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### Abstract

The syntheses, structures, and characterization of four 3d-4f defect-dicubane clusters are described. With different polyhydroxy Schiff-base ligands of 2-(((2-hydroxy-3-methoxyphenyl)methylene)amino)-2-(hydroxymethyl)-1,3-propanediol 2-(2,3-dihydroxpropyliminomethyl)-6-methoxyphenol  $(H_4L_1)$ and  $(H_{3}L_{2}),$ three self-assembled heterotetranuclear  $Ni_{2}^{II}Ln_{2}^{III}$  complexes ( $Ni_{2}^{II}Dy_{2}^{III}-L_{1}$  (1),  $Ni_{2}^{II}Tb_{2}^{III}-L_{2}$ (2),  $Ni^{II}_{2}Dy^{III}_{2}-L_{2}$  (3)) and one heterohexanuclear  $Co^{III}_{2}Dy^{III}_{4}$  complex (4) were obtained. The three heterotetranuclear Ni<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub> complexes display a central planar butterfly motif consisting of Ni<sup>II</sup><sub>2</sub>Ln<sup>III</sup><sub>2</sub>. The heterohexanuclear complex was built from defect-dicubane  $Co_{2}^{II}Dy_{2}^{II}$  clusters and two  $Dy_{2}^{II}$  ions by the bridging of pivalate. The vertices of the common face of the defect-dicubane core are occupied by transition metal ions in all four complexes. Magnetic analyses indicate that the complexes exhibit typical single-molecule magnet behaviour with anisotropy barriers of 33.7 cm<sup>-1</sup>, 60.3 cm<sup>-1</sup>, 39.6  $cm^{-1}$ , and 18.4  $cm^{-1}$  for 1–4, respectively. Ab initio calculations were performed on these complexes, and determined the low lying electronic structure of each  $Ln^{III}$  (Ln = Dy, Tb) ion and the magnetic interactions. It was found that the two Ln ions may have much more contribution to the total relaxation barrier through the stronger 3d-4f exchange couplings.



### Experimental and Theoretical Investigation of Four 3*d*-4*f*

### **Butterfly Single-Molecule Magnets**

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### Abstract

The syntheses, structures, and characterization of four 3d-4f butterfly clusters are described. With different Schiff-base polyhydroxy ligands of 2-(((2-hydroxy-3-methoxyphenyl)methylene)amino)-2-(hydroxymethyl)-1,3-propane diol  $(H_4L_1)$  and 2-(2,3-dihydroxpropyliminomethyl)-6-methoxyphenol  $(H_3L_2)$ , three heterotetranuclear  $Ni_{2}^{II}Ln_{2}^{III}$  complexes  $(Ni_{2}^{II}Dy_{2}^{III}-L_{1}$  (1),  $Ni_{2}^{II}Tb_{2}^{III}-L_{2}$  (2),  $Ni_{2}^{II}Dy_{2}^{III}-L_{2}(3)$  and one heterohexanuclear  $Co_{2}^{III}Dy_{4}^{III}$  complex (4) were obtained. The three heterotetranuclear  $Ni^{II}_{2}Ln^{III}_{2}$  complexes display a central planar butterfly topology. The heterohexanuclear complex was built from butterfly Co<sup>III</sup><sub>2</sub>Dy<sup>III</sup><sub>2</sub> cluster and two Dy<sup>III</sup> ions by the bridging of pivalate. The vertices of the body positions of the butterfly are occupied by transition metal ions in all four complexes. Magnetic analyses indicate that the complexes exhibit typical single-molecule magnet behaviour with anisotropy barriers of 33.7 cm<sup>-1</sup>, 60.3 cm<sup>-1</sup>, 39.6 cm<sup>-1</sup>, and 18.4 cm<sup>-1</sup> for 1-4, respectively. Ab initio calculations were performed on these complexes, and determined the low lying electronic structure of each  $Ln^{III}$  (Ln = Dy, Tb) ion and the magnetic interactions. It was found that the two Ln ions may have much more contribution to the total relaxation barrier through the stronger 3d-4f exchange

couplings compared to weak Ln-Ln interactions.

**Keywords:** 3*d*–4*f* heterometallic clusters; butterfly; magnetic properties; *Ab initio* calculations; single-molecule magnet

### Introduction

In the past two decades, single-molecule magnets (SMMs) have attracted great interest because of their underlying physical phenomena and potential applications such as quantum computing, high-density memory storage devices, and molecular spintronics.<sup>1-4</sup> The advantage of using lanthanide ions in the synthesis of new SMMs is that they will provide both large spin and considerable single ion anisotropy. However, the magnetic exchanges coupling interaction between 4f ions are weak and generally dipolar in nature.<sup>5</sup> A combination of two different spin carriers within the same molecular entity is a current strategy for obtaining new SMMs. The introduction of 3d ions into pure 4f systems has proven successfully in providing strong exchange interactions.<sup>6</sup> Two such examples have been reported by Murray et al. Co<sup>III</sup><sub>2</sub>Dy<sup>III</sup><sub>2</sub> and Cr<sup>III</sup><sub>2</sub>Dy<sup>III</sup><sub>2</sub> complexes that are bridged by benzoic acid show differently exchanged-couple, and result in  $U_{\rm eff}$  values of 88.8 and 77 K, respectively.<sup>7</sup> The barriers of two analogous are similar, however, the obvious magnetic hysteresis with large coercive magnetic fields was observed in the latter compound, which arises from the modification of the environment of Dy<sup>III</sup> when diamagnetic Co<sup>III</sup> ions are replaced by paramagnetic Cr<sup>III</sup> ions. Recently, Fe<sup>II</sup><sub>2</sub>Dy<sup>III</sup>, a compound with a record anisotropy barrier (459 K) for all d-f complexes, was reported by Tong et al.<sup>8</sup> This complex possesses two asymmetric and distorted Fe<sup>II</sup> ions and one quasi-D<sub>5h</sub> Dy<sup>III</sup> ion. The ferromagnetically coupled  $[Fe^{II}-Dy^{III}-Fe^{II}]$  unit together with the quasi- $D_{5h}$ symmetry of the Dy<sup>III</sup> ion are favorable for this system to show single-molecule magnets behavior. These results highlight the importance of the exchange coupling by introducing of 3d ions in lanthanide-based single-molecule magnets. Up to now, many different 3d-4f heterometal SMMs with different topological structures have been reported, such as Ni<sup>II</sup>-Ln<sup>III</sup>,<sup>9</sup> Co<sup>III</sup>-Ln<sup>III</sup>,<sup>10</sup> Cu<sup>II</sup>-Ln<sup>III</sup>,<sup>11</sup> Mn<sup>III</sup>, <sup>IV</sup>-Ln<sup>III</sup>,<sup>12</sup> Fe<sup>III</sup>-Ln<sup>III</sup>,<sup>13</sup>

