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Dy^{III} single-molecule magnets from ligands incorporating both amine and acylhydrazine Schiff base groups: the centrosymmetric {Dy₂} displaying dual magnetic relaxation behaviors

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Novel multidentate chelating ligands *N'*-(2-pyridylmethylidene)-2-(2-pyridylmethylideneamino)benzohydrazide (Hpphz) and *N'*-(2-salicylmethylidene)-2-(2-salicylmethylideneamino)benzohydrazide (H₃sshz), which incorporate both amine and acylhydrazine Schiff base groups, were synthesized and investigated in Dy^{III} coordination chemistry. The reactions of Hpphz and Dy(OAc)₃·4H₂O have yielded two {Dy₂} featuring double OAc⁻ bridges: $[Dy_2(H_2aphz)_2(OAc)_4(ROH)_2]$ [R = Me (1) and Et (2)], where the Hpphz ligands were in situ hydrolyzed into 2-amino-(2-pyridylmethylideneamino)benzohydrazide ions (H₂aphz). While the reaction between H₃sshz and Dy(NO)₃·6H₂O afforded a $[Dy_6(sshz)_4(\mu_3-OH)_4(\mu_4-O)(MeOH)_4]_2·17.5MeOH·2H₂O cluster (3). It contains two discrete {Dy₆} cores, each of which consists of a pair of {Dy₃} triangle units. All complexes display single relaxation process of single-molecule magnet (SMM) behaviors under zero dc field. Both 1 and 2 show field-induced dual magnetic relaxation behaviors. However, their diluted samples (1@Y and 2@Y) only show one-step relaxation behaviors whether under zero or applied dc field, that the dual magnetic relaxation behaviors of 1 and 2 might be ascribled to the joint contributions of the single ion anisotropy and magnetic relaxation behaviors of 1 and 2 might be ascribled to the joint contributions of the single ion anisotropy and magnetic interactions. The cases of this type were rather rare in previous studies.$ *Ab*initio calculations also suggest that the discrepancy between relaxation processes of 1 and 2 may be caused by small difference between their magnic interactions.

Introduction

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Lanthanide SMMs that can be potentially applied in ultra-high density information storage, quantum computing and molecular spintronics, are of increasing attentions in recently years.¹ Especially the Dy complexes have shown to be their ideal candidates, due to the intrinsic Kramers doublet ground state and magnetic anisotropy of the Dy(III) ion.² By optimizing the single-ion anisotropy according to symmetry strategy, great advances with growing records of efficient energy barrier (U_{eff}) and blocking temperatures (T_b) have been achieved in mononuclear Dy-SMMs.³ Note that the Dy^{III}...Dy^{III} magnetic interactions and the spatial arrangements of the Dy^{III} ions within di- and poly-nuclear systems, are also contributing factors for high SMM performace.⁴ For instances, utilizing radical-bridges that could transmit strong magnetic exchanges to suppress quantum tunnelling of magnetization (QTM), Long et. al. have deveploped a

family of {Ln₂}-SMMs with the highest T_b to 20 K.⁵ Winpenny group has reported a {Dy₅}-SMM. Its Dy^{III} ions arranging in square-based pyramidal fashion define a strong uniaxial magnetic anisotropy, giving a high U_{eff} of 528 K.⁶ Nevertheless, there are remain huge difficulties in tuning the single ion anisotropy, magnetic interactions and arrangements of the spins simultaneously.⁷ This resulted in the fact, that the well behaved di- and poly-nuclear Dy-SMMs are still limited relative to those of mononuclear. In this regard, continuous efforts should be devoted to novel di- and poly-nuclear systems, whose potential is not yet fully explored.

The magnetic relaxation processes of Dy-SMMs is another issue deserving attentions in this field. One of the most attracting type is those bearing dual relaxation behaviors. It is true that the illumination of their complicated relaxation mechanisms remains one of the challenges for researchers. But in turn, they afford ideal models to probe various factors on the relaxation besides the single-ion anisotropy, which thus can give pointed guidances to tuning the performaces.⁸ Based on previous studies, several inducements for dual relaxation behaviors have been proposed for Dy-SMMs with different structural characteristics.⁹ The most common, by far, is that the Dy^{III} centers locate in inequivalent ligand fields and have different single-ion behavior.¹⁰ Beyond that, the effects of the hyperfine interactions between nuclear spins and total angular momentum,¹¹ and the intermolecular interactions¹² were also demonstrated. It is significant that the intramolecular magnetic interactions were found

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⁺ Footnotes relating to the title and/or authors should appear here.

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to induce distinct dual relaxation behaviors in minority of Dy-SMMs whose Dy^{III} centers locate in identical ligand fields.¹³ These cases are precious, as it is usually confusing to distinguish the contributions of the single-ion anisotropy and intramolecular magnetic interactions on the relaxation in most of the Dy-SMMs.¹⁴ The studies on them would help to map the synergic effects between single-ion anisotropy and magnetic interactions on the SMM performances.

