (1). [Dy₄(μ₄- $O(HL^2)_4(SCN)_2$ $2H_2O + 4CH_3OH$ (2) and $[Dy_4(\mu_4 - O)(H_2L^3)_2(SCN)_2] + 6H_2O$ (3) were assembled by using a Schiff base ligand and its dimerized and reduced congener, respectively. These complexes share a similar μ -O bridged Dy₄ core, while, both the coordination geometry and metal-ligand interactions are slightly changed upon the modulation of the ligands, resulting in distinct single-molecular magnetic (SMM) and single-molecular toroic (SMT) properties. In complex 1, the Schiff base ligands are in antiparallel fashion and all Dy^{III} ions are in similar coordination geometry, realizing the toroidal arrangement of magnetic moments. For complex 2, the reduced ligand H_3L^2 in a parallel fashion results in double relaxation processes and 9-fold increase of the U_{eff} . Interestingly, with the use of the dimerized ligand H_{el}^{3} , we obtained complex **3**, which is similar to complex 2, while due to the slight changes of the coordination environment both the single molecular magnetic property and toroidal magnetic moments almost disappeared.

Introduction

As one of the most promising molecule-based materials, single-molecule magnets (SMMs)¹ that span chemistry, physics and material sciences have become a hot area of research due to their potential application in quantum computing and information storage.²⁻⁶ During the past two decades, hundreds of complexes showing SMM behavior have been reported.⁷⁻⁹ Especially, lanthanide based complexes have attracted increasing attention recently.¹⁰⁻¹⁸ Among these complexes, there is a special group of multinuclear clusters, namely singlemolecular toroic (SMT).^{19, 20} A basic feature of SMTs is wheel shaped distribution of magnetic moments $T = \sum_{i=1}^{N} r_i \times s_i$ (N \geq 2 spins per unit cell),²¹ whose spin carriers coupled through dipole interactions and/or exchange interactions. Thus, SMTs are a type of bistable molecules breaking both space inversion and time reversal symmetries,²²⁻²⁴ and seem to be used as multiferroic materials with magnetoelectric effect. Since the first discovery of the molecular based toroidal magnetic moments in 2006,19 a few numbers of SMTs have been reported in literature, such as Dy₃ triangles,²⁵⁻²⁷ Dy₄ squares,²⁸,

²⁹ and Dy₆ wheels.^{30, 31} In these complexes the anisotropic Dy^{III} ions are coupled through intramolecular interactions. Therefore, the toroidal magnetic moment is closely correlated to the anisotropy and magnetic interactions. Thus, we can enhance the toroidal magnetic moment by modulations of the axial anisotropy as well as the magnetic interactions.²⁰

Our previous interests have been focused on the enhancement of the toroidal magnetic moment. We have reported two decorated Dy₃ triangular compounds with tailored chemical modification of the o-vanillin group, in which the anisotropy of spin center can be significantly influenced.²⁵ Another effort to enhance the toroidal magnetic moment is the combination of multi-vortex-spin in one molecule. These fantastic works have been realized in vertex-to-vertex arranged Dy_3 triangles in Dy_6 complexes³² and the Cu^{II} bridged 1D CuDy₃ coordination polymer, 33 in which the vortex-spin in Dy₃ triangles coupled robustly through intramolecular and intra-chain interactions. Recently, we have arranged the Dy₃ triangles in an edge-to-edge arrangement, in which the very large toroidal moment has been achieved through the couplings via a μ_4 -O²⁻ ion.³⁴ With this in mind, we intend to introduce the μ_4 -O²⁻ ion in Dy₄ squares to enhance the SMT properties. With the use of bidentate Schiff base ligand H_3L^1 , we have obtained a μ_4 -O²⁻ bridged Dy₄ square. However during the course of this work, a very similar work by Rajaraman and co-workers appeared.²⁹ Therefore, we extend the modification of vortex-spin to this square arranged Dy₄ system by dimerizing and reducing the Schiff base ligands (Scheme 1). Herein, we report three μ_4 -O²⁻ bridged Dy₄ squares, namely, $[Dy_4(\mu_4-O)(HL^1)_4(H_2O)_4]_2(NO_3)_3(OH)\cdot 2H_2O\cdot 2CH_3OH$ (1), $[Dy_4(\mu_4-O)(HL^1)_4(H_2O)_4]_2(H_2O)_4(H_2O)_$ O)(HL^2)₄(SCN)₂]·2H₂O·4CH₃OH (2) and [Dy₄(μ₄- $O(H_2L^3)_2(SCN)_2] \cdot 6H_2O$ (3). Of particular interest is that the

