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# Single-Molecule Magnets Hot Paper

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# **Radical-Bridged Ln<sub>4</sub> Metallocene Complexes with Strong Magnetic Coupling and a Large Coercive Field**

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**Abstract:** Inducing magnetic coupling between 4f elements is an ongoing challenge. To overcome this formidable difficulty, we incorporate highly delocalized tetrazinyl radicals, which strongly couple with f-block metallocenes to form discrete tetranuclear complexes. Synthesis, structure, and magnetic properties of two tetranuclear  $[(Cp_2Ln)_4(tz^*)_4] \cdot 3(C_6H_6)$  $(Cp^* = pentamethylcyclopentadienyl; tz = 1,2,4,5-tetrazine;$ Ln = Dy, Gd) complexes are reported. An in-depth examination of their magnetic properties through magnetic susceptibility measurements as well as computational studies supporta highly sought-after radical-induced "giant-spin" model.Strong exchange interactions between the Ln<sup>III</sup> ions and tz<sup>\*</sup>radicals lead to a strong magnet-like behaviour in thismolecular magnet with a large coercive field of 30 kOe.

## Introduction

The field of Single-Molecule Magnets (SMMs) emerged three decades ago with the discovery of the Mn<sub>12</sub>Ac complex that exhibited magnet-like behavior of slow-relaxation of the magnetization and magnetic remanence below its blocking temperature.<sup>[1-3]</sup> Since then, an intense effort has been placed towards the goal of isolating high-performing SMMs as they are promising candidates for ultra-high density data storage devices.<sup>[4,5]</sup> For years, a common strategy to attain superior magnetic performance relied on increasing the nuclearity of transition metal complexes to isolate large spin ground state (S) intrinsic to the molecule.<sup>[6-9]</sup> As such, the energy barrier to the reversal of the magnetization  $(U_{\rm eff}; U_{\rm eff} = S^2 | D |$  and  $U_{\rm eff} =$  $(S^2-\frac{1}{4})|D|$  for integer- and half-integer-spin systems, respectively) can be increased. In this approach, the axial zerofield splitting parameter (D) was often negligible; thus, no SMM behavior was attained even with remarkably high-spin ground states. In these 3d complexes, the first-order angular momentum, a contributor to the magnetic anisotropy, is often

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quenched due to significant ligand field. Thus, achieving a large D is challenging.

In 2003, a mononuclear lanthanide (Ln) phthalocyanine complex acting as an SMM with a remarkably high  $U_{\rm eff}$  barrier was reported.<sup>[10]</sup> This was achieved through the judicious design of the ligand field around the metal center, which stabilizes the lowest degenerate substate with a large  $|J_z|$ value that provides significant separations from the higher excited states. This discovery led to a flurry of lanthanide SMMs with varying nuclearities. Polynuclear lanthanide systems are plagued by the lack of magnetic interactions between the 4f metal ions. Hence, mononuclear lanthanide SMMs reign supreme magnetic performance owing to their superior magnetic axiality (i.e., axial magnetic anisotropy).<sup>[11-18]</sup> However, magnetic axiality must be retained in the ground and excited states, otherwise it would result to the introduction of through-barrier relaxation mechanisms of the magnetization such as quantum tunneling of the magnetization (QTM), Raman and direct.<sup>[19]</sup> With that said, there is a fundamental limit to the intrinsic magnetic properties that could be extracted from a single Ln<sup>III</sup> ion. Thus, to create systems that can act as high-performing SMMs with increased magnetic hardness, strongly coupled lanthanide complexes is a challenge that deserves close attention.

To overcome the lack of strong exchange interaction between 4*f* ions, incorporating the radical bridge as a direct exchange pathway is a promising avenue. Long, Evans and coworkers elegantly demonstrated that  $N_2^{*3-}$  bridged  $Ln_2$ complexes exhibit remarkably high-blocking temperatures ( $T_B$ ) and large coercive fields indicative of magnetic hardness.<sup>[20,21]</sup> This is ascribed to strong coupling mediated through the radical  $N_2^{*3-}$  bridge. Several other complexes using radical bridges were reported,<sup>[22-27]</sup> but most of them pale in comparison to the highly delocalized and compact  $N_2^{*-}$ system. Although  $N_2^{*3-}$  is remarkable in the performance aspect, synthetically speaking, it is not trivial to rationally incorporate  $N_2^{*3-}$  into polynuclear complexes and offers no room for modification.

To overcome these issues, we turned our attention towards using the relatively unexplored unsubstituted 1,2,4,5-tetrazine (tz) as a bridging ligand. It has been shown that the very lowlying  $\pi^*$  LUMO of the tz ring easily favours the reduction and formation of the tz<sup>--</sup> radical anion.<sup>[28-35]</sup> The diffuse spin orbitals of tz<sup>--</sup>-based radicals are ideally suited to penetrate the core-like electron density of the lanthanide ion and reach the shielded 4*f* orbitals to promote stronger coupling. Moreover, its compact size and its four easily accessible nitrogen

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binding sites offer a greater possibility for the isolation of polynuclear complexes and polymeric species.