Whether for the togopogies, relaxation processes or performancs of the Dy-SMMs, the key roles of the ligands are self-evident. Among various ligands, aimine and acylhydrazine Schiff bases have been wildly favoured by the researches, respectively. They supply strong coordination fields and suitable multichelating pockets for Dy^{III} ions, having good abilities to assemble di- and poly-nuclear SMMs with novel topologies.¹⁵ Moreover, the O-donors of these ligands, could either form strong coordination bonds with the Dy^{III} ions to generate their single axial magnetic anisotropy,¹⁶ or act as the magnetic bridges to reinforce the Dy^{III}...Dy^{III} interactions efficiently.¹⁷ Typical cases include amine Schiff base which yielded serise of {Dy₂}-SMMs with the highest $U_{\rm eff}$ of 110 K,¹⁸ amine Schiff base coupling two {Dy₃} triangles into a {Dy₆}-SMM for maximizing the toroidal moment,¹⁹ and acylhydrazine Schiff base that assembled a {Dy₂}-SMM with dual relaxation processes and two high $U_{\rm eff}$ of 150 and 198 K,²⁰ etc. Surprisingly, the ligand incorporating both amine and acylhydrazine Schiff base groups was scarely employed in this field, albeit the synergism of two kinds of groups affords considerable possibility to achieve fantistic products. So far, to the best of our knowledge, only one ligand of this type has been investigated, which has constructed serise of {Mn₂Ln₄} clusters featuring chair-shaped core.²¹

On account of above and based on our previous work,²² we started to investigate the potential of the ligands containing both amine and acylhydrazine Schiff base sites. Novel ligands of Hpphz and H₃sshz featuring this structure were disigned and synthesized (Scheme 1). Their reactions with Dy^{III} salts afforded two {Dy₂} (**1** and **2**) and a {Dy₆} (**3**) complexes, all of which were found to show one-step magnetic relaxation under zero field. Field induced dual relaxation behaviors are evident in **1** and **2**, which were seldomly seen in symmetrical {Dy₂} systems. Combined with magnetic dilution and *ab* initio calculations, the relationships among the molecular structures, single-ion magnetism, magnetic interactions, relaxation processes and the SMM properties of **1-3** have been discussed.



Scheme 1 The Hpphz and H₃sshz ligands used in this work.

Results and discussion

Syntheses and Characterization



Scheme 2 The formation of H₂aphz⁻ from hydrolysis of the Hpphz.

Complexes 1 and 2 were synthesized by the same solvothermal reactions of Hpphz ligand and Ln(OAc)₃·4H₂O in the presence of triethylamine, just differ depending on the solvents. It is noteworthy that the H₂aphz⁻ ligands formed in situ, through the hydrolysis of amine Schiff bases group of the Hpphz ligand (Scheme 2). This could be supported by the change of IR spectrum between the ligand and the complexes (Figure S1). After the coordiantion, the strong absorption band of 1651 cm⁻¹ for -C=N- stretching of amine Schiff base group disappeared. New bands near 3605 and 1579 cm⁻¹ that could be assigned to the stretching and bending vibrations of the resultant -NH₂ group can be observed. However, this in situ hydrolysis didn't happened during the formation of 3, which was obtained by the solvothermal reaction of H₃sshz ligands and $Ln(NO_3)_3 \cdot 6H_2O$. In this regard, it could be speculated that either the OAc⁻ ions or the Py terminal group might be responsible for the hydrolysis of the of the Hpphz ligands in 1 and 2. On the other hand, there is one of commonalities for the IR spectrum of 1-3, that the characteritic bands near 1565 cm⁻¹ belonging to the -N=C(OH)group could be found. It suggests that the acylhydrazone groups of the ligands in 1-3 all coordianted in enol forms.

The thermogravimetric (TG) analyses of **1-3** are presented in Figure S2. Complexes **1** and **2** display very similar TG behaviors. In the temperature range of 25 to 160 °C, they undergo a weight loss of 6.0% (calcd 5.8% for **1**) and 8.0% (calcd 8.1% for **2**), respectively, which agree well with the losing of two coordinated solvent molecules. Free lattice solvent molecules of **3** lost in the temperature range of 25-181 °C with a weight loss of 9.3% (calc. 9.9%). Upon further heating, all complexes suffered continuous weight losses until final decomposition to metal oxides. In addition, their experimental power X-ray diffraction (PXRD) curves match well with the simulated profiles derived from corresponding crystal data (Figure S3), respectively. These results indicate the purities of their samples.

Structural analysis

Single-crystal X-ray diffraction data revealed that **1** crystallizes in the triclinic space group $P\overline{1}$. As shown in Figure 1a, its centrosymmetric structure consists of two Dy^{III} ions, four OAc⁻ ions, two H₂aphz⁻ ligands and two MeOH molecules. A pair of OAc⁻ ions chelate to two Dy centers, respectively. While another pair of OAc⁻ ions adopt an μ_2 - $\eta^1:\eta^2$ bridging mode, by which two Dy^{III} centers are double-bridged to form a $[Dy_2(OAc)_2]$ core (Figure 1b). All atoms of this core are almostly co-planar, with a least square value of 0.043. The Dy····Dy distance is 4.157 Å and the Dy-O-Dy angle is 112.890°. Inspection of

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the C7–O1 bond length (1.312(1) Å), the charge balance calculation and above IR analysis confirm that two H_2aphz^- ligands were involved



Figure 1. Molecular structure (a), [Dy₂(OAc)₂] core (b) and coordination geometry of the Dy^{III} ions of **1**.

in the coordination in enol forms. Each of them chelates a Dy ion with a [NON] pocket of acylhydrazone group, playing the role of terminal ligand along with two MeOH moleclues. In this way, each Dy center locates in a coordination environment consisting of five $O_{acetate}$, an O_{enol} , an O_{MeOH} and two $N_{hydrazine}$ donors (Figure 1c). The Dy-O and the Dy-N bond lengths are in the range of 2.165(5)-2.465(7) and 2.165(5)-2.465(7) Å, respectively. Continuous symmetry measure (CShM) method was employed to analyze exact coordination geometry of the Dy^{III} ion using SHAPE2.1 software.²³ The lowest CShM parameters indicat that the geometry of Dy^{III} center belongs to spherical capped square antiprism with a C_{4v} symmetry (Table S1).

