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## Exchange Interactions Switch Tunneling: A Comparative Experimental and Theoretical Study on Relaxation Dynamics via Targeted Metal Replacement

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Abstract: The magnetic relaxation and magnetization blocking barriers of tailor-made homo- and hetero-dinuclear compounds [Dy<sub>2</sub>(opch)<sub>2</sub>(OAc)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·MeOH (1) and  $[DyMn(opch)_2(OAc)(MeOH) (H_2O)_2]$  (2) were systematically investigated and the change of SMM behavior originating from the targeted replacement of one dysprosium site in Dy<sub>2</sub> compound with manganese was successfully elucidated through combined experimental and theoretical study. A detailed comparative study on theses close-related model compounds reveal the remarkable changes of the crystal field splitting and anisotropy of Dy site and the total exchange spectrum due to the replacement of Dy with Mn. And the blocking barriers in these two compounds were analyzed which explain their different blocking behavior. The two Ising doublets arising from the magnetic interaction in the case of 1 are strongly uniaxial, with tunneling splittings smaller than 10<sup>-6</sup> cm<sup>-1</sup>, leads to magnetic relaxation at temperatures exceeding the exchange energy (2.13 cm<sup>-1</sup>) which involves transition via the excited states, corresponding to local transitions on the excited doublet on Dy site. While the third and fourth exchange doublets in 2 (placed at 2.16 and 3.25 cm<sup>-1</sup>, respectively) display much larger tunneling splittings (of 10<sup>-4</sup> and 10<sup>-3</sup> cm<sup>-1</sup> respectively), opening thus an important path for magnetic relaxation.

#### Introduction

Single-molecular magnets (SMMs) that exhibit magnetic bistability of purely molecular origin approach the ultimate size

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limit for spin-based devices, making them almost immediately ideal candidate in high-density data storage technologies and molecular spintronics since its discovery in the early 1990s.<sup>[1]</sup> The requisite for such a system is the energy barrier towards reversal of the magnetization (U), which is derived from a combination of an appreciable spin ground-state (S) and magneto-anisotropy (D).<sup>[2]</sup> Apparently, the success of such technological applications hinges upon raising the blocking temperature (TB) as well as the inherent anisotropic barriers (U).

Throughout the development of SMMs,<sup>[3]</sup> transition-metal elements have acted as pioneers during a relatively long period with several remarkable results, such as magnetic hysteresis of 4.5 K and magnetization reversal of 84.6 K in a [Mn<sub>6</sub>] compound.<sup>[4]</sup> In particular, a two-coordinate cobalt imido compound was successfully explored based on the highly covalent Co=N core, where a high effective energy barrier of magnetization reversal of 594 K can be achieved and displaying magnetic blocking below 9.5 K.<sup>[5]</sup> By contrast, lanthanide-SMMs have developed at an extraordinary pace since the discovery that a mononuclear Tb<sup>III</sup> compound shows slow relaxation of the magnetization in 2003.<sup>[6]</sup> Accompanied by the establishment of the most important landmark, the threshold of 1000 K of spin relaxation barrier has been crossed by several outstanding monometallic examples in the last two years, including a few [Dy(bbpen)Br],<sup>[7]</sup> [Dy(O<sup>t</sup>Bu)<sub>2</sub>(py)<sub>5</sub>][BPh<sub>4</sub>],<sup>[8]</sup>  $[(Cp^{ttt})_2Dy][B(C_6F_5)_4]^{[9]}$  compounds. The latter represents two champions of the energy barrier and the magnetic hysteresis temperature with 1837 K and 60 K, respectively. By modulating the hyperfine interactions non-Kramers Ho<sup>III</sup> single-ion magnet (SIM) was able to suppress the fast quantum tunneling of the magnetization (QTM) at zero field to display a high energy barrier (341 K).<sup>[10]</sup> Another striking achievement is that the exceptionally strong magnetic exchange brought about by the diffuse spin of an N23- radical-bridge in dinuclear compounds hinders the QTM, creating a record blocking temperature of 14 K.<sup>[11]</sup>

In the aspect of relaxation mechanism, those dinuclear Dy<sub>2</sub> compounds have indisputably played a key role in elucidating the relaxation mechanism.<sup>[12]</sup> Retrospectively, by virtue of the diamagnetic Y2 matrix, the magnetic dilution method was employed in order to elucidate the influence of the neighboring Dy<sup>III</sup> ion in a single-ion relaxation mechanism based on a centrosymmetric dinuclear Dy<sub>2</sub> compound.<sup>[12b]</sup> The blocking mechanism principally originates from the individual Dy<sup>III</sup> sites and the exchange interaction between the sites in an asymmetric Dy<sub>2</sub> SMM was revealed by taking the advantage of combined experimental and high level ab initio calculations.<sup>[12c]</sup> On the other hand, the researches indicate that the utilization of the stronger magnetic exchange between transition-metal and lanthanide ions represents a promising route to integrate the large magnetic anisotropies and high-spin ground states, mainly because the synthesis of hetero 3d-4f system is relatively simple

compared to that of radical-containing system. It is worth mentioning that heterometallic  $[M_2Ln_2]$  (M = Co<sup>II</sup>, Cr<sup>III</sup> or Ru<sup>III</sup>, Ln = Gd<sup>III</sup>, Tb<sup>III</sup> or Dy<sup>III</sup>) model system was successfully explored where different transition-metal ions were embedded to lanthanide system to elucidate the relaxation mechanism and to enhance the blocking temperature.<sup>[13]</sup> Although the effects of different trivalent 3d ions on the relaxation dynamics have been unambiguously identified in above mentioned [M<sub>2</sub>Ln<sub>2</sub>] system, the targeted replacement of lanthanide with 3d ion in elegant dinuclear lanthanide model in order to probe the effects that 3d ions (replacing 4f) have on the relaxation dynamics have not been explored. A comparative investigation into such homo- and hetero-dinuclear models will provide insight into the influence that the 3d ions have on the system, and how they affect the static and dynamic magnetic behavior.

We therefore selected the versatile (*E*)-N'-(2-hyborxy-3methoxybenzylidene)pyrazine-2-carbohydrazide (H<sub>2</sub>opch) hydra-zone ligand in order to assemble the aforementioned two model complexes. In our previous studies, this H<sub>2</sub>opch ligand has been successfully applied to construct four polynuclear Dy<sup>III</sup>based SMMs thanks to their flexible coordination modes at different reaction conditions, as depicted in Scheme 1. Compounds **3** and **6** exhibit the butterfly-shaped topologies with peculiar mirror images of each other, and the latter has a larger anisotropic energy gap of 197 K and a longer characteristic relaxation time ( $\tau$ ) of 3.5 s.<sup>[14]</sup> Additionally double- and quadruple-CO<sub>3</sub><sup>2-</sup> bridged dinuclear Dy<sup>III</sup> cores have been obtained (compounds **5** and **4**) by spontaneous fixation of two and four atmospheric CO<sub>2</sub> molecules, respectively.<sup>[15]</sup>



Scheme 1. Six SMMs originate from the  $H_2 opch$  ligand and different  $Dy^{III}$  salts.