Our strategy involves the use of high-performing  $[Cp*_2Dy]^+$  as a building block, which provides magnetic axiality while connecting them with tz<sup>-</sup> radicals to form strongly coupled lanthanide-based complexes. Herein, we report the first employment of the unsubstituted tz<sup>-</sup> radical in lanthanide chemistry, which led to the formation of an unprecedented tetranuclear complex. This Dy<sub>4</sub> complex acts as a thermally activated SMM with very strong Dy<sup>III</sup>-tz<sup>--</sup> interactions. The calculated coupling constants of  $J_{\text{Dy-tz1}}/\text{hc} =$  $-27 \text{ cm}^{-1}$ ;  $-21 \text{ cm}^{-1}$  are comparable in strength to those reported for N2.3- bridged dinuclear systems.[21] To validate the calculated exchange parameters, the Gd analogue was synthesized. Fitting and simulation of its dc magnetic susceptibility afforded a good agreement between the experimental and computational data. As such, these coupling constants are notably the highest yet seen in "purely" organic radical-Ln interactions. Owing to this, the molecular species act as a true "giant-spin" system rather than a weakly coupled collection of metal ions, as seen in most Ln-based complexes.<sup>[36-40]</sup> Furthermore, this significant direct exchange with Ln<sup>III</sup> ions also promotes a sizeable coercive field for a SMM, the largest for any radical-bridged Dy-SMMs, leading to remarkable magnetic hardness.

#### **Results and Discussion**

The equimolar reaction of  $[Cp*_{2}Ln][(\mu-Ph_{2})BPh_{2}]$  (Ln = Dy or Gd) with 1,2,4,5-tetrazine (tz) and KC<sub>8</sub> in benzene for 24 h resulted in a dark red solution (Scheme 1). After leaving the filtrate undisturbed for two weeks at room temperature, red prism-shaped crystals of  $[(Cp*_{2}Ln)_{4}(tz')_{4}]\cdot3(C_{6}H_{6})$  (Ln = Dy (1), Gd (2)) were isolated in 30% yield. Attempts to reduce the crystallization times were unsuccessful. Due to the relatively low half-wave reduction potential of the tz ligand (-0.78 V),<sup>[28]</sup> analogous reactions without the presence of a reducing agent were performed. Although, upon mixing of the tz ligand (pink solution) with the  $[Cp*_{2}Ln][(\mu-Ph_{2})BPh_{2}]$ (Ln = Dy or Gd) (yellow slurry) a desirable colour change (dark red) was observed, no products were isolated via this synthetic route.

Single-crystal X-ray diffraction (SCXRD) analysis reveals that both complexes crystallize in the orthorhombic space group *Cmca*. X-ray data for **1** and **2**, along with selected bond



**Scheme 1.** Synthesis of 1 and 2, by reaction of 1,2,4,5-tetrazine (tz) and  $[Cp*_2Ln][(\mu-Ph_2)BPh_2]$  in the presence of KC<sub>8</sub> in benzene (C<sub>6</sub>H<sub>6</sub>).

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distances and angles are summarized in Tables S1, S2. Since both complexes are isostructural (Figure S1) only the structural description of 1 will be provided. The molecular structure (Figure 1 and Figure S2) consists of four



*Figure 1.* Molecular structure of 1. Lattice solvent molecules, H-atoms and disorder conformers have been omitted for clarity. Color code: Dy (orange), C (grey), N (blue).