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[†] Electronic Supplementary Information (ESI) available: Crystallographic data for complexes **1-3** are listed in Table S1. Selected bond lengths and angles are listed in Tables S2. Bond valence sum calculations are given in Tables S2. *SHAPE* and Magellan calculations are given in Tables S3-S4 and S5. IR and NMR spectra are depicted in Fig. S1-S4. The *M* vs *H* plots for compounds **1-3** are presented in Fig. S5-S10. Charges assigned to the ligands are given in Fig. S11. The temperature-dependent ac susceptibility and Cole-Cole plots are presented in Fig. S12-S17. See DOI: 10.1039/x0xx00000x

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vortex-spin structures and the magnetic relaxations are changed both through the modulations of the coordination environments and the square linkage motifs.



Scheme 1. Schematic drawing of the ligands H_4L (top), $H_3L^1,\ H_3L^2$ (middle) and H_6L^3 (bottom).

Experimental

Materials and measurements. All reagents and solvents were commercially obtained and used as received without any further purification. FTIR spectra were measured using a Nicolet 6700 IR Fourier spectrometer equipped with smart iTR[™] attenuated total reflectance (ATR) sampling accessory in the range from 500 to 4000 cm⁻¹ (Fig. S1). Elemental analyses for C, H, N and S were carried out on a Perkin-Elmer 2400 analyzer. ¹H NMR analyses were carried out using a Bruker Avance 400 spectrometer (Fig. S2-S4). Magnetic susceptibility measurements were measured on a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T magnet. The direct-current (dc) measurements were measured in the temperature range of 1.9-300 K with an external magnetic field of 1000 Oe. The alternating-current (ac) measurements were carried out in a 3.0 Oe ac field oscillating at different frequencies from 1 to 1500 Hz. Diamagnetic corrections were made with the Pascal's constants for all the constituent atoms as well as the contributions of the sample holder.³⁵

Synthesis of ligand H_3L^1 . Ligand H_3L^1 was synthesized by the same procedure as described previously.^{36, 37} In short, H_3L^2 obtained by the condensation of was 3methoxysalicylaldehyde 2-amino-2-methyl-1,3and propanediol in the molar ratio of 1:1 in 50 mL ethanol under heating at 80 °C for 12 h. Yield: 92%. Selected IR (cm⁻¹): 3176.35(br), 2999.94(w), 2904.66(w), 2839.63(w), 1637.22(s), 1604.98(s), 1543.54(m), 1493.99(s), 1442.01(m), 1393.77(w), 1369.34(w), 1339.11(w), 1217.02(s), 1159.77(m), 1063.38(s), 955.85(w), 925.41(m), 850.44(w), 778.52(w), 746.59(m), 719.59(w), 627.87(w).

Synthesis of ligand H_3L^2. Ligand H_3L^2 was obtained from H_3L^1 by reductive amination using NaBH₄ in dried methanol/dichloromethane. Yield: 87%. Selected IR (cm⁻¹): 3342.65(br), 2829.52(br), 1590.24(w), 1566.29(w), 1478.20(s),

1456.28(s), 1441.65(s), 1270.18(m), 1234.31(s), 1160.39(w), 1062.50(br), 887.63(w), 868.76(w), 846.31(w), 763.08(w), 729.49(m), 709.88(w), 599.84(w).