Herein we report the isolations of homo- and heterodinuclear  $[Dy_2(opch)_2(OAc)_2(H_2O)_2]$ ·MeOH (1) and [DyMn(opch)<sub>2</sub>(OAc) (MeOH)(H<sub>2</sub>O)<sub>2</sub>] (2). These two structurally close-related model complexes provide unique opportunity to probe simultaneously the contributions of 3d and 4f ions, as well as their exchange interaction to the relaxation dynamics. Ab initio calculations are applied to get insight into the influence that the individual 3d, 4f ions and their interaction have on the system, and how they affect the static and dynamic magnetic behavior. Besides detailed experimental characterization of structure and magnetism, a thorough description of the local electronic and magnetic properties of Dy sites, including the calculated crystal field parameters were given. In addition, the obtained results were correlated with the calculated charges on neighboring ligand atoms and the exchange interaction and the exchange spectrum were subsequently described. Through such a detailed comparative study, we were able to compare the 1) structural; 2) magnetic; 3) crystal field splitting and anisotropy of Dy site and 4) total exchange spectrum and exchange parameters changes due to the replacement of Dy with Mn. Finally, the blocking barriers in these two compounds were analyzed which explain their different blocking behavior.

#### **Results and Discussion**

Structural Analysis of H2 opch. The multidentate Schiffbase H<sub>2</sub>opch ligand is obtained from the reaction of pyrazine-2carbohydrazide and o-vanillin aldehyde. This ligand provides N,O,N,O,O-based multichelating sites that are especially favorable for the formation of lanthanide compounds. The molecular structure of H<sub>2</sub>opch ligand determined by sing-crystal X-ray diffraction is depicted in Figure S1 and the crystal data are summarized in Table S1. The ligand crystallizes in the monoclinic space group C2/c having eight molecules in each unit cell. The free ligand is planar and found to be in keto form as the C(9)-O(3) distance of 1.214 (5) Å corresponds to a carbon-oxygen double bond. The adjacent molecules are linked via intermolecular hydrogen bonds N2-H2····N4<sup>#1</sup>, C13-H13...N3<sup>#1</sup> and C1—H1C...O1<sup>#2</sup> (symmetry codes: #1, 1.5-x, 0.5+y, 1.5-z, #2, 2.5-x, 0.5-y, 1-z), generating a two-dimensional supramolecular plane, as shown in Figure S2.

Table 1. Selected bond lengths (Å) and angles (°) in compounds 1 and 2.

	Com	Compound 1			
Dy1–O3	2.324(1)	Dy1–O3a	2.338(1)		
Dy1-04	2.419(1)	Dy1–N3	2.566(2)		
Dy1-05	2.363(1)	Dy1–N1a	2.478(2)		
Dy1-06	2.362(1)	Dy1…Dy1a	3.891(2)		
Dy1–O2a	2.145(1)	Dy1-O3-Dy1a	113.1(2)		
Compound 2					
Mn1–O3	2.188(1)	Mn1–O10	2.079(1)		
Mn1–O5	2.314(1)	Mn1–N4	2.422(1)		
Mn1–O6	2.313(1)	Mn1–N5	2.354(2)		
Mn1–O9	2.242(1)	Mn1…Dy1	3.727(2)		
Mn1–O3–Dy1	112.5(1)	Mn1–O5–Dy1	106.6(1)		

**Structural Analysis of 1.** The reaction of  $Dy(OAc)_3 \cdot 6H_2O$  with  $H_2opch$  (1:1 ratio) in  $MeOH/CH_2Cl_2$  (1:1 ratio), in the presence oftriethylamine (3 equivalents), produces golden yellow crystals of  $[Dy_2(opch)_2(OAc)_2(H_2O)_2]\cdot MeOH$  (1) in 46% yield in one week, whose molecular structure determined by



**Figure 1.** The molecular structures of compounds **1** (top) and **2** (bottom). Hydrogen atoms and lattice solvents are omitted for clarity. Color scheme: Turquiose Dy, Dark Rose Mn, red O, blue N.

single-crystal X-ray diffraction is depicted in Figure 1 top. Compound 1 crystallizes in the triclinic space group P-1 with Z =1. Details for the structure solution and refinement are summarized in Table S1, and selected bond lengths and angles are listed in Tables 1 and S2. In this compound, molecular structure exhibits a center of symmetry with a Dy...Dy distance of 3.891(1) Å and two Dy-O-Dy angles of 113.1(2)°. Two opch<sup>2-</sup> hydrazone ligands behave as a pair of tetradentate N<sub>2</sub>O<sub>2</sub> ligands to coordinate two Dy<sup>III</sup> centers, in which the two Dy<sup>III</sup> ions are doubly bridged by the carboxy oxygen atoms ( $O_3$  and  $O_{3a}$ ), with Dy-O distances of 2.324(1) and 2.338(1) Å. Each of the  $\text{Dy}^{\text{III}}$ centers was further coordinated by one acetate anion in a bidentate fashion, as well as by one terminal water molecule to complete the N2O6 environment based on the distorted dodecahedral geometry (Figure 1 top). A closer look at the crystal structure of 1 reveals that two water molecules and two acetate groups coordinate to Dy1 and Dy1a above and below the opch<sup>2</sup>-Dy<sup>III</sup> plane, producing the hula hoop-like coordination geometry which is believed to be crucial for the observation of SMM behavior in related Dy<sub>2</sub> compounds.<sup>[12c]</sup> The Dy-O bond lengths are in the range of 2.145(1)-2.419(1) Å and the two Dy-N bond lengths are 2.478(2) and 2.565(2) Å, respectively. Only one 2.1<sub>1</sub>1<sub>1</sub>2<sub>12</sub>2<sub>2</sub> coordination mode (Harris notation<sup>[16]</sup>) can be observed for H<sub>2</sub>opch ligand in its di-deprotonated form (Scheme S1). Additionally one non-coordinated methanol molecule is located in the crystal lattice. Finally, strong inter- and intramolecular hydrogen-bonding interactions produce a twodimensional supramolecular plane with the acs net (4,4),<sup>[17]</sup> as

shown in Figure S3. The shortest intermolecular Dy...Dy distance is 8.563(1) Å.