 $[Cp_{2}^{*}Dy_{11}]^{+}$  moieties linked via four  $\mu$ -tz<sup>-</sup> ligands to form a diamond-like core. The centrosymmetric structure consists of two crystallographically independent Dy<sup>III</sup> centers. The average Dy-C<sub>Cp\*</sub> bond distance is 2.397(2) Å, while the average Cp\*<sub>cent</sub>-Dy-Cp\*<sub>cent</sub> angle is 137.86(4)°. These values are similar to those reported for other radical bridged SMMs containing [Cp\*<sub>2</sub>Dy]<sup>+</sup> moieties.<sup>[22,23,25,27]</sup> Typically, these complexes display high single-ion anisotropy due to the strong axial ligand field imposed by the Cp\* ligands. However, the Dy-Cp\*<sub>cent</sub> distances in 1 (average Dy-Cp\*<sub>cent</sub>: 2.379(2) Å) are larger when compared to the current [(Cp<sup>iPr5</sup>)Dy(Cp\*)]<sup>+</sup> benchmark<sup>[12]</sup> (Dy-Cp\*<sub>cent</sub>: 2.294(4) Å; Dy-Cp<sup>iPr5</sup><sub>cent</sub>: 2.281-(5) Å), which owes its magnetic properties to its high axiality. This further impacts the respective Cp\*-Dy-Cp\* angles (1: 139.78(2)° for Dy1 and 135.94(6)° for Dy2; [(Cp<sup>iPr5</sup>)Dy-(Cp\*)]<sup>+</sup>: 162.51(1)°) leading to an overall slight decrease in the axiality of the [Cp\*2Dy]+ moieties. The Dy-N bond distances (2.502(2) Å for Dy1 and 2.490(2) Å for Dy2) are similar to those observed for bpym- complexes (2.424(6)-2.440(6) Å)^{[22,25]} and, as expected, larger compared to  $N_2^{\cdot 3-}$ systems (2.234(1) Å).<sup>[20,21]</sup> When compared to the neutral free ligand (1.327(6) Å),<sup>[41]</sup> the N=N bonds of the reduced tetrazine rings are significantly elongated (1.351(2) Å and 1.341(3) Å), supporting its radical nature, while the average C-N bond distance remains relatively the same ( $\approx$ 1.349-(2) Å). Similar N=N bond elongation was previously reported for tz<sup>--</sup>derived radical anions.<sup>[28,31]</sup> Moreover, the shortest intramolecular Dy-Dy distance is 7.341(10) Å, while the longest distance separating the diagonals is found to be 10.715(18) Å (Figure S3). It is noteworthy that, in this centrosymmetric Dy<sub>4</sub> complex, all Dy ions lie in the same plane (Figure S4), likely imposed by the planarity of the tzradical anion. Inspection of the packing arrangement reveals that the Dy<sub>4</sub> units are in relatively close proximity. A detailed study of the supramolecular organization of the Dy<sub>4</sub> units via Hirshfeld surface analysis<sup>[42]</sup> can be found in the ESI (Figure S5 and S6). The intermolecular Dy...Dy distances vary between 10.202(10) Å and 10.601(18) Å (Figure S7). These values are slightly smaller than the largest intramolecular Dy...Dy distance of 10.715(18) Å, leading us to believe that the intermolecular interactions may impact the overall magnetic performance. With that said, the presence of bridging radical ligands is anticipated to dominate the exchange interactions and provide a giant-spin vector model intrinsic to the Dy<sub>4</sub> complex.<sup>[20,27,37,43]</sup>

To probe the magnetic interactions between the spin carriers and the potential SMM behavior, we carried out direct current (dc) and alternating current (ac) magnetic susceptibility measurements using a SQUID magnetometer. The dc magnetic susceptibility of each complex was measured between 300 and 1.8 K at 1000 Oe (Figure 2a). The room temperature  $\chi T$  products of 58.1 cm<sup>3</sup>K mol<sup>-1</sup> for **1** and  $32.9 \text{ cm}^3 \text{K} \text{ mol}^{-1}$  for 2, are in good agreement with the theoretical values of  $58.2 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$  and  $33.0 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ , respectively, for four Ln<sup>III</sup> ions (Dy: S = 5/2, L = 5, <sup>6</sup>H<sub>15/2</sub>, g =4/3,  $C = 14.17 \text{ cm}^3 \text{ K mol}^{-1}$ ; Gd: S = 7/2,  ${}^8\text{S}_{7/2}$ , g = 2, C =7.88 cm<sup>3</sup> K mol<sup>-1</sup>) and four radical species  $(S = \frac{1}{2}, C =$  $0.37 \text{ cm}^3 \text{ K} \text{ mol}^{-1}$ ). Upon decreasing the temperature, the  $\chi T$ product increases gradually until  $\approx 90$  K; below which it starts to increase rapidly to reach a maximum of  $188.8 \text{ cm}^3 \text{K} \text{ mol}^{-1}$ at 6 K for 1 and 77.4  $\text{cm}^3$  K mol<sup>-1</sup> at 4 K for 2. This trend can be attributed to the spin alignment of the metal centers caused by strong antiferromagnetic interactions between the Ln<sup>III</sup> ions and the tz<sup>-</sup> radical units. Below this temperature, the  $\chi T$  value decreases rapidly until it reaches a value of  $71.4 \text{ cm}^3 \text{ K mol}^{-1}$  at 1.8 K for 1 and 74.4 cm<sup>3</sup> K mol<sup>-1</sup> for 2. The steep downturn in the lower temperature region observed in 1, is indicative of magnetic blocking. To further confirm this, zero-field cooled/field-cooled (ZFC/FC) magnetic susceptibility measurements were performed at 1000 Oe with an average sweep rate of 0.3 K min<sup>-1</sup>. Divergence of these two data sets at 6.4 K confirms strong pinning of the magnetic moment below that temperature region (Figure 2a, insert). The blocking temperature of 6.4 K, is modest compared to other dysprosium metallocenes,<sup>[12,21]</sup> likely due to the aforementioned distortion of the Cp\*-imposed axiality on the DyIII centers. Field dependence (up to 70 kOe) of the magnetization at different temperatures (1.8 to 7 K) were measured for both complexes (Figure S8). For 1, the distinct s-shape curves of the magnetization, observed in the isotemperature lines below 5 K, further corroborate the blocking of the magnetization below this temperature. For 2, the magnetization plot shows field dependence as it increases rapidly upon increasing the field, reaching saturation at 25  $N\mu_B$ (1.9 K; 70 kOe).