There are two kinds of intramolecular hydrogen bonds in ${\bf 1}.$ The - NH_2 group in each H_2aphz^{-} ligand inverses to the other side of the acylhydrazone pockets, generating a hydrogen bond between the

N _{amine} and N _{hydrazine} [N1–H2a···N2 = 2.013(1) Å]. Two hydrogen bonds			
between the O _{MeOH} and O _{enol} [O6–H6a…O1 ⊵1.923(ഈÅ) ₩ē9€43\$5			
found, which help to reinforce the $[Dy_2(OAc)_2]$ core. However, no			
significant intermolecular interaction was found. The smallest			
Dy…Dy distance between the adjacent molecules is about 9.438 Å.			

Complex **2** also crystallizes in triclinic $P\overline{1}$ space group and displays very similar centrosymmetric structure to that of **1**, except that terminal coordinated MeOH were replaced by EtOH (Figure S4). This difference has induced tiny change of the average Dy-O and Dy-N bond lengthes, Dy...Dy distances and Dy-O-Dy angles from **1** to **2** (Table 1). It further resulted a structural dissimilarity, that the geometry of Dy^{III} center of **1** is capped square antiprism, while that of **2** is tricapped trigonal prism (Table S2).

Table 1 A summery of detailed structural parameters of 1 and 2.

Complexes	1	2
Average Dy-O bond lengthes (Å)	2.430(3)	2.431(3)
Average Dy-N bond lengthes (Å)	2.535(3)	2.530(4)
Dy…Dy distances (Å)	4.157(3)	4.167(4)
Dy-O-Dy angles (⁰)	112.898(1)	112.300(1)
Geometries of Dy ^{III} centers	capped square	tricapped
	antiprism	trigonal prism

Complex **3** belongs to the monoclinic space group $P2_1/n$. Its components per formular unit contains two discrete {Dy₆} clusters (**3a** and **3b**), together with several free MeOH and H₂O molecules. The main difference of two {Dy₆} clusters is that the directions of coordinated MeOH molecules are unidentical (Figure S5). However, they still display almost the same topologies. For brevity, only the structure of **3a** will be described in detail.

Cluster **3a** consists of six Dy^{III} ions, four sshz³⁻ ligands, an μ_4 -O²⁻ ion, four μ_3 -OH⁻ ions and four temerinal coordinated MeOH molecules (Figure 2a). Its skeleton could be regarded as the linkup of two

(d)

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Figure 2 Molecular structure (a), {Dy₆} core (b), coordination mode of the ligand (c), and geometries (d and e) of the Dy^{III} ions of 3a.

(b)

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triangle {Dy₃} units (Figure 2b), each of which was assmebled by a pairs of μ_3 -O_{hydroxyl} (O4 and O5 or O12 and O13). Trideprotonated ligands sshz³⁻ all show an μ_3 - η^1 : η^1 : η^2 : η^1 : η^2 binding mode (Figure 2c). On one hand, they contribute their μ -O_{enol} (O3, O6, O11 and O14) to bridge the adjacent Dy^{III} ions, further reinforcing each triangle unit. On the other hand, four μ -O_{phenol} (O2, O7, O10 and O15) of them link two {Dy₃} triangle units together in an edge-to-edge fashion with the help of an μ_4 -O²⁻ ion (O1), giving rise to the {Dy₆} core of **3a**. The average Dy···Dy separation and Dy···Dy···Dy angle are 3.525 Å and 60.000⁰, respectively. The dihedral angle between two meaning planes of {Dy₃} units is 49.738(1)°.

All Dy^{III} ions in **3a** are eight-coordinated and could be divided into two types in terms of their donors. The donors of the Dy1, Dy2, Dy3 or Dy4 include two O_{phenol}, two O_{hydroxyl}, an O_{enol}, a N_{hydrazine}, an μ_4 -O and an O_{MeOH} (Figure 2d). And the Dy5 or Dy6 coordinate with two O_{phenol}, two O_{hydroxyl}, two O_{enol} and two N_{imine} (Figure 2e). The bond lengths of Dy-O and Dy-N are in the ranges of 2.234(1)-2.466(1) and 2.462(1)-2.555(2) Å, respectively. Calculated lowest CShM valuses demonstrate that the geometries of Dy1/Dy3/Dy6 are distorted square antiprismatic, while those of Dy2/Dy4/Dy5 are distorted triangular dodecahedron (Table S3).