Structural Analysis of 2. The reaction of Dy(OAc)<sub>3</sub>.6H<sub>2</sub>O,  $Mn(ClO_4)_2 \cdot 6H_2O$  and the solution of  $H_2$  opch in a mixture of MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v), in the presence of triethylamine (3 equivalents), leads to the formation of dinuclear heterometallic DyMn compound after 3 weeks, namely. [DyMn(opch)<sub>2</sub>(OAc)(MeOH)(H<sub>2</sub>O)<sub>2</sub>] (2). The single-crystal X-ray diffraction studies revealed that 2 crystallizes in the monoclinic space group  $P2_1/c$  with Z = 4. A perspective view of the molecular structure of 2 is represented in Figure 1 bottom and the crystal data are summarized in Table S1 and selected bond lengths and angles are shown in Table 1 and S2. In the asymmetric molecule, two opch2- polydentate Schiff-base ligands provide N, O, N, O and O, N, O, O-based multi-chelating sites, respectively, to chelate Mn<sup>II</sup> and Dy<sup>III</sup>. In doing so two metal centers are doubly bridged by the phenol oxygen atom  $(O_3)$  and the carboxy oxygen atom  $(O_5)$  with a Mn...Dy distance of 3.726(1) Å and two Mn-O-Dy angles of 112.5(1)° and 106.6(1)°, respectively. The coordination sphere of Mn1 is completed by water and methanol molecule, generating a  $N_2O_5$ environment with nearly perfect pentagonal bipyramidal coordination geometry, whereas the Dv1 ion adopts a distorted dodecahedral geometry based on the NO7 environment resembling the Dy<sup>III</sup> ions of compound **1** (Figure 1 bottom). Here, two  $H_2$  opch ligands show  $2.1_11_12_{12}2_2$  and  $2.1_12_{12}1_23_2$ coordination modes in its di-deprotonated form (Scheme S1) with the latter is first observed for this ligand. Meanwhile, this is the first example of H<sub>2</sub>opch ligand coordinating to 3d metal ions. The Mn-O bond lengths are in the range of 2.01(1)-2.318(1) Å and the two Mn-N bond lengths are 2.358(2) and 2.425(2) Å, respectively. Additionally, the Dy-O bond lengths are in the range of 2.174(1)-2.469(1) Å and only one Dy-N bond length is 2.458(2) Å. Finally, strong intermolecular hydrogen-bonging interactions produce a one-dimensional zigzag chain of the molecules (Figure S4). The shortest intermolecular Mn…Dy distance is 6.901(1) Å.

Comparison of Molecular Structures of 1 and 2. The Dy<sub>2</sub> core of compound 1 and the DyMn core of compound 2 are embedded in two same ligands with the main differences lie in the following aspects: Firstly, only one kind of N2O6 environment can be found in compound 1 with only one binding model of the two  $H_2$ opch ligands, while the  $N_2O_5$  environment of the  $Mn^{II}$  ion and eight coordination of the Dy<sup>III</sup> ion are present in compound 2 derived from the two binding models of the ligands. Among the SMMs field, their magnetic properties are influenced not only by the coordination environments of the metal ions, but also other subtle effects induced by their nearest neighbors. Furthermore, for the lanthanide-SMMs, the geometry of the core is strongly correlated to the nature or directions of the easy axes of anisotropic ions. According to this peculiarity, the SHAPE software was implemented to quantify the geometry of the coordination center cations.<sup>[18]</sup> A systematic analysis of the resulting parameters (Table S3) reveals that an intermediate geometry between triangular dodecahedron  $(D_{2d})$  and square antiprism  $(D_{4d})$  can be observed for the octa-coordinated Dy<sup>III</sup> ions of compounds 1 and 2. The hepta-coordinated Mn" ion

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shows a nearly pentagonal bipyramid ( $D_{5h}$ ) geometry with the shape measure deviation of 0.647. On the other hand, scrutinizing these two inter-nuclear distances of the metal sites, we observed that the Dy…Mn distance (3.728(1) Å) in compound **2** is much closer than the Dy…Dy distance (3.891(1) Å) in compound **1** when the transition-metal Mn<sup>II</sup> ion successfully infiltrated into this Dy<sub>2</sub> compound, and which the short intermolecular distance has been intensely affected with the values of 8.563(1) Å and 6.901(1) Å for the compounds **1** and **2**, respectively.



Figure 2. Temperature dependence of the  $\chi_M T$  products at 1000 Oe for compounds 1 (top) and 2 (bottom). Inset: M vs. H/T plots at different temperatures below 5 K.

**Magnetic properties.** Static susceptibility measurements on polycrystalline samples of compounds **1** and **2** have been carried out in the temperature range 2 – 300 K under an applied field of 1000 Oe. The plots of  $\chi_{\rm M}T$  vs. *T*, where  $\chi_{\rm M}$  is the molar magnetic susceptibility, are shown in Figure 2. The  $\chi_{\rm M}T$  observed value at a room temperature of 28.1 cm<sup>3</sup> K mol<sup>-1</sup> for compound **1** is in good agreement with the expected value of 28.34 cm<sup>3</sup> K mol<sup>-1</sup> for two uncoupled Dy<sup>III</sup> ions (S = 5/2, L = 5,  ${}^{6}H_{15/2}$ , C = 14.17 cm<sup>3</sup> K mol<sup>-1</sup> with g = 4/3). The  $\chi_{\rm M}T$  value decreases slightly down to a minimum value of 27.4 cm<sup>3</sup> K mol<sup>-1</sup> with decreasing temperature, which is mainly ascribed to the

progressive depopulation of excited Stark sublevels. [2f, 2m, 19] With decreasing temperature further, the  $\chi_{\rm M}T$  value then increases sharply to a maximum of 38.4 cm<sup>3</sup> K mol<sup>-1</sup> at 2 K, which obviously suggesting the presence of intramolecular ferromagnetic interactions between the metal centers, as observed in other Dy<sup>III</sup> compounds.<sup>[20]</sup> For compound **2**, the  $\chi_M T$ value of 15.6 cm<sup>3</sup> K mol<sup>-1</sup> at 300 K is lower than the theoretical value of 18.55 cm<sup>3</sup> K mol<sup>-1</sup> (Mn<sup>II</sup>: S = 5/2, C = 4.375 cm<sup>3</sup> K mol<sup>-1</sup> with g = 2; and S = 5/2, L = 5,  ${}^{6}H_{15/2}$ ,  $C = 14.17 \text{ cm}^{3} \text{ K mol}^{-1}$  with g = 4/3). The  $\chi_{\rm M}T$  product gradually decreases with lowing temperature, reaching a minimum value of 17.4 cm<sup>3</sup> K mol<sup>-1</sup> at 40 K, which is a typical decrease, induced by the depopulation of excited Stark sublevels of the Dy<sup>III</sup> ions.<sup>[21]</sup> With the presence of intramolecular ferromagnetic interactions between the metal centers, the  $\chi_{\rm M} T$  value exhibits a sharp increase below 20 K (the maximum of 20.8 cm3 K mol1 at 2 K).[2n, 2o, 22] Obviously, the disparity of two curves is most likely due to the nature of the overall exchange interaction between Mn<sup>II</sup> and Dy<sup>III</sup> ions for compound 2, whereas the magnetic behavior of compound 1 depends only on the interaction between two Dy<sup>III</sup> ions.