Zn<sup>II</sup>-Ln<sup>III</sup>,<sup>14</sup> and Cr<sup>III</sup>-Ln<sup>III</sup>.<sup>15</sup>

The butterfly topology is one of the most familiar structural motifs in magneto-chemistry, and their magneto-structural correlations are often well discussed.<sup>16</sup> Among the SMMs with butterfly magnetic core,<sup>17-19</sup> the 3d-4fcompounds are very interesting from the viewpoint of the magneto-structural correlation study. They are able to show two different structure types, that is, the 4fions occupying the vertices of the body positions of the butterfly, and that of the opposite situation,<sup>20</sup> which are favorable for the investigation of the mechanism of the magnetic behaviour of 3d-4f heterometal SMM systems. In contrast, the reported 3d-4f SMMs with 3d ions occupying the vertices of the body positions of the rare.<sup>21</sup> butterfly Recently. with of are two ligands 2-(((2-hydroxy-3-methoxyphenyl)methylene)amino)-2-(hydroxymethyl)-1,3-propane diol ( $H_4L_1$ , Scheme S1) and 2-(2,3-dihydroxpropyliminomethyl)-6-methoxyphenol  $(H_3L_2)$ , we synthesized four butterfly 3d-4f heterometallic clusters with the vertices of the positions being occupied 3dbody by ions:  $[Dv_2Ni_2(H_2L_1)_2(\mu_3-OMe)_2(CH_3CN)_2(NO_3)_4]\cdot 4H_2O$ (1), $[Ln_2Ni_2(HL_2)_2(\mu_3-OMe)_2(CH_3CN)_2(NO_3)_4]\cdot 4H_2O$  [Ln = Tb (2), Dy (3)], and  $[Dy_4Co_2(HL_2)_2(\mu_3-OH)_2(piv)_{10}(OH_2)_2] \cdot 2Hpiv \cdot 2CH_3OH \cdot 5H_2O$  [Ln = Dy (4), piv = pivalate]. The magnetic investigations indicated that all the compounds display the SMMs properties. Herein, we wish to report the detailed syntheses, structures, and the experimental and theoretical investigation on the magnetic properties of these four compounds.

### **Results and Discussion**

# Description of the structure of $[Dy_2Ni_2(H_2L_1)_2(\mu_3-MeO)_2(CH_3CN)_2(NO_3)_4] \cdot 4H_2O$ (1)

Complex 1 crystallizes in the monoclinic space group  $P2_1/n$  with Z = 2. The molecule has centrosymmetric site symmetry in the crystal (Figure 1 (left)), that is 1 lies on a crystallographic inversion center and consists of a

 $[Dy_2^{III}Ni_2^{II}(\mu_2-O)_4(\mu_3-MeO)_2]^{4+}$  butterfly core with Ni<sup>II</sup> ions occupying the vertices of the body positions. The Ni ions are six-coordinated adopting distorted octahedral geometries with  $N_2O_4$  environments. The equatorial positions of Ni1 (Ni1A) is occupied by NO<sub>3</sub> donor atoms from one  $\eta^1:\eta^2:\eta^1:\eta^2:\eta^1:\mu_3$  ligand, one  $\mu_3$ -MeO<sup>-</sup> and one coordinated acetonitrile molecule. The axial positions are occupied by one oxygen atom from one coordinated methanol molecule and one nitrogen atom from the  $H_2L_1^{2-}$  ligand. The values of the Ni–O and Ni–N bond lengths cover 2.034(4)-2.095(4) and 2.012(5)-2.129(6) Å, respectively, which are comparable to those reported values.<sup>22</sup> Dy1 and its symmetry equivalent have nine coordinated oxygen atoms originating from two  $\eta^1:\eta^2:\eta^1:\eta^2:\eta^1:\mu_3$  ligands, two nitrate anions, and one  $\mu_3$ -MeO<sup>-</sup> anion. This results in nine coordinate Dy<sup>III</sup> ions with distorted capped square antiprism geometries. The Dy-O bond distances are in the range of 2.278(4)-2.566(5) Å, and the average value is 2.437 Å. It is connected to Ni1 by one  $\mu_3$ -MeO<sup>-</sup> anion bridge, one phenol oxygen atom and one alkoxyl oxygen atom. The two central Ni ions are linked by two  $\mu_3$ -MeO<sup>-</sup> anions. It is worth noting that two  $\mu_3$ -MeO oxygen atoms, two Dy atoms and two Ni atoms form a butterfly topology. Two Ni atoms (Ni1, Ni1A) and one Dy atom (Dy1 or Dy1A) form two isosceles triangle with the Ni–Ni distances of 3.071(1) Å, and Dy-Ni distances of 3.420(2) Å, respectively. Charge balance consideration reveals that  $H_4L_1$  ligand coordinates in a dianionic form with the phenol and one of the alkoxyl groups deprotonated and the other two left neutral. In addition, two methanol molecules are deprotonated and coordinated in a  $\mu_3$ -bridging form, and four nitrate anions. The uncoordinated hydroxyl group of the  $H_4L_1$  in **1** is disordered over two positions with 0.5/0.5 occupancy. These uncoordinated hydroxyl groups provide rich hydrogen bonding donors, while the coordinated nitrate anions act as acceptors, these hydrogen bonds connect the adjacent clusters along the *a*-axis. Meanwhile, the lattice water molecules link two adjacent clusters along the *c*-axis via the formation of hydrogen bonds with one coordinated oxygen atom and one uncoordinated oxygen atom of  $L_1$  ligand. The above-mentioned hydrogen bonds lead to the construction of a 2D layer structure (Figure S1, Table S1). The shortest intermolecular M.M. separation is 8.756(3) Å,