Magnetic studies

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Static Magnetic Properties

Variable-temperature dc magnetic susceptibilities of **1-3** were measured in the temperature range of 300-2 K under an applied field of 1 kOe. As shown in Figure 3, the $\chi_{\rm M}T$ values at 300 K for **1-3** are 28.02, 28.01 and 85.30 cm³ mol⁻¹ K, respectively, being close to their corresponding theoretical values calculated from two or six free Dy^{III} ions (⁶H_{15/2}, g = 4/3). Upon cooling, the $\chi_{\rm M}T$ values of three all decrease slowly up to about 15 K, which then decline sharply to the minimum values at 2 K. These results might be attributed to the weak antiferromagnetic interactions between the Dy^{III} centers and/or the thermal depopulation of Stark sublevels of the Dy^{III} centers in the systems.²⁴

The field dependence of the magnetization measured at different temperature for **1-3** were plotted as M-H (Figure 3 inset) and M- HT^{-1} curves (Figure S6). The M-H curves of all three show a rapid increase at low magnetic fields. Upon further increasing of the applied field,

Dynamic Magnetic Properties

In order to investigate the dynamic magnetic behaviors of **1-3**, the alternating current (ac) magnetic susceptibility measurements were performed at frequency range of 1-1000 Hz. In the absence of a dc field, clear frequency dependence of out-of-phase (χ'') signals relating with single magnetic relaxation process could be observed for both **1** and **2** (Figure 4a and 4b), indicative of typical SMM behaviors. Their ac susceptibilities were fitted according to generalized Debye model, affording Cole-Cole plots where most of the curves display asymmetric semicircles (Figure 4c and 4d). The ranges of the distribution coefficients α for **1** and **2** are 0.03-0.22 and 0.02-0.30 (Table S4 and S5), respectively, which reveal relatively narrow distribution of their relaxation times.

The extracted τ of **1** and **2** all obey the Arrhenius law as Eq. 1 in high-temperature range (Figure 4e and 4f, green lines), all corresponding to the Orbach process.

$$\tau = \tau_0 \exp(U_{\rm eff}/k_{\rm B}T) \quad (1)$$

As the temperature decreased, the τ values of **1** and **2** diverge from the Arrhenius law gradually. This might be attributed to the existence of the Raman, direct and QTM relaxation processes. Thus, their data over entire temperature range was fitted with Eq. 2 (Figure 4e and 4f, red lines),

$$\tau_{\rm obs}^{-1} = \tau_0^{-1} \exp(-U_{\rm eff}/k_{\rm B}T) + AT + CT^{\rm n} + \tau_{\rm QTM}^{-1}$$
 (2)

where the $\tau_0^{-1} \exp(U_{eff}/k_BT)$, AT, CTⁿ and τ_{QTM}^{-1} account for Orbach, direct, Raman and QTM processes, respectively. The best fittings of above give U_{eff} = 59 K, τ_0 = 2.75 × 10⁻⁶ s, A = 96.29 K⁻¹ s⁻¹ and τ_{QTM} = 0.0018 s for **1**; U_{eff} = 59 K, τ_0 = 2.94 × 10⁻⁶ s and τ_{QTM} = 0.0005 s for **2**.

Aiming to impress the QTM effect on the magnetic relaxation, the ac susceptibilities of **1** and **2** were further measured under optimum dc fields, which were determined to be 1 kOe for both systems



Figure 3 The plots of χ_{M} -*T* and *M*-*H* (inset) under different temperatures for **1-3**.

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Figure 4 Frequency-dependent χ'' ac susceptibilities, Cole-Cole and $\ln \tau - T^{-1}$ plots for **1** and **2** under zero dc field.

(Figure S8). Corresponding χ'' signals of **1** and **2** all show two wellresolved peaks in low temperature region, suggesting the existence of two-step relaxation processes (Figure 5a and 5b). When the temperature increases, the low-frequency peak intensities decline and only high frequency peaks are observed. These imply that there are evolutions from the fast relaxation (FR) to the slow relaxation (SR) with improvements of the temperature.²⁷ The two-step relaxation behaviors could be further verified by the Cole–Cole plots (Figure 5c and 5d), which display consecutive double-semicircle shapes at low temperatures. Accordingly, the data was fitted by the sum of two modified Debye functions (Eq 3) as following:²⁸

$$\chi_{\rm ac}(\omega) = \chi_{\rm S,tot} + \frac{\Delta \chi_1}{1 + (i\omega\tau_1)^{(1-\alpha_1)}} + \frac{\Delta \chi_2}{1 + (i\omega\tau_2)^{(1-\alpha_2)}}$$
(3)



Figure 5 Frequency-dependent χ'' ac susceptibilities, Cole-Cole and In τ - T^{-1} plots for 1 and 2 under 1 kOe dc fields.

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The best fitting gives the $\alpha_{\rm FR}$ and $\alpha_{\rm SR}$ parameters of **1** in the range of 0.15–0.38 and 0.06–0.38, respectively (Table S6), both of which are comparable to those of **2** (0.03 $\leq \alpha_{\rm FR} \leq$ 0.37 and 0.03 $\leq \alpha_{\rm SR} \leq$ 0.39; Table S7). These results reveal that the distribution of relaxation times for both systems under optimum dc fields are narrow. For the SR, the plots of lnt vs. T^{-1} were fitted well with Eq 2 (Figure 5e and 5f), respectively, affording the following parameters: $U_{\rm eff}$ = 52 K, τ_0 = 6.80 × 10⁻⁶ s, C = 16.20 s⁻¹ K^{-0.35} and n = 0.35 for **1**; $U_{\rm eff}$ = 52 K, τ_0 = 5.97 × 10⁻⁶ s, C = 31.98 s⁻¹ K^{-0.51} and n = 0.51 for **2**. However, the plots of lnt vs. T^{-1} for FR of **1** and **2** only obey the Arrhenius law as Eq. 1, which give $U_{\rm eff}$ = 3.7 K and τ_0 = 1.86 × 10⁻⁴ s for **1**, $U_{\rm eff}$ = 0.5 K and τ_0 = 2.40 × 10⁻⁴ s for **2**.