The magnetizations of the two complexes from zero dc field to 70 kOe at different temperatures are shown in the inset of Figure 2, with the corresponding maximum values reaching at 1.9 K of 10.1 (1) and 10.0  $\mu_B$  (2), where  $\mu_B$  is the Bohr magneton. These values are lower than the expected saturation value of 20 (1) and 15  $\mu_{\rm B}$  (2) for two non-interacting Dy<sup>III</sup> ions ( $g_{\rm J}$  $\times J = \frac{4}{3} \times \frac{15}{2} = 10 \ \mu_B \text{ per Dy}^{III}$ , one isolated Mn<sup>II</sup> (5  $\mu_B \text{ per Mn}^{III}$ with S = 5/2 and g = 2) and one  $Dy^{III}$  ion, respectively. This is most likely due to significant anisotropy and the crystal-field effect in the system for compounds 1 and 2.[3c] At low fields, the magnetization in compound 1 increases more rapidly than that of compound 2. Meanwhile, the non-superposition of the M vs. H/T data on a single master curve and the high-field nonsaturation suggests the presence of a significant magnetic anisotropy and/or low lying excited states in compounds 1 and 2.[23]

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5.0 K (1) 4  $\chi$ ' / cm $^3$  mol $^{-1}$ 3 25.0 K 2 1 3 5.0 K  $\chi$ "/cm<sup>3</sup> mol<sup>-1</sup> 2 25.0 K 0 1000 10 100 v∕Hz

Figure 3. Frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility of 1 under zero-dc field.

To further characterize the dynamics of magnetization, a series of ac-susceptibilities measurements at different frequencies and temperatures were carried out for compound **1** under a zero dc field, as depicted in Figures 3 and S5-S6. The strong frequency-dependence of both in-phase ( $\chi$ ') and out-of-phase ( $\chi$ '') susceptibilities reveal the onset of slow relaxation of the magnetization that is typical of SMM behavior. The  $\chi$ 'T value exhibits a rapid decrease at around 17 K for 1500 Hz, which is coincident with emerging peak of the  $\chi$ '' signal when the magnetization is blocked by the anisotropy barriers. The Cole-Cole plots of  $\chi$ '' vs.  $\chi$ ' were constructed and fitted to a generalized Debye model to obtain  $\alpha$  values and relaxation times ( $\tau$ ) in the temperature range 3.0 – 19.0 K (Figure 5 top, inset).

The result indicated a relatively narrow distribution of  $\tau$  with small  $\alpha$  parameters (0.008–0.17, Figure S7).<sup>[11]</sup> From frequency dependencies of the ac susceptibility, the magnetization relaxation times were deduced in the temperature range of 1.9 – 17.0 K and the ln $\tau$  vs  $T^{-1}$  plots obtained from these data is given in Figure 5 top. At high temperature, the relaxation follows a thermally activated Orbach mechanism<sup>[24]</sup> with  $\Delta = 95.2$  cm<sup>-1</sup> and  $\tau_0 = 4.2 \times 10^{-8}$  s based on an Arrhenius law ( $\tau = \tau_0 \exp(\Delta/kT)$ ).

Below 3 K, there is a temperature-independent characteristic time of  $\tau_{\text{QTM}} = 0.17$  s, as expected in a pure quantum relaxation regime.

For compound 2, no obvious out-of-phase signals were observed above 1.9 K under zero dc field (Supporting Information, Figure S8), indicating a very fast relaxation of the magnetization. To investigate further the relaxation behavior and study for quantum tunneling effects, the frequency-dependent ac susceptibility was measured with the application of the dc fields up to 2000 Oe at 1.9 K (see Figure S9). Remarkably, the application of dc field has a strongly influence on their dynamic behavior of magnetization, suggesting the presence of fast quantum tunneling of the magnetization.[25] As seen in ac susceptibility signals, the relaxation mode is slightly moved to higher frequency with increasing field and the Cole-Cole plot exhibits a series of evident asymmetric semicircles under variable static fields (between 600 and 2000 Oe), as depicted in Figure S10. All the above features indicate that applied field has an important effect on relaxation process.[26]



Figure 4. Frequency dependence of the in-phase (top) and out-of-phase ac susceptibility of compound 2 under a 1000 Oe dc field.

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**Figure 5.** Magnetization relaxation time,  $\ln \tau$ , versus  $\mathcal{T}^{-1}$  under 0 Oe (1, top) and 1000 Oe (2, bottom) dc field, respectively. The solid line is fitted with the Arrhenius law (see text); inset: Cole-Cole plots. The solid lines are the best fits to the experimental data.

In order to obtain quantitative information regarding the relaxation barrier of compound 2, the frequency dependence of  $\chi''$  susceptibilities under 1000 Oe applied dc field was examined below 18.0 K, as shown in Figures 4 and S11-S13. This behavior indicates the field-induced slow relaxation of the magnetization. The maximum values of the temperatures and frequencies are observed in the 1.9 - 8.0 K range. From these data, the Cole-Cole plots (Figure 5 bottom, inset) were constructed with a series of asymmetric semicircles, moreover, the generalized Debye model cannot fit these data well and gives a large  $\alpha \approx 0.24$  (see Figure S12), indicating a wide distribution of  $\tau$ .<sup>[27]</sup> All the above features suggest the presence of multiple relaxation pathways. These distinctly larger  $\alpha$  values compared to those of compound 1 may be due to the substitution of Dy<sup>III</sup> by Mn<sup>II</sup> ion and the slight changes in the ligand field caused by the replacement of the acetate with methanol. To quantify the relaxation barrier, the relaxation time was then extracted from the frequency-dependent data between 2.2 and 18.0 K and the Arrhenius plot obtained from these data is given in Figure 5 bottom. It is interesting to note that two relaxation regimes are clearly visible with a transition between them corresponding to  $\Delta$  of 3.7 and 36.2 cm<sup>-1</sup> and  $\tau_0$  of 4.9 x 10<sup>-1</sup>  $^5$  and 1.8  $\times$  10<sup>-7</sup> s for the low- and high-temperature domain, respectively. The observation of multiple relaxation processes is the result of the presence of distinct anisotropic center of single Dy<sup>III</sup> ion and the exchange interaction between the Dy<sup>III</sup> ion and Mn<sup>II</sup> ion.<sup>[13a, 13b]</sup>