indicating that the molecules are quite well isolated.



**Fig. 1.** Molecular structure of **1** (left) and **3** (right). The non-coordinated solvent molecules and the hydrogen atoms are omitted for clarity. Color code: Ni, purple; Dy, yellow; O, red; N, light blue; C, green.

# Description of the structure of $[Ln_2Ni_2(HL_2)_2(\mu_3-OMe)_2(CH_3CN)_2(NO_3)_4] \cdot 4H_2O$ (Ln = Tb (2), Dy (3))

Single crystal measurements indicated that complexes 2–3 are isostructural. Here, we will describe the structure of 3 in detail; it crystallizes in the triclinic space group *P*-1 such that the molecule has centrosymmetric in the crystal (Figure 1 (right)). Complex 3 has a planar butterfly  $Dy_2Ni_2$  core in which the two  $DyNi_2$  triangles are each bridged by a single  $\mu_3$ -MeO ligand, one lying above and the other below the Dy<sub>2</sub>Ni<sub>2</sub> plane. The Dy and Ni atoms are nonacoordinated and hexacoordinated, respectively. The Dyl cation is coordinated by one terminal alkoxo and one  $\mu_2$ -alkoxo O atom from one  $HL_2^{2^2}$ , one phenol O atom and one methoxy O from another  $HL_2^{2^2}$ , two chelate nitrate anions, and one  $\mu_3$ -MeO group with a nearly perfect monocapped square-antiprismatic geometry. The average Dy–O bond length is of 2.436 Å. The Ni centers have octahedral environments, coordinated by one phenoxide O atom, an imino atom along with a  $\mu_2$ -alkoxo O atom from one HL<sub>2</sub><sup>2-</sup>, two  $\mu_3$ -MeO groups, and one CH<sub>3</sub>CN molecule. The Dy and Ni are connected by a bridging alkoxo group and one  $\mu_3$ -MeO<sup>-</sup>, resulting in butterfly Dy<sub>2</sub>Ni<sub>2</sub> motif with Ni<sup>II</sup> ions occupying the vertices of the body positions. Hydrogen bond interactions between the coordinated hydroxyl group of the  $HL_2^{2-}$  ligands and the neighbor coordinated nitrate anions ligands, which holds molecules of **3** in chains running along *c*-direction (Figure S2, Table S2). The

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View Article Online DOI: 10.1039/C5DT03368C

closest intermolecular Dy…Dy distance is 6.322(2) Å. Dy…Dy distance along chain direction is even larger with a value of 8.747(2) Å.

# Description of the Structure of $[Dy_4Co_2(HL_2)_2(\mu_3-OH)_2(piv)_{10}(OH_2)_2]\cdot 2Hpiv\cdot 2CH_3OH\cdot 5H_2O(4)$

Single-crystal X-ray diffraction measurements revealed that complex 4 crystallize in the triclinic space group P-1. It is a heterometallic hexanuclear cluster consisting of two Co<sup>III</sup> and four Dy<sup>III</sup> ions, with the asymmetric unit containing half of the complex (one Co<sup>III</sup> ion and two Dy<sup>III</sup> ions) which lies upon an inversion center. The core of complex 4 lies on a crystallographic inversion centre and consists of a coplanar butterfly  $[Dy_2^{III}Co_2^{III}(\mu_2-O)_4(\mu_3-OH)_2]^{6+}$  core (comprising Dy1, Dy1A, Co1, and Co1A) with two Dy ions (Dy2 and Dy2A) locating above and below the Dy2<sup>III</sup>Co2<sup>III</sup> plane (Figure 2). The Co<sup>III</sup> ions occupy the vertices of the body positions of butterfly  $[Dy_2^{III}Co_2^{III}(\mu_2-O)_4(\mu_3-OH)_2]^{6+}$  core. Co1 centre is in a distorted octahedral environment. Equatorial sites are occupied by one bridging alkoxo oxygen, one bridging phenoxo oxygen, one  $\mu_3$ -OH<sup>-</sup> oxygen and an oxygen atom from 1,3 bridging pivalate ligands while axial sites are filled by an oxygen atom from  $\mu_3$ -OH<sup>-</sup> and one nitrogen from imino. Dy1 and its symmetry equivalent have eight coordinated oxygen atoms originating from two  $\eta^2:\eta^2:\eta^1:\eta^2:\eta^1:\mu_4$  ligands, three pivalate anions, and one  $\mu_3$ -OH<sup>-</sup> oxygen with distorted square antiprismatic geometry. The Dy1–O bond distances are in the range of 2.202(1)-2.530(1) Å, and the average value is 2.378 Å. It is connected to Dy2 through two pivalate anions bridges and one  $n^2:n^2:n^1:n^2:n^1:\mu_4$ ligand bridge. Furthermore, it is also connected to Co1A through one pivalate anion bridge, one  $\mu_3$ -OH<sup>-</sup> ion and  $\eta^2:\eta^2:\eta^1:\eta^2:\eta^1:\mu_4$  ligand bridge. The seven-coordinated Dy2/Dy2A ion adopts a capped trigonal prismatic geometry, with average Dv-O bond lengths of 2.323 Å. The seven oxygen atoms from one  $\eta^2:\eta^2:\eta^1:\eta^2:\eta^1:\mu_4$  ligand, one coordinated water molecule and four pivalate anions ligand which show a variety of bonding modes. Two of the four pivalate ligands coordinated to Dy1 and Dy2 with  $\mu_2$ -bridging mode. The remaining pivalate ligands connected to Dy2 with monocoordinated chelated respectively. The and mode. butterfly