Magnetic blocking occurring at 6.4 K, as observed for **1**, is a clear indication of magnet-like behavior. To validate



*Figure 2.* a) Magnetic susceptibility ( $\chi T$ ) of 1 (blue dots) and 2 (orange dots) under an applied field of 1000 Oe from 1.8 K to 300 K. The solid red line represents the fit as described in the ESI (see section 6). Insert: Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data collected under an applied *dc* magnetic field of 1000 Oe at 0.3 K min<sup>-1</sup>. b, c) Frequency dependence (0.1–1500 Hz) of the in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) magnetic susceptibility in the indicated temperature range for 1. Solid lines represent best-fits to the generalized Debye model (Tables S3 and S4). d) Arrhenius plot of the ln of the relaxation time,  $\tau$ , of the magnetization for 1 versus the inverse temperature. The red line represents the linear fit to the Arrhenius equation that affords a  $U_{eff1}/hc = 91$  cm<sup>-1</sup> for the main process and  $U_{eff2}/hc = 78$  cm<sup>-1</sup> for the minorprocess. Parameters are summarized in Table S4.

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a)

 $M(\mu_{\rm B})$ 

b) 1.0

Normalized M and  $\Delta A$ 

15

0

-15

0.5

0.0

-0.5

-1.0

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2.5 K 35K 30000 60000 -60000 -30000 0 H(Oe) -60000 -30000 30000 60000 0 H(Oe) Figure 3. a) Hysteresis sweep from 1.8 K to 6 K in a field range of 70

whether the observed blocking is of molecular origin, ac susceptibility measurements were performed in the 0.1 to 1500 Hz frequency range. A temperature-dependent ac susceptibility signal indicative of SMM behavior was observed in the absence of an applied field  $(H_{dc} = 0 \text{ Oe})$ (Figure 2b and c) in the temperature range of 7.2 to 13.4 K. The relaxation times for both the in-phase  $(\chi')$  and out-ofphase susceptibilities  $(\chi'')$  were extracted using the generalized Debye model (Tables S3 and S4; Figure S9) from 13.4 to 11 K. However, below 10.8 K a second, minor, relaxation process appears which requires the sum of two generalized Debye terms to fit the asymmetric peaks. The presence of two relaxation processes of the magnetization for Ln-based SMMs is not uncommon as it has been observed in strongly coupled  $N_2^{3-}$  radical bridged dilanthanide SMMs<sup>[21,25,44]</sup> as well as other polynuclear Ln-based SMMs.<sup>[45]</sup> In 1, the evident exponential temperature dependence of the relaxation times implies that the relaxation of the magnetization occurs through an Orbach relaxation-guided pathway. Consequently, the data were fit to an Orbach process, using Equation (1):

$$\tau^{-1} = \tau_0^{-1} \exp\left(-\frac{U_{\rm eff}}{k_{\rm B}T}\right) \tag{1}$$

The fit of these relaxation times revealed two effective barriers to spin reversal;  $U_{\rm effl}/\rm hc = 91~\rm cm^{-1}$  with a  $\tau_0 = 1.0 \times$  $10^{-8}$  s for the main process and  $U_{\rm eff2}/{\rm hc} = 80~{\rm cm}^{-1}$  with a  $\tau_0 =$  $1.9 \times 10^{-9}$  s for the minor process (Figure S10). Accordingly, the Arrhenius plots of the  $ln(\tau)$  versus the inverse temperature for both processes were made to verify these findings (Figure 2d). The linear fit of the relaxation times reveals an effective barrier of spin reversal of  $U_{\rm eff1}/{\rm hc} = 91 \ {\rm cm}^{-1}$  for the main process and  $U_{eff2}/hc = 78 \text{ cm}^{-1}$  for the minor process, which are consistent with the fits obtained using Equation (1). Attempts to incorporate terms that would account for QTM and/or Raman relaxation process failed to yield a better fit, further supporting that the Orbach relaxation mechanism is the primary relaxation for 1. Although these  $U_{\rm eff}$  values are smaller than the  $N_2\mbox{-}radical$  bridged systems,  $^{[20,21]}$  they are among the highest values reported for organic radical bridged Dy<sup>III</sup> complexes.<sup>[22–27]</sup> The lower energy barriers are likely due to tz<sup>-</sup> radicals lying in the equatorial plane, subsequently competing with the axiality imposed by the Cp\* ligands.

To probe the effect of an applied static field in the relaxation process, ac measurements were undertaken at various static fields (0-2600 Oe) at 10 K (Figure S11). Fitting of the  $\chi''$  via a double Debye model yielded the fielddependent relaxation times, which, as expected, for both the main and minor processes were relatively constant and not affected by the change in the applied field (Figure S12 and Table S5). This, in addition to the superposition of the fielddependent ac susceptibility signals and the non-improvement of the signal with the increase of the applied field, undoubtedly confirms the presence of an Orbach-only process of the magnetic relaxation, which is, as expected, extremely weakly field-dependent.

