

# A rational approach to the modulation of the dynamics of the magnetisation in a dysprosium–nitronyl-nitroxide radical complex†

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A control of the dynamics of the magnetisation is chemically achieved in a ring-like Dy-radical based molecule, allowing the estimation of the quantum tunnelling frequency with a <sup>4</sup>He-cooled susceptometer.

In recent decades the discovery of compounds showing at the molecular scale magnetic properties previously found in classical 3D magnets, such as magnetic hysteresis (hence called single molecule magnets – SMMs),<sup>1</sup> aroused deep interest from both applicative and theoretical points of view. Although much chemical effort has been devoted to the design of novel SMMs with tunable properties, the rational control of the relaxation mechanisms, especially the quantum tunnelling (QT) of the magnetisation, is an objective which has not been completely reached. Previous evidences of its reduction have been reported in zero applied magnetic field by creating a superexchange bias potential afforded by feeble antiferromagnetic coupling of two identical SMMs.<sup>2</sup> Our approach deals with an induced chemical and magnetic coupling between two identical lanthanide-radical subunits by means of molecular engineering.

As radicals of the nitronyl-nitroxide family show good coordination ability with 3d and 4f ions,<sup>3,4</sup> the radical 2-(4-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazolyl-3-oxide (NITpPy), was chosen as a building block. The spin density on the pyridine nitrogen is significantly smaller than on the oxygen atoms and therefore NITpPy is able to give rise to very different magnetic interactions, depending on its coordination mode. Lanthanide ions are, on the other hand, very well suited for building new SMMs since they possess an intrinsic uniaxial anisotropy, and have shown slow relaxation of the magnetisation in zero and one-dimensional magnetic materials.<sup>5–8</sup>

Reaction of Dy(hfac)<sub>3</sub>·2H<sub>2</sub>O (hfac = hexafluoroacetylacetonate), with NITpPy produced crystals of complex [Dy(hfac)<sub>3</sub>{NITpPy}]<sub>2</sub> **1**,<sup>†</sup> isostructural with its Gd(III) analogue, previously investigated by some of us.<sup>9</sup> Its dinuclear structure, shown in Fig. 1,

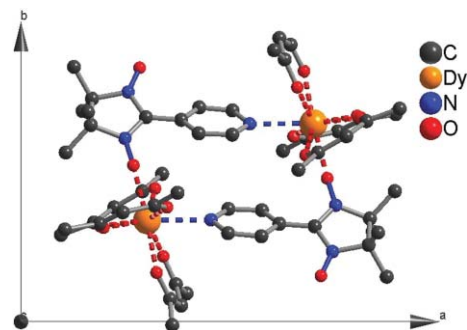


Fig. 1 Schematic view of the [DyNITpPy]<sub>2</sub> structure along the crystallographic *c* axis. Fluorine and hydrogen atoms are not shown for the sake of clarity. Dotted lines highlight Dy(III) coordination bonds.

possesses an inversion centre and comprises two bridging NITpPy radicals, each one coordinating two lanthanide ions *via* an oxygen and the nitrogen of the pyridine ring.

The Dy centres are hence octa-coordinated, with the O<sub>Rad</sub> and N<sub>py</sub> at 2.38 and 2.61 Å, respectively. The tilting between the aromatic and the imidazole planes, about 33°, is similar to that previously observed in other N-coordinated NITpPy compounds.<sup>10</sup>

Dc-magnetic characterization of **1** was carried out with a Cryogenic SQUID S600 magnetometer in the 2–300 K temperature range, by pressing the microcrystals in a pellet to avoid orientation in the magnetic field.

Above 160 K (Fig. 2) the compound follows the Curie law, showing a  $\chi T$  value at room temperature of 27.7 emu K mol<sup>-1</sup>, slightly lower than expected for two uncorrelated Dy(III) (a <sup>6</sup>H<sub>15/2</sub> ion) and two uncorrelated *S* = 1/2 spins, but in good agreement with literature data.<sup>6</sup> Between 160 and 25 K the  $\chi T$  product decreases from 27.7 to 25.6 emu K mol<sup>-1</sup>, due to crystal-field

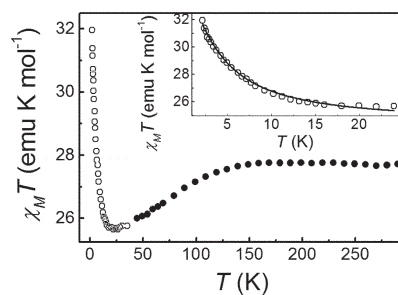


Fig. 2 Temperature dependence of the  $\chi T$  product in the 2–300 K range, in 0.1 kOe and 1 kOe (empty and filled circles, respectively) fields. The fitting of the data between 24 and 2 K, as described in the text, is shown in inset.