 $[Dy_2^{III}Co_2^{III}(\mu_2-O)_4(\mu_3-OH)_2]^{6+}$  cores are held together primarily via two  $\mu_3$ -OH<sup>-</sup> and  $\mu_2$ -bridging pivalate ligands. Obviously, these small ligands are able to stabilise the hexametallic core by coating inside and outside the metals. The two lattice water molecules O2W and O3W connect the adjacent clusters along the crystallographic *b*-axis (Fig S3, Table S4). The coordinated water molecule O4W connect two pivalate anions through O–H···O interactions along the crystallographic *a*-axis (Fig S4, Table S4). These result in 2D hydrogen-bonded sheet (Fig S5, Table S4). The closest intermolecular Dy···Dy distance is 5.871(2) Å. In particular, complexes 2–4 are the first example of 3d-4f complexes with 2-(2,3-dihydroxpropyliminomethyl)-6-methoxyphenol as ligand.



**Fig. 2.** Molecular structures of the coordination cluster in complex **4**. The non-coordinated solvent molecules and the hydrogen atoms are omitted for clarity. Color code: Ni, purple; Dy, yellow; O, red; N, light blue; C, green.

### **Magnetic Properties**

The temperature dependence of the magnetic susceptibilities of complexes 1–4 were each measured on powdered samples over the temperature range 2-300 K under an applied direct current magnetic field of 1000 Oe (Figure 3). For complex 1, the DC studies reveal a room temperature  $\chi_M T$  value of 29.89 cm<sup>3</sup> K mol<sup>-1</sup>, which is lower than that expected value of 30.34 cm<sup>3</sup> K mol<sup>-1</sup> for the noninteracting ions. The  $\chi_M T$  products of 1 increase slightly with decreasing temperature, reaching maximum values of 63.93 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. The  $\chi_M T$  value of 26.57 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K for the complex 2 is slightly higher than the value of 25.84 cm<sup>3</sup> K mol<sup>-1</sup> expected for two

Ni<sup>II</sup> (S = 1) and two Tb<sup>III</sup> ( ${}^{4}f_{8}$ , J = 6, S = 3, L = 3,  ${}^{7}F_{6}$ ) magnetically isolated ions. On lowering the temperature, the  $\chi_M T$  value increases gradually to reach a maximum value of 105.28 cm<sup>3</sup> K mol<sup>-1</sup> at 3 K and then decreases abruptly. For **3**, the  $\chi_{\rm M}T$  value of 30.42 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K for the Ni<sup>II</sup>-Dy<sup>III</sup> complex is close to the expected value of 30.34 cm<sup>3</sup> K mol<sup>-1</sup> for two Ni<sup>II</sup> and two Dy<sup>III</sup> (4f<sup>9</sup>, J = 15/2, S = 5/2, L = 5,  $^{6}\text{H}_{15/2}$ ) magnetically isolated ions, and the  $\chi_{\rm M}T$  value increases gradually to reach a maximum value of 57.78  $\text{cm}^3$  K mol<sup>-1</sup> at 10 K and then decreases to 48.21  $\text{cm}^3$  K  $mol^{-1}$  at 2 K. In complexes 1–3, the Ni–O–Ni angles range from 94.45 to 95.46°, and Ni<sup>II</sup>...Ni<sup>II</sup> distances range from 3.067 to 3.071 Å, respectively. Evidently, ferromagnetic coupling occurs between the two Ni<sup>II</sup> ions. The shape of the  $\chi_M T$  vs T plots for 1-3 also indicates intramolecular ferromagnetic interactions between the paramagnetic centers within the butterfly units.<sup>23</sup> For 4, the product  $\chi_{M}T$  at 300 K is  $58.52 \text{ cm}^3 \text{ K mol}^{-1}$ , which is in agreement with the expected value for non-interacting spins of four Dy<sup>III</sup> and two diamagnetic Co<sup>III</sup> ions.<sup>24</sup>  $\chi_M T$  gradually decreases with the lowering of temperature from 300 to 180 K and then further gradually increases to reach *ca*. 63.72 cm<sup>3</sup> K mol<sup>-1</sup> at 14 K. On lowering the temperature, the  $\gamma_{\rm M}T$  value abruptly decreases, finally reach the minimum value of 45.35  $\text{cm}^3$  K mol<sup>-1</sup> at 2 K. This thermal evolution may suggest the presence of ferrimagnetic interactions between the spin carriers. However, it is difficult to comment on the interactions of Dy-Dy in 4, with the Dy<sup>III</sup> ions having their intrinsic complicated magnetic characteristics which include the presence of spin-orbit coupling and magnetic anisotropy.<sup>25</sup> The slight decrease in  $\chi_{\rm M}T$  on decreasing the temperature from 300 to 180 K can be ascribed to the thermal depopulation of Stark sublevels of the Dy<sup>III</sup> ions.<sup>26</sup> Between 180 and 14 K, the  $\chi_M T$  product increases to reach 63.72 cm<sup>3</sup> K mol<sup>-1</sup> before plummeting to reach a value of 45.35 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K. If the latter variation is probably associated with the presence of magnetic anisotropy or weak antiferromagnetic interaction between hexanuclear complexes, the increase of the  $\chi_{\rm M}T$ product between 180 and 14 K suggests the presence of a high-spin ground-state for this complex that could be the result of either a ferri- or ferromagnetic arrangement of the Dy(III)-Co(III)-Dy(III) spins.