Magnetic remanence and hardness are critical when it comes to evaluating the overall performance of a magnet. Hysteresis loop measurements were performed using variato -70 kOe with a coercive field of  $\approx$  30 kOe. b) Hysteresis sweep obtained with SQUID (orange line) and MCD (blue line) at 1.8 K to 6 K in a field range of 70 kOe to -70 kOe with an average sweep rate of 25  $Oes^{-1}$  (SQUID) and 23  $Oes^{-1}$  (MCD).

ble-field magnetization measurements with an average sweep rate of 25 Oes<sup>-1</sup>. Hysteresis loops were observed for **1** from 1.8 K to 6 K, above which the loops are no longer open (Figure 3a). The opening of the loop up to 6 K is consistent with the 6.4 K blocking temperature obtained via ZFC/FC studies. The step-like features seen in the loop suggest the presence of ground state (at 0 Oe) and resonant quantum tunneling (30 kOe) of the magnetization for 1. At 1.8 K, the opening of the loop at zero-field reveals a coercive field of  $\approx$  30 kOe. To the best of our knowledge, this coercive field of 30 kOe is the highest, yet reported, among the family of Dybased radical bridged metallocenes in the literature (Table 1).<sup>[20-23,25,27]</sup>

To validate that the observed magnetic behavior of 1 is of molecular origin, frozen solution measurements were attempted but, due to the insoluble nature of 1, were not successful. In such a case, magnetic dilution (i.e. 5% Dy and 95% Y) could be employed instead.<sup>[46,47]</sup> However, due to the presence of two crystallographically independent Dy<sup>III</sup> ions (Dy1 and Dy2) in 1, with two different exchange couplings, magnetic dilution would have resulted in a statistical mixture of products, adding another level of complexity to the system by fragmenting the system and as such this route was not further explored herein.

To further probe the origin of the magnetic hysteresis and hardness, magnetic circular dichroism (MCD) studies were performed on a polycrystalline sample of 1 at 1.8 K under fields ranging from 70 to -70 kOe (Figure S13). MCD technique is per se a dilution method, as only molecules with

Table 1: Key magnetic properties of radical bridged Dy-SMMs. For comparison reasons, only those exhibiting coercive field are presented.

	$J_{Ln-rad}/hc [cm^{-1}]$	$U_{\rm eff}/{ m hc}~[{ m cm}^{-1}]$	$ au_0[s]$	H <sub>c</sub> [kOe]	References
$[(Cp*_{2}Dy)_{4}(tz)_{4}]\cdot 3(C_{6}H_{6})$	$J_{Dy-tz1} = -27$ $J_{Dy-tz2} = -21$ $J_{Gd-tz1} = -24$	$U_{\rm eff1} = 91$ $U_{\rm eff2} = 80$	$ au_{01} = 1.0 \times 10^{-8} \  au_{02} = 1.9 \times 10^{-9}$	30 <sup>[a]</sup>	This work
$\begin{split} & [K(18\text{-}crown\text{-}6)] \{ [(Me_3Si)_2N]_2(THF)Dy \}_2(\mu\text{-}\eta^2\text{-}N_2\text{-}) \\ & [K(crypt\text{-}222)] [(Cp^{Me4H}_2Dy)_2(\mu\text{-}N_2\text{-})] \\ & [Cp^*_6Dy_3(\mu_3\text{-}HAN\text{-})] \\ & [Cp^*_2Dy)_2(\mu\text{-}tppz\text{-})] (BPh_4) \end{split}$	$\int_{Gd-t_22} = -15 \\ \int_{Gd-r_ad} = -54 \\ \int_{Dy-r_ad} = -14.6 \\ \int_{Gd-r_ad} = -10 \\ \int_{Gd-r_ad} = -6.91$	123 108 51 35.9	$8 \times 10^{-9}$ $1.7 \times 10^{-8}$ $1.2 \times 10^{-8}$ $2.1 \times 10^{-7}$	15 <sup>[b]</sup> 10 <sup>[c]</sup> 8 <sup>[d]</sup> 1 <sup>[e]</sup>	[20] [21] [27] [23]
$\label{eq:constraint} \begin{split} &[(Cp*_2Dy)_2(\mu\text{-}5,5'\text{-}Me_2bpym^{*})](BPh_4) \\ &[(Cp*_2Dy)_2(\mu\text{-}bpym^{*})](BPh_4) \\ &[(Cp*_2Dy)_2(\mu\text{-}5,5'\text{-}F_2bpym^{*})](BPh_4) \end{split}$	$J_{Gd-rad} = -19.1$ $J_{Gd-rad} = -20$ $J_{Gd-rad} = -21.8$	82 87.8 93	$3.2 \times 10^{-7}$ $1.0 \times 10^{-7}$ $2.0 \times 10^{-7}$	0.76 <sup>[f]</sup> 0.6 <sup>[g]</sup> 0.58 <sup>[f]</sup>	[25] [22] [25]
[(Cp* <sub>2</sub> Dy) <sub>2</sub> (μ-5,5'-(OEt) <sub>2</sub> bpym')](BPh <sub>4</sub> ) [(Cp* <sub>2</sub> Dy) <sub>2</sub> (μ-5,5'-(NMe <sub>2</sub> ) <sub>2</sub> bpym')](BPh <sub>4</sub> )	$J_{ m Gd-rad} = -7.8$ $J_{ m Gd-rad} = -5.8$	$U_{eff1} = 40$ $U_{eff2} = 94$ $U_{eff1} = 31$ $U_{eff2} = 46$	$\tau_{01} = 5.0 \times 10^{-7}$ $\tau_{02} = 3.2 \times 10^{-8}$ $\tau_{01} = 3.2 \times 10^{-6}$ $\tau_{02} = 4.0 \times 10^{-7}$	0.43 <sup>[r]</sup> 0.04 <sup>[f]</sup>	[25] [25]