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effects on the Dy(III) Stark sub-levels, as already evidenced in other Dy(III) based compounds.<sup>11</sup> Below 25 K there is a pronounced increase of the  $\chi T$  value up to 32.0 emu K mol<sup>-1</sup> at 2 K, with no evidence of any levelling. This suggests parallel alignment of the two Dy(III) magnetic moments, as confirmed by the magnetisation vs. field curve, whose second derivative  $d^2M/dH^2$  changes sign only in zero field (see ESI†).

As the Dy centres can be treated at low-temperature, as  $S = 1/2$  spins with high anisotropy the curve was fitted using an Ising spin-Hamiltonian:

$$H = -J_1(S_1^z s_1^z + S_2^z s_2^z) - J_2(S_1^z s_2^z + S_2^z s_1^z) - 2\mu_B(GS + gs)H^z$$

where  $S_i$  are the Dy(III) spins,  $s_1$  and  $s_2$  the NO and N<sub>py</sub> bounded to Dy<sub>1</sub> radical spins respectively,  $G$  and  $g$  the Landé factors of Dy and radical spins,  $\mu_B$  the Bohr magneton and  $J_1$  and  $J_2$  are the exchange interactions transmitted by the NO group and the pyridine nitrogen, respectively. All quantities are considered as scalars, and the spin variables can take only two values,  $\pm 1/2$ . A diagonal energy matrix is thus obtained and the magnetic properties are calculated from the distribution function, giving the expression reported in the ESI† for the  $\chi T$  curve. The polycrystalline behaviour is simulated taking one third of the  $\chi T$  value calculated with this Hamiltonian.

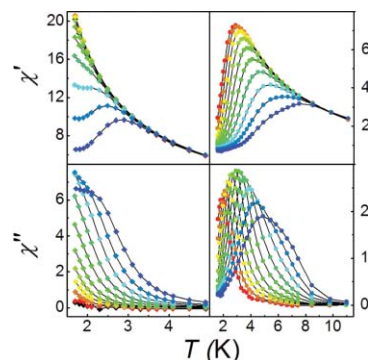
The Ising approximation is expected to be well-suited to the low-temperature regime of Dy(III), as the low-symmetry components of the crystal field are forced to behave as a  $S = 1/2$  spin system, with very anisotropic values of  $G$ .<sup>12</sup> On the other hand the radical is better described by an isotropic Heisenberg center with  $g = 2.00$ . Anyway, as the  $\chi T$  product depends on the square of the gyromagnetic factors and  $G$  is about one order of magnitude bigger than  $g$ , such a Hamiltonian is a reasonable choice. This model allowed us to fit the  $\chi T$  vs.  $T$  curve in the 2–25 K temperature range, yielding two ferromagnetic interactions of  $13.5 \pm 0.9$  and  $0.28 \pm 0.01$  cm<sup>-1</sup>, with an agreement factor  $R^2 = 0.997$ . Above 25 K population of excited Stark sublevels, neglected in the model, becomes important. The obtained values are in good agreement with those reported for the Gd analogue,<sup>9</sup> and have been interpreted as the result of a spin-polarization mechanism of the radicals' unpaired electrons on the Ln(III) empty orbitals.

Even though, for the symmetry of the Hamiltonian, it is *a priori* impossible to attribute the coupling constants to the Dy–O or Dy–N exchange pathways it is reasonable to assume that the strongest coupling ( $J_1$ ) occurs *via* the NO group of the ligand.

The dynamic magnetic behaviour of **1** was investigated using a homemade ac-probe working in the 100 Hz–25 kHz frequency range.<sup>13</sup> In a  $H = 0$  static field the system shows a frequency dependence of the imaginary part ( $\chi''$ ) of the susceptibility, as reported in Fig. 3. There is no evidence of frequency independent  $\chi''$  peaks, typical of long-range ordering.