Fig. 3. Plots of  $\chi_M T$  vs T for 1–4 under applied dc magnetic field of 1000 Oe.

The field dependence of magnetization (0–50 kOe) for complexes **1** and **4** each show an initial rapid increase up to a field of 10 kOe, followed by almost linear increase with field, finally reaching values of 17.05  $N\beta$  (**1**) and 39.31  $N\beta$  (**4**) at 50 kOe and 2 K, but without saturation. For complexes **2**–**3**, upon increasing the applied external magnetic field, the magnetization increases up to 19.75  $N\beta$  and 24.06  $N\beta$  very close to the expected saturation value of 22  $N\beta$  and 24  $N\beta$  (9  $N\beta$  for Tb<sup>III</sup> ion, 10  $N\beta$  for Dy<sup>III</sup> ion and 2  $N\beta$  for Ni<sup>II</sup> ion) at 5 T, respectively. The sharp increase of *M* values at lower dc field indicates the presence of intramolecular ferromagnetic interactions. Furthermore, the *M* vs *H*/T (Supporting Information, Figures S6-S9) plots of **1**–**4** at different temperatures are not superposed, indicating the presence of low lying energy states and/or anisotropy in the system.<sup>27</sup>

The magnetic properties of complexes 1-3 are governed by three factors: the thermal population of the Stark components of Ln<sup>III</sup>, the Ni<sup>II</sup>...Ni<sup>II</sup> interaction, and the Ni<sup>II</sup>-Ln<sup>III</sup> interaction. To probe the slow relaxation of the magnetization and quantum tunneling effects within these systems, variable temperature and frequency ac magnetic measurements were performed for complexes 1-4, utilizing a 2.5 Oe oscillating field and a zero-applied dc magnetic field (Fig 5). A strong frequency-dependence of the in-phase ( $\chi'$ ) (Figure S10) and out-of-phase ( $\chi''$ ) (Figure 5) signals was observed for these complexes. The blocking temperatures at 1000 Hz



for 1-4 could be observed at 4.3, 3.2, 4.5 and 4.8 K, respectively.





Fig. 5. Temperature dependent out-of-phase ac susceptibility for 1-4 in the absence of a dc field ( $H_{ac} = 2.5 \text{ Oe}$ ).

Linear Arrhenius fitting ( $\tau$  vs 1/*T*) of the data for complexes 1–4 measured under zero applied magnetic field (Figure 6) results in energy barriers of 33.7 cm<sup>-1</sup> (1), 60.3 cm<sup>-1</sup> (2), 39.6 cm<sup>-1</sup> (3) and 18.4 cm<sup>-1</sup> (4) with relaxation times  $\tau_0 = 3.6 \times 10^{-8}$  (1),  $2.3 \times 10^{-7}$  (2),  $3.3 \times 10^{-8}$  (3) and  $8.7 \times 10^{-6}$  (4) s. We summed up the magnetic data of 3*d*-4*f* SMMs with the 3*d* ions occupy the vertices of the body positions of the butterfly up to now (Table S5). The complexes 1–3 display relatively higher anisotropy barrier, especially, the complex 2 exhibits the highest anisotropy barrier of 60.3 cm<sup>-1</sup> (86.71 K) among the Ni–Tb SMMs reported so far.



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Fig. 6. Arrhenius semilog plots of the relaxation time vs 1/T of complexes 1–4. The solid lines correspond to a linear fit in the thermally activated range of temperatures.

Data for the complexes 1–4 are a clear signature of SMMs behavior. From the position of the maximum of the imaginary component of the susceptibility,  $\chi''$ , we extracted the relaxation time, defined as  $\tau(T_{max}) = 1/(2\pi v)$ . Plotting these data as  $\tau$  versus 1/T and fitting them using the Arrhenius law afforded the plot depicted in the Figure 6. The Cole-Cole diagram can be used to study the distribution of the relaxation process, which is frequently characterized and discussed for SMMs. The data of 1–4 plotted as Cole-Cole diagrams are shown in Figure S11. The shape of the Cole-Cole plot of 1–4 are relatively symmetrical and can be fitted to the generalized Debye model with a parameter  $\alpha$  ranging from 0.12 to 0.08 for 1, 0.15-0.11 for 2, 0.21-0.15 for 3, and 0.19-0.13 for 4, respectivelly, The relatively small  $\alpha$  value indicates that a single relaxation time is mainly involved in the present relaxation process independently of the temperature.

To confirm the SMM behavior, magnetic hysteresis measurements were

performed using a conventional SQUID magnetometer on polycrystalline samples of 1-3 between -5 and 5 T at 2 K. Although were hardly observed, narrow hysteresis loops could still be seen from Figure S12–S14, which evidenced the behavior of 1-3 as molecular magnets. The hysteretic behavior of complex 4 is different to that of complexes 1-3, in this case, no hysteresis loop was observed at 2 K using a conventional SQUID magnetometer (Figure S15). The existence of quantum tunneling at zero field would explain why the loops observed at 2 K are small.