Synthesis of ligand H_6L^3. Ligand H_6L^3 was synthesized by the same procedure as H_3L^1 , using 1,3-bis(3-formyl-2-hydroxyphenoxy)propane to replace 3-methoxysalicylaldehyde. Yield: 92%. Selected IR (cm⁻¹): 3249.86(br), 2921.68(br), 1626.95(s), 1608.35(s), 1510.28(s), 1468.10(m), 1347.22(w), 1224.15(s), 1166.24(m), 1140.55(m), 1044.12(m), 944.71(w), 911.00(w), 731.76(m), 622.36(w), 571.70(m).

Synthesis of complex 1. The reaction of Dy(NO₃)₃·5H₂O (0.1 mmol) with H₃L¹ (0.1 mmol) in the presence of triethylamine (0.2 mmol), with 5:10 mL methanol/dichloromethane as the media was stirred at room temperature for one hour, then filtrated and left un-disturb, produced yellow crystals of **1** after 5 days in ~ 67% yield. Selected IR (cm⁻¹): 2992(w), 2900(w), 2832(w), 1644(s), 1620(s), 1579(s), 1549(w), 1474(s), 1329(s), 1253(m), 1224(s), 1173(w), 1078(m), 1036(w), 972(w), 862(w), 740(s), 621(w), 428(w). Anal. Calcd for $\{[Dy_4(\mu_4-O)(HL^1)_4(H_2O)_4]_2(NO_3)_3(OH)\}\cdot 2H_2O\cdot 2CH_3OH$

 $(C_{98}H_{149}Dy_8N_{11}O_{56},\ MW\ =\ 3677.28);\ C,\ 32.01\%;\ H,\ 4.08\%;\ N,\ 4.19\%.\ Found:\ C,\ 31.52\%;\ H,\ 4.16\%;\ N,\ 4.05\%.$

Synthesis of complex 2. The reaction of $Dy(SCN)_3 \cdot 6H_2O(0.1 mmol) with <math>H_3L^2(0.1 mmol)$ in the presence of KOH (0.1 mmol), with 10:10 mL methanol/acetonitrile as the media was stirred at room temperature for three hours, then filtrated and left un-disturb, produced colourless crystals of **2** after 7 days in ~ 59% yield. Selected IR (cm⁻¹): 3537.99(br), 3272.25(w), 3248.91(w), 3222.18(w), 2971.78(br), 2362.35(w), 2065.80(vs), 1481.96(s), 1382.41(m), 1309.52(m), 1253.18(w), 1228.18(m), 1188.02(w), 1088.75(m), 1060.11(m), 1034.01(w), 966.05(w), 890.29(w), 855.05(w), 768.43(w). Anal. Calcd for $[Dy_4(\mu_4 - O)(HL^2)_4(SCN)_2] \cdot 2H_2O \cdot 4CH_3OH$ (C₅₄H₈₈Dy₄N₆O₂₃S₂, MW = 1903.42): C, 34.06%; H, 4.63%; N, 4.33%, S, 3.37%. Found: C, 33.98%; H, 4.71%; N, 4.46%, S, 3.35%.

Synthesis of complex 3. Complex 3 was obtained from solvothermal reaction. A mixture of Dy(SCN)₃·6H₂O (0.2 mmol) with H_6L^3 (0.1 mmol) in the presence of triethylamine (0.4 mmol), with 6:6 mL methanol/acetonitrile as the solvent was sealed in a 20 mL Teflon-lined reactor and heated at 90 °C for 3 days and then cooled to room temperature at 5 $^{\circ}C \cdot h^{-1}$. Colourless block crystals were collected in 50% yield based on Dy(SCN)₃·6H₂O. Selected IR (cm⁻¹): 3271.88(br), 2970.04(w), 2923.01(w), 2836.27(w), 2041.89(vs), 1644.63(s), 1601.51(m), 1557.60(w), 1455.26(vs), 1388.65(s), 1286.48(s), 1258.28(w), 1218.69(m), 1196.00(m), 1174.72(w), 1088.17(s), 1066.80(m), 1032.74(m), 990.74(w), 932.83(w), 861.39(w), 841.53(w), 819.44(w), 777.74(w), 732.05(m0, 633.21(w), 614.95(w). Anal. Calcd for $[Dy_4(\mu_4-O)(H_2L^3)_2(SCN)_2]\cdot 6H_2O$ $(C_{52}H_{68}Dy_4N_6O_{23}S_2,$ MW = 1859.24): C, 32.49%; H, 3.59%; N, 4.59%, S, 3.31%. Found: C, 33.61%; H, 3.71%; N, 4.48%, S, 3.40%.