In order to make insights into the two steps magnetic relaxation behaviors of 1 and 2, the ac susceptibilities of their diluted samples (1@Y and 2@Y) were further investigated. Under zero field, both 1@Y and 2@Y show one-step relaxation behaviors as 1 and 2. In comparison with those of **1** and **2**, however, their maxima χ'' peaks shift to higher frequency region, and the χ'' peaks for the QTM process become more incomplete and widened (Figure 6a and 6b). Accordingly, the arcs of their Cole-Cole curves become less asymmetric (Figures 6c and 6d). Fitting of the Cole–Cole plots afford α values in the ranges of 0.14-0.49 for **1@Y** and 0.25-0.47 for **2@Y** (Table S8 and S9). Treating the data of $In\tau$ vs. T^{-1} with Eq 2 give following sets of parameters: $U_{\rm eff}$ = 62 K, τ_0 = 2.57 × 10⁻⁷ s and $\tau_{\rm QTM}$ = 0.0005 s for **1@Y** (Figure 6e); U_{eff} = 63 K, τ_0 = 6.51 × 10⁻⁸ s and τ_{OTM} = 0.0003 s for **2@Y** (Figure 6f). These results suggest that the QTM in 1@Y and 2@Y is suppressed but not completely guenched.²⁴ In this case, the ac susceptibilities of 1@Y and 2@Y were further recorded under applied dc field, which was optimized to be 0.4 kOe

(Figure S10). As shown in Figure 7a and 7b, samples 100 Aard 200 Y still present one-step relaxation behaviors inder 0.43 KO2 CO46 Mds. The χ'' signals all show clear peaks, and shift to lower frequency range relative to those under zero field. Meanwhile, the lack of overlapping peak maxima at low temperatures imply that the QTM have been supressed efficiently under the optimized dc field. The Cole–Cole plots show approximate semicircles (Figure 7c and 7d), from which the fitting afford α values in the range of 0.14-0.49 for 100 Y and 0.25-0.47 for 200 Y (Table S10 and S11). These results further confirm the single relaxation behaviors of 100 Y and 200 Y. Fitting of the Int vs. T^{-1} data to Eq 2 led to $U_{eff} = 60$ K, $\tau_0 = 1.0 \times 10^{-5}$ s, A = 0.65 K⁻¹ s⁻¹, $C = 5.60 \times 10^{-4}$ s⁻¹ K^{-6.83} and n = 6.83 for 100 Y (Figure 7e); $U_{eff} = 51$ K, $\tau_0 = 5.2 \times 10^{-6}$ s, A = 2.26 K⁻¹ s⁻¹, $C = 1.25 \times 10^{-3}$ s⁻¹ K^{-6.48} and n = 6.48 for 200 Y (Figure 7f).

As for **3**, its χ'' susceptibilities show obvious frequency-dependent peaks under zero field, indicating the slow relaxation of magnetization in association with SMM properties (Figure 8 a). Semicircular shapes are observed in its Cole-Cole diagrams (Figure 8 c). The fitting with generalized Debye model provides the α values in the range of 0.03-0.23 (Table S12), which suggests a narrow distribution for the relaxation time. The lnr vs. T^{-1} only obey the Arrhenius law as Eq. 1 (Figure 8e), affording $U_{eff} = 14$ K and $\tau_0 = 1.23 \times 10^{-5}$ s. When an optimum dc fields of 2 kOe was applied (Figure S12), the temperature range where the χ'' peaks could be identified became much wider than that under zero dc field (Figure 8b), and the Cole-Cole plots show more symmetric arcs (Figure 8d). The simulation gives α values from 0.21 to 0.32 (Table S13). The lnr vs. T^{-1} curve is nonlinear at whole temperatures. Fitting to Eq 2 afforded $U_{eff} = 15$ K, $\tau_0 = 4.36 \times 10^{-5}$ s, C = 4.36 s⁻¹ K^{-2.39} and n = 2.39 (Figure 8f).



Figure 6 Frequency-dependent χ'' ac susceptibilities, Cole-Cole plots and $\ln \tau - \tau^{-1}$ plots under zero dc field for **1@Y** and **2@Y**.

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Figure 7 Frequency-dependent χ'' ac susceptibilities, Cole-Cole diagrams and $\ln \tau - T^{-1}$ plots for **1@Y** and **2@Y** under 0.4 kOe dc fields.



Figure 8 Frequency-dependent χ'' ac susceptibilities, Cole-Cole plots and $\ln\tau$ - T^{-1} plots for 3 under zero and 2 kOe dc fields.

Theoretical Calculations

The calculations using complete-active-space self-consistent field (CASSCF) on individual Dy^{III} fragments (Figure S13) of **1–3** derived from single-crystal structures have been conducted with MOLCAS 8.4²⁹ and SINGLE_ANISO programs (see the Supporting Information for computational details).³⁰ The energy levels (cm⁻¹), $g(g_x, g_y \text{ and } g_z)$

tensors and the predominant m_J values of the lowest eight Kramers doublets (KDs) for each Dy^{III} fragment are list in Table S14, where the **3a_Dy1** and **3a_Dy5** possess the smallest (33.8 cm⁻¹) and the largest (214.6 cm⁻¹) energy gaps between the lowest two KDs, respectively. The calculated g_x and g_y values for **1_Dy1** are close to the corresponding values of **2_Dy1**, which show that **1** and **2** have almost the same transverse anisotropy components. The predominant m_J