To analyze the dynamics of this system we extracted the relaxation time at all temperatures by fitting the  $\chi''$  vs. frequency curves (see ESI†). Plotting the extracted time vs. the inverse of the temperature afforded the Arrhenius plot in Fig. 4.

Above 2.5 K the relaxation follows a thermally-activated mechanism while at lower  $T$  a gradual cross-over to a temperature-independent regime is observed, a behaviour associated to the appearance of quantum effects on the relaxation process.<sup>14,15</sup> For the first time for a magnetic compound, an

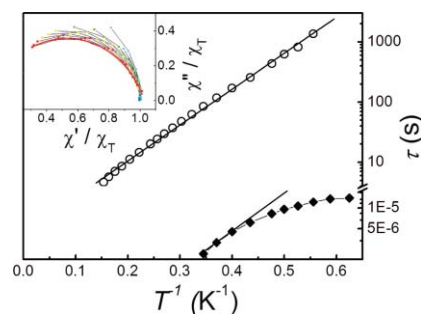


**Fig. 3** Temperature dependence of  $\chi'$  (top) and  $\chi''$  (bottom), expressed in emu mol<sup>-1</sup> and measured in zero static field (left), and  $H = 2$  kOe (right) for ten logarithmically-spaced frequencies, ranging from 100 Hz (red points) to 25 kHz (blue points).

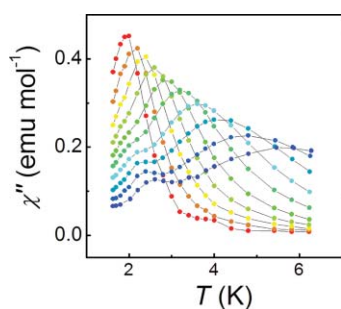
estimation of the tunnelling frequency is achieved with a <sup>4</sup>He-liquid refrigerated ac-susceptometer and revealed to be about 14 kHz. This prevents the opening of a magnetic hysteresis loop, even at <sup>3</sup>He temperature, as reported in the ESI†

From the Argand plot ( $\chi''$  vs.  $\chi'$  at constant  $T$ ) reported in the inset of Fig. 4, we can have direct access to the width of the distribution of the relaxation rate by introducing the  $\alpha$  parameter in the Debye formula.<sup>16,17</sup> When  $\alpha = 0$  a single relaxation time is present. SMMs often feature a very broad distribution in the tunnelling regime,<sup>18</sup> while **1** displays a narrow distribution: only a moderate increase of the dispersion on lowering  $T$ , with  $\alpha$  passing from 0.03 at 2.9 K to 0.21 at 1.6 K.

It is well known<sup>19</sup> that for SMMs the tunnelling mechanism can be suppressed by applying a static magnetic field removing the degeneracy of the states connected by the tunneling mechanism. We thus measured the dynamic susceptibility in  $H = 2$  kOe (right part of Fig. 3). The ac data on the right show an overall reduction in height due to saturation effects that depress the susceptibility. More interesting is the shift of the  $\chi''$  maxima to higher temperatures, typical of a slowing down of the relaxation mechanism. The Arrhenius plot in  $H = 2$  kOe field, also reported in Fig. 4, is linear over the entire temperature range, confirming that the application of an external static field is sufficient to fully suppress the QT process. Linear regression on the basis of the Arrhenius law for a thermally activated mechanism,  $\tau = \tau_0 \exp(\Delta/k_B T)$ , afforded a barrier  $\Delta = 13.7 \pm 0.1$  K and  $\tau_0 = (6.7 \pm 0.2)$



**Fig. 4** Arrhenius plot in zero and 2 kOe static field (filled squares and empty circles, respectively). Lines show the linear fit of the data (only the three highest temperatures are considered in zero field). The inset shows the Argand plot taken from zero-field measurements normalized with respect to the isothermal susceptibility  $\chi_T$ . Only the 1.6 K fit is shown for clarity.



**Fig. 5** Temperature dependence of  $\chi''$  measured in  $H = 2$  kOe static field in the 100 Hz–25 kHz range for a polycrystalline sample of **1** doped with Y(III).