Crystallography. Single-crystal X-ray data of the title complexes (Table S1) were collected on a Bruker Apex II CCD diffractometer equipped with graphite-monochromatized Mo-K α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXTL-97.^{38, 39} All non-hydrogen atoms

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were determined from the difference Fourier maps and refined anisotropically. Hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. Crystallographic data are listed in Table 1. CCDC 1432430-1432432 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data request/cif</u>.



Fig. 1 Structures of $[Dy_4(\mu_4-OH)]$ (a), **1** (b), **2** (c) and **3** (d) with azure, dark, blue, red and orange spheres representing Dy, C, N, O and S, respectively; hydrogen atoms and solvents have been omitted for clarity.

Results and discussion

With the combination of bidentate Schiff base ligand H_3L^1 and $Dy(NO_3)_3$ ·5H₂O, in the presence of triethylamine, yellow crystals of complex {[Dy₄(μ_4 -

 $O(HL^{1})_{4}(H_{2}O)_{4}]_{2}(NO_{3})_{3}(OH)\}\cdot 2H_{2}O\cdot 2CH_{3}OH, 1, were obtained.$ Single crystal structure study reveals that complex 1 shows a μ_4 -O bridged Dy₄ square core, which is similar with the [Dy₄(μ_4 -OH)] reported by Rajaraman (Firure 1, a). The Dy₄ square is sandwiched by four deprotonated ligands HL¹, each two of which on the same sides of the square bridging the four $\mathrm{Dy}^{\mathrm{III}}$ ions in antiparallel fashion through two phenoxy oxygen atoms from the o-vanilins and two alkoxy oxygen atoms from hydroxymethyl arms. All the Dy^{III} ions adopt in similar monocapped square antiprism coordination geometry (Fig. 2). While due to the rigid Schiff base ligands and the asymmetric configuration of the square, the four Dy^{III} ions are not coplanar. Therefore, the Dy^{III} ions and the μ_4 -bridging O atom construct Dy₁-O₁-Dy₃ and Dy₂-O₁-Dy₄ angles of 164.86° and 166.06° (Table S2), which are smaller than the values (166.03° and 166.52°, respectively) reported in $[Dy_4(\mu_4-OH)]^{29}$ The relatively small angles of Dy-O-Dy can be properly attributed to the change of the μ_4 -O bridges and the secondary coordination environment. In complex 1, the bidentate hydroxymethyl arms replaced the tridentate hydroxymethyl group in $[Dy_4(\mu_4-OH)]$, resulting in a less deprotonated of ligands and the entire protonation of μ_4 -O²⁻ bridge. Thus, the average Dy-O and Dy-Dy distances (2.50 and 3.57 Å) are a litlle shorter than $[Dy_4(\mu_4 -$ OH)] (2.51 and 3.58 Å).²⁹ Although the bond valence sum calculations (BVS = 1.107) suggest that the valence of the center O atom should be OH⁻ (Table S3), the large space in the square make it difficult to form short Dy-O bonds (average bond of 2.28 Å for BVS = 2.02), which is consistent with the μ_{4} -O²⁻ bridged dysprosium compounds.⁴⁰⁻⁴² Herein, the coordination enviroment of the Dy centers for both complexes **1** and $[Dy_4(\mu_4-OH)]$ are almost the same (Table S4), the slight change on the metal-ligand interactions would influence the toroidal moments and magnetic relaxations significantly (see below).