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components for the lowest two KDs of each single-Dy^{III} moiety show that their ground KDs are all mostly composed by $m_1 = \pm 15/2$ state (Table S15). Their first excited states are also mostly composed by several m_J states severely, apart from those of the **3a_Dy5**, **3a_Dy6** and **3b_Dy6** being all mostly composed by $m_J = \pm 13/2$. From the magnetization blocking barriers of individual Dy^{III} fragments (Figure S14), it could be found that the transversal magnetic moments in the ground states of the 3a Dy5, 3a Dy6, 3b Dy5 and 3a Dy4, 3b Dy3, **3b** Dy6 are about 10^{-3} and 10^{-3} μ_B , respectively. These results indicate that the QTMs in their ground states could be suppressed at low temperature. On the other hand, the transversal magnetic moments in the first excited states of **1**–**3** are mostly about $10^{-1} \mu_{\rm B}$, therefore resulting in fast QTM in their first excited KDs.

Despite the magnetic anisotropies of the lanthanide SMMs mainly stem from the individual Dy^{III} fragments, the Dy^{III}...Dy^{III} interactions have non-negligible influence on their slow magnetic relaxation processes. Thus, the Dy^{III}...Dy^{III} interactions of **1** and **2** were further investigated. Considering the results that the calculated ground g_z values for their single-Dy^{III} moieties are all near 20 (Table S14), the Dy^{III}...Dy^{III} interactions were treated as Ising type in simulations. In this premise, the program of POLY ANISO³⁰ was applied to simulate the magnetic susceptibilities. Relevant intramolecular magnetic interaction parameters (Table 2) include the total coupling parameter J_{total} , its components of the exchange coupling (J_{exch}) and dipole-dipole interaction (J_{dip}) , all of which were fitted with respect to a pseudospin ($S^{\%}$) of 1/2 on the Dy^{III} sites. The intermolecular interactions were also considered in the fitting. Relevant intermolecular coupling constants between the nearest Dy^{III} ions of **1** and **2** are 0.006 and -0.048 cm⁻¹, respectively (Table S16).

Table 2. Fitted J_{exch} , J_{dip} and the J_{total} between magnetic center ions in 1 and 2 (cm⁻¹).

Complexes	J _{exch}	J _{dip}	$J_{\rm total}$
1	0.50	-2.15	-1.65
2	0.25	-2.06	-1.81

The experimental and calculated $\chi_{\rm M}T$ -T plots of **1** and **2** are shown together in Figure S15. Two sets of data for each system are close to each other. The fitted results within the Lines model³¹ indicate that the intramolecular interactions J_{total} and J_{dip} are all antiferromagnetic, while the exchange couplings J_{exch} of **1** and **2** are ferromagnetic (Table 2). And the J_{total} primarily depend on J_{dip} , as the calculated values of J_{dip} all overcome corresponding values of J_{exch} . Between 1 and 2, there is no obvious difference no matter for the J_{total} or J_{dip} values. However, the J_{exch} value for **1** (0.50 cm⁻¹) is just twice as large as that of 2 (0.25 cm⁻¹).

In addition, the exchange energies, the energy differences between each exchange doublets Δ_t and the main values of the g_z for the lowest two and four exchange doublets of 1 and 2 were also calculated (Table S17). Their g_z values of the ground-state exchanges are all 0.000. This further confirms the antiferromagnetic Dy^{III}...Dy^{III} interactions in both systems. The main magnetic axes were also drawn on the Dy^{III} ions for **1** and **2**, respectively, where the magnetic axes for both complexes are all antiparallel (Figure S16).

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In the family of these {Dy₂}-SMMs, the dual relaxation behaviors generally occurred in those asymmetric systems that two DV#4645 locate in inequivalent sites,¹⁰ and could be ascribed to different single-ion magnetism relating to weak exchange limit.³² Obviously, different single-ion magnetism of two Dy^{III} centers should not be the inducement for dual relaxation behaviors of 1 and 2 featuring centrosymmetric structures. From above ac susceptibilities data, it is clearly observed that both 1@Y and 2@Y show single relaxation behavior not only under zero field but also under applied dc field. In other word, the dual relaxation behaviors of 1 and 2 are absent along with the weaken/vanishment of the magnetic interactions after the dilution. It is thus suggested that the dual relaxation behaviors of 1 and 2 might be related with the magnetic interactions in the systems. Similar cases can also be found in previous literature. For instances, Tang group has stated that the presence of two relaxation processes in a {Dy₂}-SMM might be ascribed to the weak intramolecular exchange and dipolar interactions.^{13c} Ho and Chibotaru have proved that the existence of a sufficiently wide dipolar field distribution is the main cause for the appearance/disappearance of the multiple maxima in magnetic relaxation processes.³³ Within 1 and 2, the magnetic interactions are dominated by those of intramolecular as indicated by above theoretical calculation. However, the contributions of the intermolecular interactions on the relaxation processes of 1 and 2 might still exist, though they all show rather small values coupling constants. Because even when two Dy ion reside far away from each other, the dipolar coupling between each other may affect the magnetic properties of the systems.^{33,34} Therefore, the intramolecular and intermolecular magnetic interactions, as well as the single ion anisotropy of Dy ions, might jointly contribute to the dual relaxation behaviors of 1 and 2.