Comparison of Magnetic Properties of 1 and 2. The temperature dependence of the susceptibility for compounds 1 and 2 shows similar intramolecular ferromagnetic interactions between the metal centers at temperatures below ~ 40 K, while the  $\chi_{\rm M}T$  product conspicuously decreases from 300 to 40 K in compound 2 and slight decline tendency observed along the same temperature range in compound 1. This variation of  $\chi_{\rm M}T$  at higher temperatures is directly correlated to the replacement of Dy<sup>III</sup> ion with Mn<sup>II</sup> ion. In ac susceptibility aspect, for compound **1**, a single slow relaxation of the magnetization process can be detected, giving a thermal energy barrier for the reversal of magnetization of 95.2 cm<sup>-1</sup> without the external dc field. In contrast, compound 2 exhibits a complex behavior of the twostep relaxations by providing a small dc field. In order to interpret the origin of their magnetic properties, we performed ab initio theoretical calculations on 1-2, a method that is very applicable for the investigation of lanthanide compounds.<sup>[2f, 2g, 28]</sup>

**Table 2**. Energies (cm<sup>-1</sup>) and *g* tensors of the low-lying Kramers doublets (KD) of Dy sites in compounds 1 and 2 obtained within the largest computational model employed.

KD		Dy in Dy <sub>2</sub> (1)		Dy in DyMn <b>(2)</b>		
		E	g	E	g	
1	g <sub>×</sub> g <sub>y</sub> g <sub>z</sub>	0.000	0.00656 0.01297 19.47883	0.000	0.00377 0.00746 19.60838	
2	g <sub>x</sub> g <sub>y</sub> g <sub>z</sub>	191.727	0.20683 0.24975 16.64449	204.075	0.09764 0.14829 16.68307	
3	g <sub>x</sub> g <sub>y</sub> g <sub>z</sub>	333.817	1.73682 3.00333 15.63005	365.896	2.43880 4.01876 15.24130	
4	g <sub>x</sub> g <sub>y</sub> g <sub>z</sub>	353.559	1.66865 5.31728 11.80336	423.700	8.30491 5.18753 1.34074	
5	g <sub>x</sub> g <sub>y</sub> g <sub>z</sub>	415.434	1.44494 3.80855 12.14542	537.958	8.37729 6.74977 2.28868	
6	g <sub>x</sub> g <sub>y</sub> g <sub>z</sub>	442.544	1.19377 2.07300 16.24514	585.852	1.92027 3.15284 15.15655	
7	g <sub>x</sub> g <sub>y</sub> g <sub>z</sub>	513.722	0.44372 1.15980 15.03593	671.784	0.30107 0.52062 17.15311	
8	g <sub>x</sub> g <sub>y</sub> g <sub>z</sub>	579.318	0.23857 0.53052 18.07661	754.154	0.12276 0.14069 19.33366	

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Computational Details. Fragment ab initio CASSCF calculations were performed on the compounds 1 and 2 with MOLCAS program package.<sup>[29]</sup> Two basis set approximations have been employed a) a medium-sized DZP-quality and b) a large TZP-quality basis set corresponding to the following contractions: for the DZP basis: [7s6p4d2f1g] for Dy<sup>III</sup> ions, [3s2p] for all N and C, and [2s] for H; for the basis TZP: [8s7p5d4f2g1h] for Dy<sup>III</sup> ions, [4s3p1d] for N and C from the first and second coordination spheres, [3s2p] for distant C, and [2s] for H (see Table S2). For Dy<sup>III</sup>, the active space of the CASSCF method included the 9 electrons from the last shell spanning seven 4f orbitals, CAS(9,7). All active molecular orbitals contain ~99.8% contribution from the 4f basis functions of the Dy site. Stateaverage CASSCF calculations were performed for all possible spin states. All spin sexted states (<sup>6</sup>H, <sup>6</sup>F and <sup>6</sup>P manifolds), some of the spin quartet states (128 out of 224) and spin doublet states (130 out of 490) were further mixed by the spin-orbit interaction within the restricted active space state interaction (RASSI) method, resulting in a spin-orbital spectrum comprising 898 states, grouped in doublets (Kramers doublets, KD). On the basis of the resulting spin-orbital multiplets the SINGLE ANISO program<sup>[30]</sup> computed local magnetic properties (*q*-tensors, main magnetic axes. local magnetic susceptibility, parameters of the crystal-field for the ground atomic multiplet, etc). Exchange spectrum and magnetism of the binuclear compounds was simulated using the POLY\_ANISO software,<sup>[30]</sup> on the basis of the ab initio results. More details are given in the Experimental & Computational Section.



Figure 6. Calculated orientations of the local magnetic axes (dashed lines) and the magnetic moments in the ground exchange state (green arrows) on the metal sites in 1 and 2.

All BS-DFT calculations were done with ORCA program package<sup>[31]</sup> using the B3LYP exchange correlation functional. All atoms were described by relativistic Split-Valence + Polarization basis sets (SVP-DKH) or by large relativistic def2-Triple-Zeta Valence + Polarization basis (def2-TZVPP).<sup>[32]</sup> Relativistic corrections were accounted for in the Douglas-Kroll-Hess formalism, truncated at the second order (default implementation). The strictest convergence criteria for the selfconsistent field energy minimization was employed (VeryTightSCF) in combination with the most accurate angular grids for the grid integration accuracy (Grid7).

**Table 3.** Exchange interactions between  $Dy^{III}$  ions in compounds 1 and 2 obtained within the largest computational modes employed. zJ is the parameter describing the intermolecular interaction. All values are given in cm<sup>-</sup>

	Dy <sub>2</sub> (1)	DyMn ( <b>2</b> )
$J_{total}^* = J_{exch} + J_{dipolar}$	0.185	0.454
J <sub>exch</sub>	-0.023	0.330
J <sub>dipolar</sub> *	0.208	0.124
zJ	-0.0024	-0.0146
J <sub>exch</sub> from BS-DFT	-0.06	0.54

\* Only J<sub>exch</sub> was fitted to experimental data, while the value of the dipoledipole interaction J<sub>dipolar</sub> is given here just for illustration, estimated as the difference J<sub>total</sub>\*-J<sub>exch</sub>. In practice, the dipole-dipole magnetic Hamiltonian was computed using the *ab initio* results and added to the Lines exchange Hamiltonian. We mention here that this estimation of J<sub>dipole</sub> was possible only because the dipole-dipole interaction is close to Ising type in these two particular cases, due to strong Ising anisotropy of the Dy sites in these compounds.