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In contrast with the metal-ligand interactions, the coordination sphere can affect the magnetic anisotropy more directly and effectively. To investigate the influence, we used the reduced ligand H_3L^2 , in which the flexible hydroxymethyl arms can release the tension on the Dy₄ plane, to replace ligand H_3L^1 and Dy(SCN)₃·6H₂O to replace Dy(NO₃)₃·5H₂O. As expected, complex $[Dy_4(\mu_4-O)(HL^2)_4(SCN)_2]\cdot 2H_2O\cdot4CH_3OH$, **2**,

with μ_4 -O²⁻ bridging four Dy^{III} ions in the Dy₄ square, was obtained. Due to the rotatable C-N bond in ligand H₃L², the structure of **2** are totally different with complex **1** (Fig. 1). Firstly, complex **2** is centrosymmetric and the four Dy^{III} ions and the μ_4 -O²⁻ ion are coplanar in conplex **2** with average Dy-O and Dy-Dy distances of 2.48 and 3.51 Å, which are a little longer than the ones in **1**. Secondly, the two ligands on the

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same side of the square in complex 2 are arranged in a parallel fashion rather than antiparallel in complex 1, linking the four Dy^{III} ions through phenoxy oxygen atoms and alkoxy oxygen atoms. What's more, the four Dy^{III} ions in complex **2** are in two different types of coordination environment, that is, Dy1 is wraped by two hydroxymethyl arms from two ligands and adopts a nine coordinate tricapped trigonal prismic coordination geometry (Table S5), while Dy2 is wraped by phenoxy and methoxyls oxygen atoms from the o-vanillina part, and further charge balanced by one coordinated SCN⁻, forming an eight coordinate bicapped trigonal prismic coordinate sphere. More over, the distance of Dy1-O1 (2.494 Å) is longer than Dy2-O2 (2.466 Å), suggesting a compression along Dy2-Dy2A direction. These changes probably have a great impact on the magnetic anisotropy.



To modulate the coordination environment further, we designed a bi-Shiff bases ligand H_6L^3 , which can be regarded as methylene linked two ligand H_3L^1 . With utilization of ligand $H_6L^3,$ complex $[Dy_4(\mu_4\text{-}O)(H_2L^3)_2(SCN)_2]\cdot 6H_2O,$ 3, was obtained. Be similar with complex **2**, the structure of **3** also contains a μ_{4} - O^{2-} bridged Dy₄ square with two deprotonated ligands H₂L³ sandwiching the square on both sides and two coordinated SCN⁻ balancing the positive charge on the terminal sides. The coordination environment around Dy^{III} ions in complex **3** is similar with the corresponding Dy^{III} in complex **2**, while, due to the rigid methylene linker, the ligands are slight twisted and the methoxyls of the o-vanillin are close to each other with O-O distance of 2.80 Å, which is shorter than the one in 2 (3.06 Å), indicating a shrinkage of the coordinate sphere on Dy2, which is contrary to complex 2. What's more, the rigid C=N bonds of the ligand make the Dy₄ square a little compressed along Dy1-Dy1A direction with Dy1-O1 and Dy2-O2 distances of 2.453 and 2.532 Å, respectively. Herein, all the ligands in complexes 1, 2 and 3 (half of the ligand in 3) are in the same binding mode (Fig. 3), while the coordination motif of each ligand in these complexes is different. This can be ascribed to the dimerization and reduction of the Schiff base ligands.



Fig. 4 Temperature dependence of x_{MT} products at 1 kOe between 2 and 300 K for 1 (red), 2 (dark) and 3 (blue). Inset represents the plots of magnetization M versus *H*/*T* for **1-3** at 1.9 K.

All the differences both on the coordinate geometry and metal-ligand interactions probably make a significant influence on the magnetic relaxation as reported in the mononuclear and binuclear lanthanide systems. 43-48 In this work we intend to probe the influence on the toroidal magnetic moment in these Dy₄ square complexes. Therefore, direct current (dc) magnetic susceptibility measurements were performed on complexes 1-3 in the temperature range 2-300 K, in an applied field of 1000 Oe (Fig. 4). The $\chi_{\rm M}T$ product ($\chi_{\rm M}$ = molar magnetic susceptibility) versus T plots for all three complexes show similar tendency: the $\chi_{\rm M} \tau$ decrease slowly from the values of 54.70, 55.52 and 56.78 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **1**, **2** and **3** at room temperature, which are in good agreement with the value of 14.17 cm³·K·mol⁻¹ for each Dy^{III} ion, indicating the free-ion approximation applies, then decrease sharply when lowering the temperature, reaching the minimal values of 2.07, 7.33 and 12.97 cm³·K·mol⁻¹ at 2 K. The sharp decrease in $\chi_{\rm M}T$ at low temperature region can be probably attributed to the thermal depopulation of the excited m_1 states of the Dy^{III} ions and intramolecular antiferromagnetic exchange interactions.^{49,}