Average sweep rates: [a] 25  $Oes^{-1}$ ; [b] 800  $Oes^{-1}$ ; [c] 100  $Oes^{-1}$ ; [d] 40  $Oes^{-1}$ ; [e] 30  $Oes^{-1}$ ; [f] 82  $Oes^{-1}$  for |H| > 10 kOe and 24  $Oes^{-1}$  for |H| < 10 kOe and [g] 20  $Oes^{-1}$ . Cp\*=pentamethylcyclopentadienyl; Cp<sup>Me4H</sup>=tetramethylcyclopentadienyl; HAN = hexaazatrinaphthylene; tppz = 2,3,5,6-tetra(2-pyridyl)pyrazine; bpym = 2,2'-bipyrimidine; THF = tetrahydrofuran. The Gd-rad exchange provided in the table is the coupling constant for the isostructural Gadolinium complexes.

a specific orientation to both magnetic field and light propagation direction are excited.<sup>[48]</sup> MCD spectra of 1 show broad bands in the UV region. The presence of broad bands is likely due to the high density of excited 4f states of the Dy<sup>III</sup> ion (Figure S14). In addition to the obtained spectra, magnetization curves were collected for 1 by recording the MCD intensity at 325 nm (30769 cm<sup>-1</sup>,  ${}^{6}P_{3/2} \leftarrow {}^{6}H_{15/2}$  transition) as a function of the applied field (Figure 3b), which allows for qualitative comparison with the data obtained via SQUID magnetometry (Figure S15). Although the shape of the hysteresis loop is very similar, the decrease in the coercive field is likely due to the sample preparation in the Parabar cryoprotectant, which may influence the sample concentrations and molecular arrangement. Further studies are required to provide a direct quantitative comparison. With that said, it is clear that the overall magnetic hardness is evidently intrinsic to the molecule, with all four Dy<sup>III</sup> and tz<sup>--</sup> radicals forming a molecular entity with a giant-spin rather than weakly coupled individual spin centers.

In an attempt to shed light on the magnetic performance of 1, its electronic structure was studied by a combination of ab initio multireference calculations<sup>[49,50]</sup> to treat the local magnetic properties of the Dy ions and by broken symmetry density functional theory (BS-DFT) calculations<sup>[51-55]</sup> to estimate the exchange interactions. The  $\mathbf{D}\mathbf{y}^{\text{III}}$  ions were treated by calculating the ab initio crystal-field (CF) parameters<sup>[56]</sup> for systems where the radical ligands had two or no electrons instead of the one unpaired electron. The CF of the Dy<sup>III</sup> ion in the presence of the tz<sup>-</sup> radicals was then estimated as the average of the two calculated cases. Further information is given in the ESI (see section 6). The exchange interactions were treated using a spin-scaling approach; the respective exchange coupling constants were calculated for an isostructural system where the Dy<sup>III</sup> ions were replaced by Gd<sup>III</sup> ions. The resulting exchange parameters were scaled to account for the smaller total spin of the Dy<sup>III</sup> ion.<sup>[57]</sup> These values were then mapped onto a pseudospin Ising-type Hamiltonian acting on the ground Kramers doublet (KD) of the Dy<sup>III</sup> ions. It should be noted that while the scaling approach has been shown to provide rather good results in the presence of weak exchange interactions, it is heuristic in nature and its validity cannot be guaranteed. In the case of relatively strong exchange interaction, the nature of the interaction can be complicated and cannot be necessarily reduced to a single effective parameter.<sup>[58,59]</sup> Thus, the resulting exchange parameters should be taken rather as order-of-magnitude estimates than as quantitative values (Figure S16).

The asymmetric unit of the crystal structure of 1 contains two Dy ions labeled as Dy1 and Dy2. In both cases, the ground KD is strongly axial in character with small, but nonnegligible transverse components in the g tensor (Tables S8-S11). In general, for an isolated ion, the transverse components would be large enough to enable significant QTM. This would be clearly evident in hysteresis loop measurements, where a zero-field tunneling step would be prevalent. To validate the giant-spin vector model, the close inspection of the energy levels reveals that the lowest excited doublets lie at 188 cm<sup>-1</sup> and 170 cm<sup>-1</sup> for Dy1 and Dy2, respectively. These values are much higher than the experimentally obtained effective barriers (91 cm<sup>-1</sup> and 80 cm<sup>-1</sup>); thus, the system cannot be considered as a set of weakly coupled DyIII ions relaxing separately, but rather as a coupled spin system relaxing as a single "giant-spin".