Ab initio investigation of local electronic and magnetic properties of Dy sites in 1 and 2. Ab initio calculations on the individual Dy<sup>III</sup> magnetic sites were performed in order to find the local electronic structure and magnetic anisotropy. Tables 2, S5 and S6 show the obtained spectrum of the low-lying Kramers doublets arising from the crystal field splitting of the free ion J =15/2 manifold of the Dy<sup>III</sup> and their magnetic anisotropy. We notice the large energy separation between the ground and first excited doublet, of ca 190-200 cm<sup>-1</sup>, as well as the strong uniaxial magnetic anisotropy of the ground doublet states  $(g_{x,y})$  $\langle g_z \rangle$ ; see Figure S14). The main magnetic axis  $(g_z)$  of the ground doublets on the dysprosium sites are making a small angle with the shortest Dy-O2 chemical bonds (dashed lines in Figure 6), lying approximately in the plane formed by the two bridging oxygen atom and two dysprosium ions. The reason for this orientation is the electrostatic and covalent effects arising from the O2 oxygen ligand atom, which apparently produces the strongest effect on the Dy site. The ab initio calculated LoProp atomic charges<sup>[33]</sup> on all atoms are shown in Tables S7-S8. Note that the O2 oxygen atom is not the one exerting the largest electrostatic effect, in both compounds. The angle between the main magnetic axes  $(q_7)$  of the ground and first excited Kramers doublets is larger in 1 than in 2 (20.4° and 8.6°, respectively,

Tables S9-S10), denoting a slighter larger contribution to tunneling in the first excited state. For both investigated compounds, the calculated excitation energy between the ground and first excited state is higher than the value of a single thermally activated relaxation regime extracted from the *ac*-susceptibility data (95.2 cm<sup>-1</sup>). We can assume that in the high temperature regime magnetic relaxation of the Dy<sub>2</sub> compound occurs via several relaxation processes, some of them having lower activation barrier, which results in an effective activation barrier extracted in *ac* measurements (Figures 7 top and 8 top).

Ab initio investigation of magnetic coupling in 1 and 2. In order to get an estimation of the sign and magnitude of exchange coupling in 1 and 2, we have performed BS-DFT calculations (as described above). On the other hand, exchange coupling was found from the fitting of experimental data within the POLY\_ANISO program. On the basis of calculated exchange spectrum, the temperature-dependent magnetic susceptibility (see Figure 2) and high-field magnetization at low temperatures (see Figure 2, inset) are described. Tables 3 and S11 show a comparison of the extracted exchange coupling parameters in the investigated compounds.

In the case of 1, we notice that both BS-DFT calculations and the fitting of the experimental data predict quite small antiferromagnetic exchange coupling (Tables 3 and S12). However, the total magnetic interaction between Dy sites in 1 is ferromagnetic due to the strong dipolar magnetic interaction between large moments on the Dy<sup>III</sup> sites, which stabilizes their parallel arrangement (Figure 6). The latter in its turn, originates from a near-parallel alignment of the local anisotropy axes and the axis connecting the Dy<sup>III</sup> ions.

Table 4. The low-lying exchange spectrum (cm<sup>-1</sup>) arising from the exchange interaction of the lowest Kramers doublets on magnetic centers in the compounds 1 and 2.

Dy <sub>2</sub> (1)			DyMn ( <b>2</b> )		
Е	$\Delta_{t}$	gz	Е	$\Delta_{t}$	gz
0.0000 0.0000	5.7377E-07	38.96	0.0000 0.0000	6.900E-11	29.54
2.1389 2.1389	1.0403E-06	0.00	1.0822 1.0822	1.1333E-08	25.56
191.9828 191.9828	3.6103E-06	35.56	2.1646 2.1649	3.5167E-04	21.59
192.1815 192.1815	2.8020E-05	35.56	3.2469 3.2481	1.2282E-03	17.63
193.4588 193.4588	1.9685E-05	0.00	4.3305 4.3305	3.5175E-07	13.69
193.5632 193.5632	1.5421E-05	0.00	5.4138 5.4138	7.4000E-11	9.81
334.2725 334.2740	1.5107E-03	27.30	204.6030 204.6030	4.2800E-10	26.56

In the case of **2**, both exchange interaction is much stronger than the magnetic dipolar coupling, which is natural for a 4f-3d

interaction. BS-DFT calculations also predict ferromagnetic coupling. Calculated energy spectrum for both compounds is shown in Table 4. We notice that the two Ising doublets arising from the magnetic interaction in the case of **1** are strongly uniaxial, with tunneling splittings smaller than  $10^{-6}$  cm<sup>-1</sup>. This explains why **1** is showing blocking the magnetization. Magnetic relaxation at temperatures exceeding the exchange energy (2.38 cm<sup>-1</sup>) must involve transition via the excited states, corresponding in this case to local transitions on the excited doublet on Dy site (Figure 7 bottom).

The low-lying exchange spectrum of **2** is formed by six Ising doublets (Figure 8 bottom), originating from the exchange interaction of the ground doublet on Dy and the S = 5/2 on Mn (Table 4). Here we see that the third and fourth exchange doublets in **2** (placed at 1.94 and 2.91 cm<sup>-1</sup>, respectively) display much larger tunneling splittings (of  $10^{-4}$  and  $10^{-3}$  cm<sup>-1</sup> respectively), opening thus an important path for magnetic relaxation in this compound. We can associate this energy with the extracted exchange barrier of magnetic relaxation (3.7 cm<sup>-1</sup>).



Figure 7. Top: the magnetization blocking barrier of Dy in Dy2 (1). The thick black lines represent the Kramers doublets in accordance with the value of its magnetic moment. The green dashed lines correspond to diagonal quantum tunneling of magnetization (QTM); the blue dashed lines represent Orbach

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relaxation processes; the red arrows show the most probable path for magnetic relaxation. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment. Bottom: the low-lying exchange spectrum arising from the exchange interaction of the lowest Kramers doublets on magnetic center ( $\Delta_{tun}$  are corresponding tunneling gaps).



Figure 8. Top: the magnetization blocking barrier of Dy in DyMn (2). The thick black lines represent the Kramers doublets in accordance with the value of its magnetic moment. The green dashed lines correspond to diagonal quantum tunneling of magnetization (QTM); the blue dashed lines represent Orbach relaxation processes; the red arrows show the most probable path for magnetic relaxation. The numbers at each arrow stand for the mean absolute value of the corresponding matrix element of transition magnetic moment. Bottom: the low-lying exchange spectrum arising from the exchange interaction of the lowest Kramers doublets on magnetic center ( $\Delta_{tun}$  are corresponding tunneling gaps).