### Ab initio Calculations for 1-4

Complete-active-space self-consistent field (CASSCF) calculations on individual lanthanide (Ln) fragments of complexes 1-4 on the basis of X-ray determined geometry have been carried out with MOLCAS 7.8<sup>28</sup> and SINGLE ANISO<sup>29</sup> program package (see Supporting Information for computational details). The other Ln (Dv<sup>III</sup> for 1, 3 and 4;  $Tb^{III}$  for 2) and transition metal (Ni<sup>II</sup> for 1, 2 and 3; Co<sup>III</sup> for 4) ions were replaced by diamagnetic Lu<sup>III</sup> and Zn<sup>II</sup>, respectively. For complexes 1, 2 and 3, there is only one type of Ln fragment. Thus, we only calculated one Ln fragment for each of them. For 4, however, there are two types of Dy fragments which were both calculated by us. The basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for DyIII and TbIII ions; VTZ for close O; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set and the spin-orbit couplings were handled separately in the restricted active space state interaction (RASSI-SO) procedure. The active electrons in 7 active spaces include all f electrons (CAS(9 in 7) for Dy<sup>III</sup>-based complexes of 1, 3 and 4; CAS (8 in 7) for Tb<sup>III</sup>-based complex of 2) in the CASSCF calculation. To exclude all the doubts we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 21 sextets; 128 from 224 quadruplets; 130 from 490 doublets for the Dy<sup>III</sup> fragments of complexes 1, 3 and 4). For the Tb<sup>III</sup> fragment of complex 2, we mixed the roots coming from the following spin-free states: all from 7 septets; all from 140 quintets; 68 from 500 triplets.

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The lowest spin-orbit energies and the g tensors of  $Dy^{III}$  or  $Tb^{III}$  ion of four complexes are shown in Table S6. The main magnetic axes on two  $Dy^{III}$  or  $Tb^{III}$  ions are indicated in Figure S16 where the magnetic axes are parallel to each other for each complex. From Table S6, the energy separations between the ground and the first excited doublets of **1**, **2**, and **3** are all larger than 150 cm<sup>-1</sup> which indicates that the  $Dy^{III}$ - $Dy^{III}$ ,  $Dy^{III}$ - $Ni^{II}$  and  $Tb^{III}$ - $Ni^{III}$  exchange interactions will be mainly of the Ising type.

The magnetic susceptibilities of complexes 1-4 were simulated with the program POLY ANISO <sup>30</sup> (see Figure S17) using the exchange parameters from Table 1. For four complexes, the total coupling parameters J (dipolar and exchange) were included to fit the magnetic susceptibilities. All parameters from Table 1 were calculated with respect to the pseudospin  $\tilde{S} = 1/2$  of the Dy<sup>III</sup> ions. The calculated and experimental  $\chi_{\rm M}T$  versus T plots of four complexes were shown in Figure S17 in Supporting Information, where a slight discrepancy of the fit to the experimental data for 1, 2 and **3** because the long relaxation times which make the measured  $\chi_{\rm M}T$  to be lower than the isothermal susceptibility.7b The computational details of BS-DFT on four complexes can be found in Supporting Information. From Table 1, the calculated couplings between Dy<sup>III</sup>-Ni<sup>II</sup>, Tb<sup>III</sup>-Ni<sup>II</sup>, Ni<sup>III</sup>-Ni<sup>II</sup>, and Dy<sup>III</sup>-Dy<sup>III</sup> of four complexes using BS-DFT and those by fitting using Lines model are all ferromagnetic. However, the fitting J values are all a little larger than those calculated by BS-DFT since BS-DFT methods often underestimate ferromagnetic couplings.<sup>30, 31</sup> From Figure S16, the orientations of the local main magnetic axes of the ground doublets on Dy<sup>III</sup> or Tb<sup>III</sup> ions of 1, 2 and 3 have a little difference, but they have much larger difference for the two types of Dy<sup>III</sup> in **4**.

**Table 1**. Calculated exchange coupling constants  $(J = J_{exp} + J_{dip})$  (cm<sup>-1</sup>) using BS-DFT and the fitted exchange coupling parameters (cm<sup>-1</sup>) within the Lines model of complexes 1–4.

Complex		BS-DFT	Fitting
1	Dy-Ni	7.9	11.0
	Ni-Ni	17.2	20.3
	Dy-Dy	4.7	7.1

2	Tb-Ni	8.5	20.4
	Ni-Ni	17.6	20.5
	Tb-Tb	5.3	6.8
3	Dy-Ni	9.5	21.6
	Ni-Ni	17.8	20.5
	Dy-Dy	4.9	5.7
4	Dy1-Dy2	5.8	13.0
	Dy3-Dy4	5.8	13.0

The calculated exchange spectrum and the corresponding tunneling gaps and  $g_z$  values were given in Table S6. According to a recent proposal by Ungur and co-workers,<sup>32</sup> the relaxation paths can be related to the tunneling gaps. The relaxation paths of **1**, **2**, **3** and **4** were shown in Figures 7 and S18, respectively. The blocking barrier can be defined by the shortest paths, where these quantities are the largest. Thus, the derived blocking barriers of **1**, **2**, **3** and **4** are 35.1 cm<sup>-1</sup>, 61.4 cm<sup>-1</sup>, 40.3 cm<sup>-1</sup>, and 18.8 cm<sup>-1</sup>, respectively, which are close to the corresponding experimental fitting values.



**Fig. 7.** The magnetization blocking barrier in complexes **1** (left) and **2** (right). The arrows show the connected exchange states. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of the transversal magnetic moment.

For 4, the relaxation barrier is only 18.4 cm<sup>-1</sup> although the energy separation between the ground and the first excited Kramers doublets of one  $Dy^{III}$  ion is up to 305.2 cm<sup>-1</sup> (see Table S7). For 1, 2 and 3 which have stronger 3d-4f interactions, however, their energy barriers are much larger than that of 4 whose  $Dy^{III}-Dy^{III}$  interactions are relatively much weaker. Especially for 2, the energy barrier is up to

60.3 cm<sup>-1</sup>. The above results show that the two Ln<sup>III</sup> ions may have much more contribution to the total relaxation barrier through the stronger 3d-4f exchange couplings compared to those with weak Ln-Ln interactions.