The principal magnetic axes of the ground KDs of all ions are almost collinear, with an angle of 5.7° between those calculated for Dy1 and Dy2 (Figure S17). The axes are perpendicular to the molecular plane, clearly showing that the strong axiality of the CF arising from the Cp\* ligands is stronger than the equatorial contribution to the CF arising from the bridging tz<sup>-</sup> ligands. The isotropic exchange parameters calculated for the two different Dy-tz<sup>-</sup> exchange interactions are  $-21 \text{ cm}^{-1}$  and  $-27 \text{ cm}^{-1}$ , which correspond to the respective exchange parameters of  $-104 \text{ cm}^{-1}$  and  $137 \text{ cm}^{-1}$  when mapped to an Ising type Hamiltonian acting on the ground KD of a Dy<sup>III</sup> ion. The nearest-neighboring radicals also have short contacts, which lead to exchange interaction with exchange coupling constants of  $-50 \text{ cm}^{-1}$  and  $-31 \text{ cm}^{-1}$ . Due to the larger values of the Ising-type parameters, the Dy-tz<sup>-</sup> interaction dominates the spin configuration of the ground state, leading to an antiferromagnetic configuration with all Dy<sup>III</sup> spins in the same direction and all radical spins in the opposite direction. This is consistent with the observed magnetic susceptibility.

To validate the aforementioned findings, the exchange coupling parameters of 2 were calculated using broken symmetry density functional theory (BS-DFT). Four different exchange couplings were considered: two different metalradical interactions for the two different exchanges in the asymmetric unit:  $J_1 = -24 \text{ cm}^{-1}$  and  $J_1' = -15 \text{ cm}^{-1}$ ; and two nearest-neighbor radical-radical interactions:  $J_2 = -42 \text{ cm}^{-1}$ and  $J_2' = -23 \text{ cm}^{-1}$ . A susceptibility plot simulated from the calculated exchange coupling constants reproduces the observed susceptibility reasonably well (Figure S18), although the simulated susceptibility rises more rapidly and at a slightly lower temperature than the measured susceptibility. A good fit of the susceptibility data was only possible using a single metal-radical exchange parameter  $J_1 = J_1' = -19.6 \text{ cm}^{-1}$ , which is in excellent agreement with the average of the two calculated metal-radical exchange parameters  $(-19.5 \text{ cm}^{-1})$ (Figure 2a). Any attempt to include more parameters in the fit leads to physically unreasonable values of some of the parameters. Further information is given in the ESI (see section 6).

A model of the energy level structure of the full complex 1 was constructed on the basis of four pseudospin doublets describing the local ground KDs of the Dy<sup>III</sup> ions and four isotropic effective spin doublets describing the tz-radical bridges. Further information is given in the ESI (see section 6). It should be noted that while the Dy-tz<sup>--</sup> exchange splitting is smaller than the splitting between the ground and first excited local KD at each Dy<sup>III</sup> ion, it is still of the same order of magnitude. Thus, the omission of the excited doublets in the simulation of the energy level structure means that the results are necessarily only qualitative. Treatment of the problem taking into account the full 16-dimensional Jmanifold of each Dy ion would, however, lead to a Hamiltonian with a dimension of over a million that would not be tractable. In the model, all metal-radical interactions were taken as purely Ising type, so that each state of the full system retains at least two-fold Ising-type degeneracy. The ground state consists of a doublet corresponding to the two ferrimagnetic states where all Dy<sup>III</sup> spins are aligned in the same direction and the radical spins to the opposite direction. The lowest excited manifold at 78 cm<sup>-1</sup> is a two-fold degenerate consisting of states where one of the radical spins is flipped. The next two excited manifolds are both fourfold degenerate and lie at 84 cm<sup>-1</sup> and 85 cm<sup>-1</sup>, respectively. They correspond to a situation where either two DyIII spins and two radical spins or one Dy<sup>III</sup> spin and two radical spins have been flipped relative to the ground manifold. This energy range of 75 cm<sup>-1</sup> to 85 cm<sup>-1</sup> within the first excited manifold suggests that there is a dispersion of about 10 cm<sup>-1</sup> within it. The relaxation of magnetization is most likely initiated via these sets of states, which are in relatively good agreement with the observed

barriers for the relaxation of magnetization considering the approximation involved. As previously mentioned, the two crystallographically distinct Dy ions lead to two possible values for the Dy-radical and radical-radical exchange coupling constants. Once the full Hamiltonian model corresponding to the full system is constructed and diagonalized, the slightly different values of the exchange coupling constants lead to dispersion in the energies of each exchange manifold. This then allows different pathways for the relaxation of magnetization within each manifold that can lead to different relaxation times, that is, the presence of two relaxation processes. Although there is a dispersion in the exchange manifold due to the different possible values of the exchange coupling parameters, the manifold itself arises as a consequence of the exchange coupling. Therefore, both relaxation times correspond to the relaxation of the whole system. The relatively large splitting between the ground spin configuration and the excited configuration means that the ground state of 1 can be described as a single "giant-spin". The relaxation proceeds by stepwise flipping of the individual spins, which leads to the destruction of the "giant-spin" state and to eventual relaxation of the magnetization.