#### Conclusions

A particularly telling pair of tailor-made centrosymmetric dinuclear  $Dy_2$  compound and its heterometallic derivative DyMn compound has been successfully developed to probe systematically the magnetic relaxation mechanism. Single-

crystal X-ray diffraction demonstrates that the molecular structures of compounds 1 and 2 are priori comparable. Compound 1 shows typical single-molecule magnet behavior with an energy gap ( $\Delta$ ) of 95.2 cm<sup>-1</sup> and a pre-exponential factor  $(\tau_0)$  of 4.2 × 10<sup>-8</sup> s under zero dc field, while no out-of-phase alternating-current signal was observed for compound 2. Through a detailed comparative study on these close-related model compounds, the structural and magnetic properties, especially the changes of the crystal field splitting and anisotropy of Dy site and the total exchange spectrum due to the replacement of Dy with Mn were investigated and finally the blocking barriers in these two compounds were rationalized which explain their different blocking behavior. The Ising interaction in 1 suppress the tunneling efficiently and the magnetic relaxation at temperatures exceeding the exchange energy (2.13 cm<sup>-1</sup>) must involve transition via the excited states, corresponding to local transitions on the excited doublet on Dy site. While in the case of 2, the third and fourth exchange doublets in placed at 2.16 and 3.25 cm<sup>-1</sup>, respectively, display much larger tunneling splittings (of 10<sup>-4</sup> and 10<sup>-3</sup> cm<sup>-1</sup> respectively), switching on thus an important path for magnetic relaxation in this compound.

This analysis was made possible by taking advantage of deliberate design of dinuclear model compounds with targeted metal replacement. Such a deep exploration enhances the understanding of magnetic interactions in elucidating the relaxation dynamics of lanthanide-containing system and will then direct the rational design of new SMMs with high performance.

#### **Experimental & Computational Section**

General Considerations. All reagents employed in the experiments were analytical grade and used without further purification. The elemental analyses for C, H, and N were performed with a Perkin-Elmer 2400 analyzer. The IR measurements were recorded on a VERTEX 70 Fourier transform infrared (FTIR) spectrophotometer using the reflectance technique (4000-300 cm-1); the samples were prepared as KBr disks.

X-ray Crystallographic Analysis and Data Collection. Crystallographic data and refinement details are given in Table 1. Suitable single crystals with dimensions of  $0.30 \times 0.30 \times 0.20$  mm3,  $0.30 \times 0.25 \times 0.21$  mm3 and 0.25 x 0.25 x 0.30 mm3 for H2opch, 1 and 2, respectively, were selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at temperatures of 293 K (H<sub>2</sub>opch and 1) and 273 K (2) on a Bruker ApexII CCD diffractometer with graphite monochromated Mo K $\alpha$ radiation ( $\lambda$  = 0.71073 Å). Data processing was accomplished with the SAINT processing program. The structure was solved by the direct methods and refined on F2 by full-matrix least squares using SHELXTL97.<sup>[34]</sup> All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. CCDC 1030999 960070 and 960071 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif

Magnetic Measurements. Magnetic susceptibility measurements were performed in the temperature range 2-300 K using a Quantum Design

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MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. The dc measurements were collected from 300 to 2 K and the ac measurements were carried out in a 3.0 Oe ac field oscillating at various frequencies from 1 to 1500 Hz. The diamagnetic corrections for the compounds were estimated using Pascal's constants,<sup>[36]</sup> and magnetic data were corrected for diamagnetic contributions of the sample holder.

Computational Methodology. Electronic and magnetic properties of individual metal centers in the Dy2 and DyMn compounds have been studied by fragment ab initio calculations using the MOLCAS-8.0 program package.<sup>[29]</sup> We have employed the fragment approach because of the limitations the current ab initio methods and our computers have, being not vet suitable to treat at this moment such binuclear complexes entirely ab initio. In this connection, the question arises to build suitable mononuclear fragments from the molecules, and which would not change significantly the energy structure on the magnetic centre. In order not to introduce additional errors, the full molecular structure of both molecules was employed. Since we aim at direct comparing the calculated magnetism with experimental measured one on crystalline samples, no geometry optimization on the fragments have been done, all atomic coordinates being taken from the X-ray analysis. Magnetic interaction is cancelled by substituting neighboring metal sites (containing unpaired electrons) by their diamagnetic equivalents. In 1, the neighboring Dy<sup>III</sup> ion has been simulated by the closed shell Lu<sup>III</sup> ion while in 2 the Mn<sup>II</sup> site has been simulated by the closed shell ZnII. In other words, a mononuclear Dy fragment is in fact the entire molecule where all neighboring metal sites are substituted by their diamagnetic equivalents. All atoms were described by all-electron relativistic ANO-RCC basis sets available in MOLCAS package.<sup>[36]</sup> Relativistic basis sets are suitable for the description of scalar relativistic effects by means of Douglas-Kroll-Hess formalism.<sup>[37]</sup> These basis functions were used to optimize the electronic spin states of the individual metal sites within the active space of the complete active space self-consisting field (CASSCF) method.[38] The active space of the CASSCF calculation of the Dy included the 4f orbitals (CAS (9 in 7)) since we are interested in the ligand field states only. The 4f orbitals are well localized on the Ln site, which allows us to consider the metal-to-metal or metal-to-ligand charge transfer states much higher in energy, thus being not relevant for the magnetism. The optimized spin states for ground and excited manifolds within CASSCF calculations were further mixed by the spin-orbit interaction within the restricted active space state interaction (RASSI) method. [37b, 39] In this approach, the spin-orbit interaction is included by means of the atomic mean field approach (AMFI).<sup>[37b]</sup> Matrix elements of the orbital momentum over the spin states are also computed within RASSI method. Ab initio calculated spectrum and orbital momentum are further employed by the SINGLE\_ANISO module<sup>[30]</sup> in MOLCAS to calculate the powder susceptibility, molar magnetization and the g-tensors for the ground and several excited Kramers doublets of isolated metal fragments. In calculations of magnetic properties, all spin-orbit multiplets included within spin-orbit coupling in RASSI are taken into account. Therefore, including a large number of spin states in the spin-orbit mixing in RASSI method is important for an accurate description of magnetism, in particular in cases of strong magnetic anisotropy.

For the simulation of magnetic properties of binuclear compounds we used an approach combining the calculated electronic and magnetic properties of individual metal fragments with the model description of the anisotropic exchange interaction between metal sites, achieved within the Lines model.<sup>[40]</sup> In this model, the isotropic Heisenberg exchange interaction is included between the true spins on neighboring metal sites ( $\hat{H}_{exch} = -J_{exch}\hat{S}_1\hat{S}_2$ , where  $S_{12} = 5/2$  for Dy and Mn) in the absence of spin-orbit coupling. Considering explicitly (non-perturbatively) the spin-orbit interaction on the individual metal sites and expanding the interaction matrix in terms of product of localized spin-orbitals on

individual metal sites, the resulting exchange matrix describes in fact the anisotropic exchange interaction. To this matrix we also added the dipolar-magnetic coupling between local magnetic moments. Diagonalization of the total interaction matrix (exchange + dipolar) provides the exchange (coupled) spectrum. These coupled eigenstates are further used to compute all measurable properties (magnetic susceptibility, molar magnetization, g-tensors of the low-lying coupled eigenstates, etc.) of the entire binuclear systems within the POLY\_ANISO program.<sup>[30]</sup> The exchange parameters J<sub>ii</sub> are usually extracted from the comparison between the calculated and measured magnetic data (magnetic susceptibility, molar magnetization) through minimization of the standard deviation, and are the only fitting parameters used in this approach. In the present case, this is just one fitting parameter describing the interaction between metal sites. Intermolecular interaction is accounted for in the mean field approximation, using one parameter describing the average exchange interaction between the considered molecule and neighboring ones (zJ).