On the other hand, the theoretical calculation has also shown some difference between the magnetic interactions of 1 and 2, which should be induced by substitution of coordinated solvent molecules. These results confirm the previous reports that the magnetic interactions in {Dy₂}-SMMs can be tuned through subtle structural variations not only in the aspect of the bridging factors, but the terminal coordinated groups. For examples, Wang et. al has reported a transition between antiferromagnetic and ferromagnetic interaction states when terminal coordinated dimethylacetamide (DMA) were changed to dimethylformamide (DMF),³⁵ Murugesu et. al suggested that the dipolar and exchange components of the magnetic interactions could be turned by the dihedral angle of the terminal amido ligands,^{10a} and so on. Given the calculated results that 1 and 2 have negligible dissimilarity between their single ion anisotropy of individual Dy^{III} fragments, the tiny change of the magnetic interactions could also be regarded as the possible reason for the discrepancy between their relaxation processes.

Experimental section

Syntheses of the Hpphz and H₃sshz ligands

A solution of 2-amino-benzohydrazide (10 mmol) in an anhydrous EtOH was added to a solution of pyridine-2-aldehyde or salicylaldehyde (20 mmol) in an anhydrous EtOH (Scheme S1). The reaction

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mixture was stirred and refluxed for 3 h. Upon cooling to room temperature, yellowish needle-like crystals were obtained. Then the crystals were collected by filtration and recrystallized with EtOH, giving Hpphz or H_3 sshz ligands, respectively.

Hpphz: Yield: ca. 83%. ¹H NMR (*d*₆-DMSO, δ/ppm): 8.67 (s, 1H), 8.59 (d, *J* = 4.5 Hz, 1H), 8.48 (d, *J* = 4.1 Hz, 1H), 7.99 (d, *J* = 3.3 Hz, 1H), 7.91-7.92 (m, 1H), 7.79-7.88 (m, 2H), 7.74 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.39-7.42 (m, 1H), 7.26-7.32 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.76-6.70 (m, 1H), 6.67 (d, *J* = 3.4 Hz, 1H). Elemental analyses (%) calcd for C₁₉H₁₅N₅O: C, 69.29; H, 4.59; N, 21.26. Found: C, 69.35; H, 4.39; N, 21.12. Selected IR (KBr, cm⁻¹): 3348(s), 1660(m), 1576(s), 1504(s), 1447(s), 1364(s), 1255(w), 1158(m), 1058(m), 1013(w), 959(w), 931(w), 874(w), 758(m), 679(m), 529(m), 413(m).

H₃sshz: Yield: ca. 79%. ¹H NMR (d_6 -DMSO, δ/ppm): 11.45 (s, 1H), 10.24 (s, 1H), 8.46 (s, 1H), 7.81 (d, J = 6.8 Hz, 1H), 7.49 (d, J = 2.3 Hz, 1H), 7.40 (dd, J = 7.7, 1.4 Hz, 1H), 7.32-7.27 (m, 2H), 7.15-7.12 (m, 1H), 6.99 (d, J = 7.6 Hz, 1H), 6.93-6.83 (m, 5H), 6.76 (t, J = 7.5 Hz, 1H), 6.70 (t, J = 7.5 Hz, 1H). Elemental analyses (%) calcd for C₂₁H₁₇N₃O₃: C, 70.18; H, 4.77; N, 11.69. Found: C, 70.30; H, 4.65; N, 11.52. Selected IR (KBr, cm⁻¹): 3369(s), 3188(s), 1643(s), 1614(s), 1491(s), 1456(m), 1405(s), 1405(s), 1365(m), 1273(w), 1236(m), 1155(s), 1097(m), 962(m), 754(s), 694(w), 650(w), 588(w), 526(w), 476(w).

Syntheses of 1 and 2

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A mixture of $Dy(OAc)_{3}$ ·4H₂O (0.2 mmol), Hpphz (0.1 mmol) and 5 drops of triethylamine in 7 mL MeOH solvent was sealed in a Teflonlined stainless autoclave after stirring for several minutes. The autoclave was heated to 60 °C for 48 h followed by cooling to room temperature at a rate of 0.5 °C min⁻¹. Yellowish crystals of **1** suitable for X-ray diffraction analysis were obtained.

The preparation of **2** followed the same procedure as **1**, except that the solvent was EtOH.

 $\label{eq:constraint} \begin{array}{l} \mbox{[Dy}_2(H_2aphz)_2(OAc)_4(MeOH)_2] (1). Yield: 32% (based on the Hpphz ligand). Elemental analysis (%) calcd. for C_{36}H_{42}Dy_2N_8O_{12}: C, 39.17, H, 3.83, N, 10.15; found: C, 39.31, H, 3.94, N, 10.33. Selected IR (KBr, cm^{-1}): 3614 (s), 3348 (s), 1576 (s), 1504 (s), 1446 (s), 1364 (s), 1255 (w), 1157 (m), 1058 (m), 758 (m), 678 (m). \end{array}$

 $[Dy_2(H_2aphz)_2(OAc)_4(EtOH)_2]$ (2). Yield: 29% (based on the Hpphz ligand). Elemental analysis (%) calcd. for $C_{38}H_{46}Dy_2N_8O_{12}$: C, 40.33, H, 4.10, N, 9.90; found: C, 40.87, H, 4.21, N, 10.15. Selected IR (KBr, cm⁻¹): 3615 (s), 3348 (s), 1573 (s), 1502 (s), 1443 (s), 1365 (s), 1255 (w), 1154 (m), 1057 (m), 755 (m), 680 (m).

Preparation of diluted samples of 1 and 2.