In the presence of an external magnetic field directed along the principal magnetic axis, one of the states in the ground doublet gets mixed with one of the states in the lowest excited doublets resulting in a crossing of the energy levels at a field of about 23200 Oe (Figure 4). In the presence of a transverse component to the field, the crossing will lead to



**Figure 4.** The splitting of the electronic states of 1 under an external magnetic field applied along the principal magnetic axes shown a) for all states considered in the spin model; b) for the low-lying states near the crossings of the energy levels.

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an avoided crossing and to significant QTM. A further crossing takes place at around 33300 Oe. Considering the approximation involved in the calculation, this is in qualitative agreement with the observed steps in the hysteresis at approximately 16000 Oe and 30000 Oe (Figure 3 and S19). As no crossings take place at lower fields, the observed minor steps (Figure S19) can be attributed to intermolecular dipolar interactions. The shortest intermolecular contacts between Dy<sup>III</sup> ions with collinear magnetic axes are 10.346(11) Å and 10.426(4) Å. Assuming perfectly collinear magnetic axes, and using the calculated *g* tensors, the magnetic field in the direction of the principal axis can be calculated as roughly 1000 Oe.<sup>[60]</sup>

# Conclusion

In summary, we successfully isolated the first examples of tetranuclear radical-bridged lanthanide metallocene complexes, Ln4, using a tz<sup>-</sup> radical anion. Owing to its highly delocalized electron density, the tz<sup>--</sup> radical strongly couples to the metal center affording a  $J_{\text{Dy-tz1}}/\text{hc} = -27 \text{ cm}^{-1}$  and  $J_{\text{Dy-tz2}}/\text{cm}^{-1}$  $hc = -21 cm^{-1}$ , as determined by computational studies. These strong coupling constants with  $Dy^{\ensuremath{\text{III}}}$  ions places  $tz^{\text{--}}$ radical the second most efficient radical bridge after the wellknown diatomic N2.3- radical anion. As such, 1 acts as a molecular entity, with giant-spin, rather than weakly coupled individual spin centers. Thus, strong magnetic interactions can be seen as a route to surpass the throughbarrier relaxation of the magnetization (via QTM or Raman) which usually vitiate the blocking of the magnetization. This feature is reminiscent of transition metal complexes with strong intramolecular interactions akin to the well-known Mn<sub>12</sub>Ac complex. The same strong interactions also lead to one of the largest coercive fields ( $\approx 30$  kOe) in the hysteresis loops reported to date.

Through computational studies, simulation and fitting of the experimental dc magnetic susceptibility of the Gd<sub>4</sub> analogue (2), further supports the strong exchange coupling between the Gd<sup>III</sup> ions and the tz<sup>-</sup> radical ligands. Furthermore, the relaxation mechanism was probed, revealing that thermally activated relaxation proceeds by stepwise rotation of the local spins with respect to the total giant-spins of the system, which ultimately leads to the removal of the giantspin state and to eventual relaxation of the magnetization. The energy barrier of this rotation of the local spins, with respect to one another, is determined by the exchange coupling between the spins, thus explaining the barrier in the 80 to 91 cm<sup>-1</sup> range. Such an Orbach-only process is similar to 3d metal systems, and otherwise uncommon in lanthanide ions, which tend to be dominated by significant QTM and Raman.

All these attributes point towards **1** being one of the highest performing magnets in terms of magnetic hardness, a critical aspect when envisioning storage application. This is due to the Dy-tz<sup>--</sup> interaction that efficiently couples the metal centers to become one single molecular unit with a giant-spin. Although some of the N<sub>2</sub>.<sup>3-</sup> bridged Ln<sub>2</sub> systems outperform our example, controlled incorporation of N<sub>2</sub>.<sup>3-</sup> to

form a targeted molecular structure with specific design and nuclearity is far from trivial, as serendipity plays a critical role in the synthesis. In comparison, the tz<sup>-</sup> radical anion is highly versatile and offers greater stability, tunability and control for the synthesis of molecular and low-dimensional materials. This 1,2,4,5-tz<sup>-</sup> radical system provides a glimpse into the potential of cluster-based SMMs to outperform smaller mono or dinuclear systems. With this strategy, large spin ground state SMMs could be achieved, where the radical-lanthanide units behave as a magnetic entity rather than a collection of spins, while the Ln ions preserve their inherent spin-orbit coupling.<sup>[61]</sup>

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# **Conflict of Interest**

The authors declare no conflict of interest.

**Stichwörter:** coercive fields · giant-spin model · organic radical bridges · single-molecule magnets · tetrazine

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