An alternative approach to extract the exchange coupling constants employs the broken-symmetry DFT calculations.<sup>[41]</sup> Since the orbitally near-degenerate ground state of the Dy<sup>III</sup> sites complicates much the DFT calculations, it has to be replaced computationally by the closest atom with non-degenerate ground state. It was reported recently<sup>[13b]</sup> that broken-symmetry calculations performed on the same molecular structure as initial compounds involving computational substitution of the Dy by Gd provides accurate values for the exchange couplings. In this approach, the exchange values obtained for the isostructural Gd-Gd compound (two interacting spins of 7/2) have to be rescaled for the Dy-Dy (two interacting spins of 5/2) by a factor of 7/5 × 7/5 =49/25. For the Dy-Mn the rescaling involves only the spin of one metal site, therefore, the rescaling coefficient is 7/5.

Synthesis of H<sub>2</sub>opch. The pyrazine-2-carboxylic acid methyl ester was prepared by a literature procedure described elsewhere.  $^{\left[ 15a\right] }$  A mixture of pyrazine-2-carboxylic acid methyl ester (2.07 g, 15 mmol) and hydrazine hydrate (85%, 20 ml) in methanol (30 ml) was refluxed overnight, at a temperature somewhat below 80 °C. The resulting pale-yellow solution set aside 15 h. During this period, a colorless product, i.e. pyrazine-2carbohydrazide, was precipitated from the reaction mixture as crystalline solid (yield = 1.35 g, 65%). Pyrazine-2-carbohydrazide (0.276 g, 2 mmol) was suspended together with o-vanillin (0.304 g, 2 mmol) in methanol (20 ml), and the resulting mixture was stirred at the room temperature overnight. The pale yellow solid was collected by filtration. Then 0.054 g product (0.2 mmol) was dissolved into 25 ml CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) giving a pale yellow solution. Pale yellow single crystals, suitable for Xray diffraction analysis, were formed after 2 h (yield = 0.037 g, 68%). <sup>1</sup>H NMR (400 MHz, DMSO) δ 12.62 (s, 1H), 10.97 (s, 1H), 9.28 (d, J = 1.6 Hz, 1H), 8.94 (d, J = 2.8 Hz, 1H), 8.85 (s, 1H), 8.80-8.81 (m, 1H), 7.12 (dd, J<sub>1</sub> = 1.2 Hz, J<sub>2</sub> = 8.0 Hz, 1H), 7.05 (dd, J<sub>1</sub> = 1.2 Hz, J<sub>2</sub> = 8.0 Hz, 1H), 6.87 (t, J = 8.0 Hz, 1H), 3.82 (s, 3H). Elemental analysis (%) calcd for  $C_{13}H_{12}N_4O_3$ : C, 57.35, H, 4.44, N, 20.58: found C, 57.64, H, 4.59, N, 20.39. IR (KBr, cm<sup>-1</sup>): 3415(w), 3258(w), 1677(vs), 1610(s), 1579(m).  $1530(s),\ 1464(s),\ 1363(m),\ 1255(vs),\ 1153(s),\ 1051(w),\ 1021(s),\ 986(w),$ 906(m), 938(w), 736(s), 596(m), 498(w).

Synthesis of  $[Dy_2(opch)_2(OAc)_2(H_2O)_2]$ ·MeOH (1). The solution of Dy(OAc)<sub>3</sub>·6H<sub>2</sub>O (0.357 g, 0.1 mmol) and H<sub>2</sub>opch (0.0405 g, 0.15 mmol) in 20 ml CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) was stirred with Et<sub>3</sub>N (0.014 ml, 0.3 mmol) for 5 h. The resultant golden yellow solution was left unperturbed to allow the slow evaporation of the solvent. Golden yellow single crystals, suitable for X-ray diffraction analysis, were formed after one week. Yield: 18 mg (46%, based on metal salt). Elemental analysis (%) calcd for C<sub>32</sub>H<sub>38</sub>Dy<sub>2</sub>N<sub>8</sub>O<sub>14</sub>: C, 35.47, H, 3.53, N, 10.34: found C, 34.96, H, 3.41, N, 10.42. IR (KBr, cm<sup>-1</sup>): 3389(br), 3057(w), 2841(w), 1607(vs), 1561(m),

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Synthesis of [DyMn(opch)<sub>2</sub>(OAc)(MeOH)(H<sub>2</sub>O)<sub>2</sub>] (2). The solution of Dy(OAc)<sub>3</sub>·6H<sub>2</sub>O (0.0357 mg, 0.1 mmol) and H<sub>2</sub>opch (0.0405 mg, 0.15 mmol) in 20 ml CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> (1:1 v/v) was stirred with Et<sub>3</sub>N (0.014 ml, 0.3 mmol). After 3 h, Mn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (36.2 mg, 0.1 mmol) was added to the solution. Then the mixture was stirred for another 2 h, followed by filtration. The solution was left unperturbed to allow the slow evaporation of the solvent. Dark red single crystals, suitable for X-ray diffraction analysis, were formed after three weeks. Yield: 24 mg (52%, based on Dy(OAc)<sub>3</sub>·6H<sub>2</sub>O). Elemental analysis (%) calcd for C<sub>29</sub>H<sub>32</sub>DyMnN<sub>8</sub>O<sub>11</sub>: C, 39.31, H, 3.64, N, 12.65: found C, 39.47, H, 3.56, N, 12.81. IR (KBr, cm<sup>-1</sup>): 3352(br), 3047(w), 2944(w), 2861(w), 1605(m), 1578(s), 1562(m), 1477(s), 1463(w), 1455(s), 1417(m), 1389(m), 1346(w), 1301(m), 1289(w), 1247(m), 1217(s), 1162(m), 1079(w), 1033(w), 972(w), 921(w), 869(w), 781(w), 739(s), 689(w), 665(w), 627(w), 587(w), 457(w), 429(m).

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**Keywords:** single-molecule magnet • ab initio calculations • magnetization blocking barrier • exchange interaction • relaxation dynamics

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