The diluted samples **1@Y** and **2@Y** were synthesized as the same method of **1** and **2**, respectively, except that the Dy(OAc)₃·4H₂O was substituted with a mixture of Dy(OAc)₃·4H₂O and Y(OAc)₃·4H₂O with a molar ratio of 1:9. The purity of the diluted samples was confirmed by a comparison between the experimental PXRD pattern and those simulated from the single-crystal data (Figure S3). The contents of Dy^{III} and Y^{III} in the final crystalline products were 10.83% and 89.07% for **1@Y** as well as 8.38% and 91.62% for **2@Y**, which were determined by energy dispersive spectroscope (EDS) of field-emission scanning electron microscope (Table S18).

Synthesis of 3

A mixture of $Dy(NO_3)_3 \cdot 6H_2O$ (0.15 mmol), $H_3^{OS}h_2^{10}(0.1976)H_3^{10}h_3^{$

 $\label{eq:ssh2} \begin{array}{l} \mbox{[Dy_6(ssh2)_4(\mu_4-O)(\mu_3-OH)_4(CH_3OH)_4]_2$-17.5MeOH+2H_2O (3). Yield: 29% (based on the H_3sshz ligand). Elemental analysis (%) calcd. for C_{193.5}H_{226}Dy_{12}N_{24}O_{61.5}: C, 39.92, H, 3.91, N, 5.77; found: C, 40.12, H, 3.78, N, 5.87. Selected IR (KBr, cm^{-1}): 3394 (m), 3152 (m), 1605(s), 1528 (s), 1472 (m), 1443 (m), 1394 (m), 1345 (m), 1197 (w), 1181 (w), 1152 (w), 755 (m). \end{array}$

Materials and general methods

All reagents were used as received without further purification. IR spectra were taken on a Perkin-Elmer spectrum One FT-IR spectrometer in 4000~400 cm⁻¹ region with KBr pellets. Elemental analyses for C, H and N were carried out on a Model 2400 II, Perkin-Elmer elemental analyzer. NMR spectra were obtained on BRUKER Ascend-500. Thermal analyses were performed on a Netzsch STA 449C thermal analyzer from room temperature at a heating rate of 10°C min⁻¹ under a continuous stream of N₂. Powder X-ray diffraction (PXRD) patterns were recorded using Cu- $K\alpha$ radiation on PANalytical X'Pert PRO diffractometer. Energy dispersive spectroscope (EDS) were measured using field emission scanning electron microscopy (SEM, HITACHI, SU5000).

Magnetic measurements

The magnetic susceptibility measurements were carried out on a Quantum Design SQUID magnetometer MPMS-XL 7 operating between 2.0 and 300 K for dc-applied fields ranging from 0-7 T. Polycrystalline samples were dispersed in Vaseline in order to avoid torquing of the crystallites. The sample mulls were contained in a calibrated gelatine capsule held at the centre of a drinking straw that was fixed at the end of the sample rod. Alternating current (ac) susceptibility measurements were carried out under an oscillating ac field of 3.5 Oe and frequencies ranging from 1 to 1000 Hz using both zero and optimized static dc fields.

Crystallographic refinement and structure solution

All the data were collected with an Agilent Supernova diffractometer by using graphite monochromatic Mo-K α radiation (λ = 0.71073 Å) at 298.15 K (150.00 K for **3**). Absorption effect was corrected by semiempirical methods. The structures were solved by direct methods and were refined by full-matrix least-squares methods with a suite of SHELX programs via the Olex2 interface.³⁶ The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined by using a riding model. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. ORTEP-style drawings showing ADPs of **1-3** are provide in Figure S18-S20. The detailed parameters for the structures are shown in Table S19. The related structural data such as bond lengths and angles for **1-3** are presented in Tables S20-

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S22, respectively. CCDC 1964713-1964715 for **1-3**, respectively, can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, which is free of charge.

Conclusions

In summary, by employing novel ligands incorporating both amine and acylhydrazine Schiff base groups, a pair of {Dy₂} (1 and 2) and a {Dy₆} (3) SMMs have been prepared. They all display one-step slow relaxation processes under zero dc field. Both 1 and 2 were further found to show distinct dual relaxation behaviors when 1 kOe dc field were applied. However, the dual relaxation behaviors were not observed in their diluted samples whether under zero or applied dc field. Given these facts and combined with ab initio calculation, it could be inferred that the synergism between the single ion anisotropy and magnetic interactions might be the inducement for their dual relaxation behaviors. Moreover, the change of coordinated solvent molecules between 1 and 2 has induced tiny difference of the magnetic interactions, as indicated by theoretical calculations. This might be responsible for the discrepancy between the relaxation processes of 1 and 2. This work thus demonstrates the potential of ligands incorporating both amine and acylhydrazine Schiff base groups in the achievement of novel di- and poly-nuclear Dy-SMMs, and provides new insight for the dual relaxation behaviors of the Dy-SMMs.

Conflicts of interest

There are no conflicts to declare.

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Dy^{III} single-molecule magnets from ligands incorporating both amine and acylhydrazine Schiff base groups: the centrosymmetric {Dy₂} displaying dual magnetic relaxation behaviors

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Using novel ligands incorporating both amine and acylhydrazine Schiff base groups, two $\{Dy_2\}$ and a $\{Dy_6\}$ SMMs has been synthesized. Two $\{Dy_2\}$ show dual magnetic relaxation behaviors, which could be ascribed to the joint contributions of the single ion anisotropy and magnetic interactions.



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