$\times 10^{-7}$  s with  $R = 0.998$ , values in good agreement with those found for the three highest temperature points taken in the zero field measurement, shown in Fig. 4 ( $\Delta = 13.2 \pm 0.5$  K and  $\tau_0$  of  $(2.3 \pm 0.3) \times 10^{-8}$  s,  $R = 0.9995$ ). While the barrier under field remains, within the error, unchanged,  $\tau_0$  increases appreciably, in accordance with the behaviour of other SMMs.<sup>16</sup>

Compound **1** constitutes a nice example of a well-characterized dynamics in both the thermal and quantum relaxation regimes. Parallel investigation on monomeric  $\text{Dy}(\text{hfac})_3(\text{NITR})_2$  units, featuring the metal ion surrounded by the three hfac and by two oxygen atoms from two different radicals, revealed that in zero field the tunnelling is so fast that no  $\chi''$  is detected.<sup>20</sup> In our case, the interaction between two metal centres through the pyridine appears to be at the origin of the reduction of the tunnelling rate in zero field. To confirm this hypothesis we suppressed this interaction by substituting most of the Dy centers with diamagnetic Y(III). Owing to the similar ionic radius of Y(III) the doped compound was found to be isostructural (see ESI†). We used a starting Y : Dy molar ratio of 9 : 1, giving a room-temperature value of  $\chi T$  of  $4.15$  emu K mol<sup>-1</sup>, corresponding to an effective 5.7 : 1 ratio. Assuming a random distribution of Dy(III) and Y(III) ions inside the doped compound, Dy–Y and Dy–Dy pairs represent 25.5 and 2.25% respectively. The ac-susceptibility of this compound in zero field revealed only very weak  $\chi''$  features which well correspond to that observed for **1** (see ESI†). These indicate a slightly larger Dy<sub>2</sub> species content (about 4%), possibly due to its lower solubility compared with the Y<sub>2</sub> and DyY species, as suggested by the measured Dy(III) content compared to the stoichiometry of the starting mixture. By applying a static magnetic field the curves become more complex. In the 3–6 K temperature range peaks in  $\chi''$  are observed (Fig. 5) resembling those shown by the pure compound, but at lower temperature a second feature appears which we attribute to the faster relaxing Dy–Y dimer.

Comparing the pure and doped samples it appears that the weak Dy–Dy interaction, mediated by the small spin density delocalized on the radical's N<sub>py</sub> atom, has the effect of reducing the QT rate to a value that can be investigated with our experimental set-up. Under a magnetic field, where the QT mechanism is partially suppressed, this interaction slows the dynamics down.

This is not at all an obvious conclusion. Some of us have investigated the dynamics behaviour of Dy–M–Dy trimeric units where M is paramagnetic Ni(II) or diamagnetic low-spin Fe(II).<sup>21</sup> The former features fast QT in zero field and a smaller barrier for the reversal of the magnetisation, compared to that of the

Dy–Fe–Dy cluster, despite the weak ferromagnetic Dy–Ni interaction. The major difference between the two systems resides in the symmetry of the molecules. In fact in **1** the two anisotropic Dy(III) ions are related by an inversion centre, having therefore collinear anisotropy tensors, while an idealized binary axis relates the lanthanide ions in Dy–M–Dy species.

In conclusion, the investigation of **1** has revealed that this compound represents a text-book example of molecular systems showing a cross-over to the tunnelling regime in the <sup>4</sup>He temperature region with a well defined tunnelling rate of the magnetisation, phenomenon that can be suppressed applying an external magnetic field. The investigation of the Y-analogue doped with Dy reveals the key role played by the weak Dy–Dy interaction mediated by the N<sub>py</sub> atom of the NIT-R radical. The investigation of other species with different spin density on the third coordination site of the radical is planned to quantify the relation between the tunnelling rate and the exchange interaction.

## Notes and references

† The synthesis was carried out dissolving 0.1 mmol of  $\text{Dy}(\text{hfac})_3 \cdot 2\text{H}_2\text{O}$  in 20 ml of boiling *n*-heptane; the solution was then cooled to 70 °C and 0.1 mmol of microcrystalline NITpPy was added, affording compound **1**. The reagents were synthesized according to the literature.<sup>22,23</sup> Analysis: C<sub>54</sub>H<sub>38</sub>Dy<sub>2</sub>F<sub>36</sub>N<sub>6</sub>O<sub>16</sub>: calc.: C 31.86, H 1.88, N 4.13; found: C 31.93; H 1.69; N 4.11%. Rhombic crystals suitable for X-ray analysis were obtained with the same procedure using 3 ml of CHCl<sub>3</sub>.

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