 $^{\rm 50}$ Interestingly, the minimal $\chi_{\rm M} {\it T}$ products for 1-3 are much smaller than the one in $[Dy_4(\mu_4-OH)]$ (25.4 cm³·K·mol⁻¹). Actually, the relatively small $\chi_{M}T$ products for all these complexes, especially for **1** (2.07 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$), probably result from strong intramolecular antiferromagnetic exchange interactions and/or toroidal arrangement of magnetic moments.



Fig. 5 M versus H plots for 1 (red), 2 (dark) and 3 (blue) at 1.9 K.

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To probe this effect, isothermal magnetization (M) measurements have been also performed on complexes 1-3. Both the magnetization versus field and H/T plots at 5 K (Fig. S5-S7) reveal quick increase without saturation until 7 T for all complexes, indicating magnetic anisotropy possibly presenting. While, when the measurement performed at 3 and 1.9 K, the magnetizations increase slowly at low field, then rise sharply before a smooth increase at high field, showing S shaped plots for all complexes. The slopes (d(M/Ms)/dH) of magnetization versus field data suggest less steep at low field and obvious inflection around 8 kOe for 1 (6, and 5 kOe for 2 and 3, respectively), at which field the field dependent out-of-phase (χ'') susceptibility maxima was identified (Fig. S8-S10). The M versus *H* plot of complex **1** displaying clear step at 1.9 K (Fig. 5) also evidences the toroidal arrangement of the magnetic moments.^{19, 27, 28} Furthermore, we calculated the anisotropy axes of these compounds using the Magellan $program^{51-53}$ (Fig. 6, Fig. S11 and Table S6). The results indicate that complex 1 shows net toroidal moment SMT behavior, while complexes 2 and 3 show similar parallel arranged anisotropy axes. Herein, the calculation was based on electrostatic model and didn't include the intramolecular interaction and excited states, further quantitative evaluation of the anisotropy axes and Dy-Dy coupling J values (dipolar and exchange interactions) through *ab initio* calculations is definitely needed.⁵⁴⁻⁵⁷



Fig. 6 Ground-state magnetic anisotropy of compounds 1 (a), 2 (b), and 3 (c). The green arrows represent the orientations of the anisotropic axes for each Dy^{III} ion, as calculated by the electrostatic model

The magnetic relaxation dynamics of all complexes were also investigated. Under a zero dc field, the variable temperature and frequency ac susceptibilities show the temperature and frequency dependent maximum for complexes 1 (Fig. S12) and 2 (Fig. S13), which is typical for SMM behavior. Alike to most SMT, the in-phase (χ') and outof-phase (χ ") susceptibilities show broad shoulders at low temperature region and drop suddenly upon further cooling. The sudden drop corresponds to the sharp decrease in $\chi_{M}T$ at low temperature, indicating a nonmagnetic ground state.³⁴ The broad shoulders at low temperature suggest the coalescence of the two peaks, indicating the possible presence of two relaxation processes.^{58, 59} Indeed, frequency dependent@@ac susceptibility measurements show broad peaks for complex 1 and two distinct peaks for complex 2 in the frequency dependent out-of-phase (χ ") susceptibilities (Fig. 7). To investigate the relaxation processes, the relaxation times were extracted from the frequency dependent ac susceptibility. The τ for complex **1** (Fig. S14) showing an exponential dependence on temperature was analysed by the Arrhenius law, giving the effective energy barriers (U_{eff}) of 6.5 K with pre-exponential factor (τ_0) of 2.7 × 10⁻⁵ s. While, for complex **2**, the two distinct peaks for the χ " give two relaxation regimes, namely fast relaxation phase (FR, with relatively short relaxation time) and slow relaxation phase (SR, with relatively long relaxation time). The plots were fitted using the equation shown below: 60-62

$$\frac{1}{\tau_{obs}} = \frac{1}{\tau_{QTM}} + AH^2T + CT^n + \tau_0^{-1} \exp(-U_{eff} / k_B T)$$
(1)