### Conclusion

In conclusion, we have successfully synthesized four new 3d-4f heterometallic butterfly SMMs by applying two polyhydroxy Schiff-base ligands. In all four complexes, the 3d ions occupy the vertices of the body positions of the butterfly. Experimental and theoretical investigations indicate that there exist stronger magnetic exchanges in the complexes of 1-3. All four complexes exhibit SMMs properties, and the complexes 1-3 showing stronger ferromagnetic coupling display relatively higher anisotropy barrier. *Ab initio* calculations have been performed. The results suggest that  $Dy^{III}/Tb^{III}$  ions exhibit high axial anisotropy, and the two  $Ln^{III}$  ions may have much more contribution to the total relaxation barrier through the stronger 3d-4fexchange couplings compared to weak Ln-Ln interactions. These results highlight the importance of the exchange coupling in 3d-4f SMMs, and the synthesis of 3d-4fheterometallic systems with enhanced exchange interactions may be an important avenue in pursuit of SMMs with excellent magnetic performance.

### **Experimental section**

### Materials and methods

All chemicals were commercially available and used as received without further purification. The Schiff-base ligand 2-(((2-hydroxy-3-methoxyphenyl)methylene)amino)-2-(hydroxymethyl)-1,3-propane diol ( $H_4L_1$ ), was prepared by a condensation of tris(hydroxymethyl)aminomethane o-vanillin and 1:1 molar ratio hot methanol. in а in 2-(2,3-dihydroxpropyliminomethyl)6-methoxyphenol (H<sub>3</sub>L<sub>2</sub>) was prepared based on reported procedures.<sup>33</sup> IR spectra were recorded in the range of 4000-400 cm<sup>-1</sup> on Perkin-Elmer Spectrum Two FT/IR spectrometer using a KBr pellet. Elemental

analysis (C, H, N) was performed on a Elementar Micro cube CHN elemental analyzer. Magnetic susceptibility measurements were performed in the temperature range of 2–300 K, using a Quantum Design MPMS SQUID-XL-5 magnetometer equipped with a 5 T magnet. The diamagnetic corrections for these complexes were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.<sup>34</sup> Alternating current susceptibility measurements were taken of powdered samples to determine the in-phase and out-of-phase components of the magnetic susceptibility. The data were collected by increasing temperature from 2 K to 10 and/or 15 K, with no applied external dc field and a drive frequency of 2.5 Oe, with frequencies between 1 and 1000 Hz. In the samples where free movement of crystallites were prevented, silicone grease was employed for the embedding.

Single-Crystal X-ray Crystallography. Diffraction data for these complexes were collected on a Bruker SMART CCD diffractometer (Mo K $\alpha$  radiation and  $\lambda = 0.71073$  Å) in  $\Phi$  and  $\omega$  scan modes. The structures were solved by direct methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques on  $F^2$  using SHELXL-97.<sup>35</sup> All other non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. X-ray crystallographic data and refinement details for the complexes are summarized in Table 2. Full details can be found in the CIF files provided in the Supporting Information.

Synthesis of  $[Dy_2Ni_2(H_2L_1)_2(\mu_3-OMe)_2(CH_3CN)_2(NO_3)_4]\cdot 4H_2O$  (1). Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (22.83 mg, 0.05 mmol), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (14.5 mg, 0.05 mmol), H<sub>4</sub>L<sub>1</sub> (6.38 mg, 0.025 mmol), CH<sub>3</sub>OH (0.8 mL), CH<sub>3</sub>CN (0.2 mL) and Et<sub>3</sub>N (0.03 mL) were placed in a thick Pyrex tube (ca 20 cm long). The tube was frozen using liquid N<sub>2</sub>, evacuated under vacuum and flame-sealed. It was allowed to warm to room temperature and heated at 70 °C for 72 h, then cooled to room temperature to give light green block crystals of 1 in 23% yield (based on Dy). Anal. Calc. for C<sub>30</sub>H<sub>52</sub>Dy<sub>2</sub>Ni<sub>2</sub>N<sub>8</sub>O<sub>28</sub>: C, 25.46%; H, 3.70%; N, 7.92%; Found: C, 25.51%, H, 3.76%, N, 7.97%. IR data (KBr pellet, cm<sup>-1</sup>): 3404 (s), 2934 (w), 1634 (s), 1457 (s), 1384 (s), 1299 (vs), 1221 (s), 1031 (vs), 740 (vs).

Synthesis of  $[Tb_2Ni_2(HL_2)_2(\mu_3-OMe)_2(CH_3CN)_2(NO_3)_4] \cdot 4H_2O$  (2). Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (22.65 mg, 0.05 mmol), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (14.5 mg, 0.05 mmol), H<sub>3</sub>L<sub>2</sub> (0.05mol/L, 1 mL), CH<sub>3</sub>OH (0.5 mL), CH<sub>3</sub>CN (0.6 mL) and Et<sub>3</sub>N (0.02 mL) were placed in a thick Pyrex tube (ca 20 cm long). The tube was frozen using liquid N<sub>2</sub>, evacuated under vacuum and flame-sealed. It was allowed to warm to room temperature and heated at 80 °C for 72 h, then cooled to room temperature to give light green block crystals of **6** in 36% yield (based on Tb). Anal. Calc. for Tb<sub>2</sub>Ni<sub>2</sub>C<sub>32</sub>H<sub>44</sub>N<sub>10</sub>O<sub>22</sub>: C, 28.34%; H, 3.27%; N, 10.33%; Found: C, 28.39%, H, 3.35%, N, 10.38%. IR data (KBr pellet, cm<sup>-1</sup>): 3331(s), 2950(m), 2833(w), 1647(s), 1471(s), 1381(m), 1305(m), 1222(s), 1116(m), 1036(m), 953(m), 853(m), 784(w), 743(m), 645(w), 515(w).

Synthesis of  $[Dy_2Ni_2(HL_2)_2(\mu_3-OMe)_2(CH_3CN)_2(NO_3)_4] \cdot 4H_2O$  (3). The preparation of 3 is similar to that of 2 using Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O instead of Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, giving light green block crystals of 3 in 29% yield (based on Dy). Anal. Calc. for Dy<sub>2</sub>Ni<sub>2</sub>C<sub>32</sub>H<sub>44</sub>N<sub>10</sub>O<sub>22</sub>: C, 28.20%; H, 3.25%; N, 10.28%; Found: C, 28.26%, H, 3.30%, N, 10.31%. IR data (KBr pellet, cm<sup>-1</sup>): 3328(s), 2948(m), 2832(w), 1643(s), 1468(s), 1382(m), 1301(m), 1218(s), 1112(m), 1033(m), 951(m), 858(m), 783(w), 740(m), 645(w), 513(w).

# Synthesis of the complex $[Dy_4Co_2(HL_2)_2(\mu_3-OH)_2(piv)_{10}(OH_2)_2]\cdot 2$ Hpiv·2CH<sub>3</sub>OH·5H<sub>2</sub>O (4).

A general synthetic protocol was applied for the preparation of all the complex **4** as follows.  $H_3L_2$  (2 mL, 0.05 mol/L) was dissolved in methanol (15 mL).  $Dy(NO_3)_3 \cdot 6H_2O$  (0.5 mmol), pivalic acid (0.30 g, 3.0 mmol) and triethylamine (0.12 mL, 0.90 mmol) were added to this solution. The reaction mixture was stirred for 30 min. At this stage,  $Co(NO_3)_2 \cdot 6H_2O$  (0.1455 g, 0.5 mmol) was added, and the reaction

mixture was stirred for a further period of 30 min at room temperature to afford a clear solution. A dark red solution was obtained which was evaporated and red-brown block-shaped crystals were obtained from the resulting solution after one week. The characterization data for complex **4** is given below. Yield: 23% (based on Dy). Anal. Calc. for  $Dy_4Co_2C_{84}H_{156}N_2O_{43}$ : C, 38.07%; H, 5.93%; N, 1.06%; Found: C, 38.31%, H, 6.02%, N, 1.13%. IR data (KBr pellet, cm<sup>-1</sup>): 3406(s), 2966(m), 2742(w), 2678(m), 2491(w), 1704(m), 1643(s), 1607(w), 1542(s), 1480(s), 1385(s), 1302(m), 1230(s), 1109(w), 1077(m), 1037(m), 963(m), 904(w), 866(m), 738(m), 616(w), 599(w).

Table 2. Details of the Data Collection and Refinement Parameters for Complexes 1-4

	Complex 1	Complex 2	Complex 3	Complex 4
chemical formula	$Dy_{2}Ni_{2}C_{30}H_{50}N_{8}O_{28} \\$	$Tb_2Ni_2C_{32}H_{44}N_{10}O_{22}\\$	$Dy_2Ni_2C_{32}H_{44}N_{10}O_{22}\\$	$Dy_4Co_2C_{84}H_{156}N_2O_{43}\\$
Formula weight	1413.16	1349.98	1357.14	2650.02
crystal system	monoclinic	Triclinic	Triclinic	Triclinic
space group	P2 <sub>1</sub> /n (#14)	P-1 (No. 2)	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
<i>a /</i> Å	11.5441(4)	8.7774(19)	8.7471(4)	12.5549(17)
b / Å	10.2056(4)	11.403(3)	11.3799(5)	14.5434(9)
<i>c</i> / Å	21.1065(7)	12.193(3)	12.1659(6)	17.2581(12)
α / °	90	72.702(3)	72.730(4)	112.329(6)
β/°	102.089(3)	85.036(4)	84.913(4)	91.119(8)
γ/°	90	83.513(4)	83.476(4)	107.560(8)
$V/\text{\AA}^3$	2431.5(2)	1155.9(5)	1146.99(10)	2746.7(5)
Ζ	2	1	1	1
$D_{\text{calcd}}$ / g cm <sup>-3</sup>	1.930	1.939	1.965	1.554
$\mu$ / mm <sup>-1</sup>	3.897	3.914	4.119	3.060
<i>F</i> (000)	1396	662	664	1284
T / K	293(2)	296	293	293
reflections total	22115	10032	23623	20373
Theta Min-Max	3.0, 25.0	1.8, 26.4	2.9, 26.4	2.9, 25.1
[Deg]				
Min. and Max. Resd.	-0.61, 0.77	-0.55, 0.87	-0.51, 0.61	-0.84, 1.62
Dens. [e/Ang^3]				
reflections unique	4268	4670	4676	9758
R <sub>int</sub>	0.049	0.031	0.046	0.038
GOF on $F^2$	1.06	1.05	1.05	1.07
$R_1 [I > 2\sigma(I)]$	0.0372	0.0310	0.0247	0.0441
$wR_2$ (all reflections)	0.0938	0.0822	0.0580	0.1243
CCDC	1036116	1036141	1036145	1036142

### Acknowledgements

This work was support by National Natural Science Foundation of China (No. 21271050 and 51572050), Guangxi Natural Science Foundation (No. 2015GXNSFDA139007), the State Key Laboratory Cultivation Base for the Chemistry and Molecular Engineering of Medicinal Resources, Ministry of Science and Technology of China (CMEMR2014-A07), and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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