Where τ_{QTM} , AH^2T , CT^n , and $\tau_0^{-1}exp(-U_{eff}/k_BT)$ represent quantum tunnelling, direct, Raman, and Orbach relaxation processes, respectively. The best fit gives the $U_{\rm eff}$ of 57.6 K with $\tau_0 = 1.4 \times 10^{-7}$ s, $\tau_{QTM} = 9.9 \times 10^{-5}$ s, for FR phase and U_{eff} of 5.7 K with $\tau_0 = 1.2 \times 10^{-4}$ s, and $\tau_{QTM} = 4.8 \times 10^{-2}$ s for SR phase (Fig. 8). The Cole–Cole plots for complexes 1 and 2 was fitted well with the generalized Debye functions, 63 giving α values of 0.21–0.39 for 1 (Fig. S15), which is relatively large suggesting a multiple relaxation processes, and α_1 values of 0.04–0.27 and α_2 values of 0.12–0.22 for FR and SR phase, respectively, for 2 (Fig. S16).



Conclusions

rearrangement of the toroidal magnetic moments in SMMs and SMTs.

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Notes and references

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‡ The authors declare no competing financial interest.

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In contrast with complex 1 and 2, complex 3 just shows

slow magnetic relaxation behavior with none out-of-phase χ''

peak at zero field (Fig. S17). The change of the magnetic

properties in this series of compounds could be likely

attributed to the modulation of the ligand fields and

coordination environments. For complex **1** and $[Dy_4(\mu_4-OH)]$,

all the Dy^{III} ions reside in the equivalent position in the

anamorphic Dy₄ plane and share the similar coordinate sphere

of capped square antiprism (Table S4), which is beneficial for

the arrangement of magnetic moment in toroidal fashion.

Replacing Schiff base ligand with reduced H_3L^2 in complex 2,

the Dy₄ square becomes planar resulting in a shorter distance

between neighboring Dy^{III} ions, while the Dy^{III} ions are no

longer similar to each other. This leads to a regular parallel

arrangement of anisotropy axes. The structure of complex 3 is

similar with 2, while due to the rigid methylene linker and C=N

bond, the coordinate sphere of Dy2 is contracted and the Dy_4

square is compressed along Dy1-Dy1A direction, which is likely

to modify the anisotropy of Dy2 ions as well as the magnetic

interaction between the neighboring Dy^{III} ions, resulting in the

disappearance of the SMM behavior and toroidal magnetic

moment. Further theoretical calculations are planned to

elucidate more in-depth the non-collinear magnetic structure

In conclusion, modifying both the coordination geometry and

metal-ligand interactions by dimerizing and reducing the Schiff

base ligands have been realized in three μ_4 -O²⁻ bridged Dy₄

squares. With Schiff base ligand H_3L^1 bridging the four Dy^{III} ions

in an antiparallel fashion in complex 1, the Dy₄ square arranges

the magnetic moments in a net toroidal fashion; the utilization

of reduced ligand H_3L^2 in complex **2** makes the ligands bridge

the Dy^{III} ions in parallel fashion, resulting in a 9-fold increase of

the U_{eff} ; However, with the use of dimerized ligand H_6L^3 , we

obtained the isostructural complex 3, in which both the single

molecular magnetic property and toroidal magnetic moment

of such interesting systems.^{54, 55, 64-67}

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SYNOPSIS TOC

Modulations of the first and secondary coordination geometry by dimerizing and reducing the Schiff base ligands result in the enhancement of the magnetic relaxation and rearrangement of the magnetic moments in μ_4 -O²⁻ bridged Dy₄ squares.



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