Single-Molecule Magnets

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Magnetic Memory in an Isotopically Enriched and Magnetically Isolated Mononuclear Dysprosium Complex**

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Abstract: *The influence of nuclear spin on the magnetic hysteresis of a single-molecule is evidenced. Isotopically enriched Dy^{III} complexes are synthesized and an isotopic dependence of their magnetic relaxation is observed. This approach is coupled with tuning of the molecular environment through dilution in an amorphous or an isomorphous diamagnetic matrix. The combination of these approaches leads to a dramatic enhancement of the magnetic memory of the molecule. This general recipe can be efficient for rational optimization of single-molecule magnets (SMMs), and provides an important step for their integration into molecule-based devices.*

Single-molecule magnets (SMMs) are intensively studied from a fundamental point of view because they can act as a storage unit and they can behave as quantum objects. Potential applications cover high-density data storage devices, spintronics, and quantum computing.[1] One of the main objectives in the design of SMMs is to increase the temperature at which a molecule operates as a magnet since, to date, the highest temperature at which an isolated molecule stores magnetic data, with no external field, is 14 K.[2] Chemists are particularly eager to trap the magnetic moment in one particular direction, to ensure magnetic bistability within the molecule, by increasing the energy barrier at which relaxation occurs. The temperature dependence of the magnetic relaxation is then expected to follow an Arrhenius law, and the relaxation time tends to infinity as the temperature tends to zero. However, in most cases, a temperature-independent regime is observed (where quantum tunneling is the dominant relaxation mechanism) and is too fast to ensure magnetic bistability on a reasonable time scale. Typically, butterfly-shaped hysteresis loops are observed with the characteristic constriction at zero field.[3] This is a consequence of a transverse internal field created in condensed phases by neighboring molecules as well as the coupling with nuclear spins. In fact, these two factors are known to induce fast relaxation between quasi-degenerate Kramer's doublets.[4] Accordingly, the suppression of this regime is a prerequisite to improve magnets performance (i.e. magnetic bistability) regardless of the energy barrier between states.

To improve SMMs performance the internal field has to be minimized, that is, the magnetic molecules must be moved away from each other. The first strategy is to dissolve the molecule into an amorphous matrix (an organic solvent). The main drawback is that solubilization may induce a distribution of the molecular geometry and so a modification of the magnetic anisotropy.[5] The second strategy is to synthesize the compound as an isomorphous crystalline matrix (the diamagnetic analogue) doped with SMMs to create a solid-solution.[6] A common feature of these two strategies is that optimization resides in the modification of the environment of the molecule and not in the molecule itself. A fundamentally different strategy is to reduce quantum tunneling of the magnetization, by minimizing the hyperfine coupling between nuclei of different spins. This strategy can be achieved using metal-centered isotopic enrichment.[4b,7] This new approach may offer the possibility to intrinsically improve the magnetic bistability of existing SMMs, by decreasing the number of relaxation pathways. To tune the zero-field relaxation, various isotopes of lanthanide with ($I \neq 0$), or without ($I = 0$), nuclear spin can be used. Herein it is demonstrated that it is possible to open the hysteresis loop at zero-field and produce a genuine magnet using the three previously mentioned strategies, including metal-centered isotopic substitution.

In the last decade, lanthanide-based complexes have given a new impetus to the community of SMMs designers.[8] Among others, Dy^{III}-based complexes appeared to be ideal candidates to retain the magnetic data in zero field. However, Dy^{III}-based complexes which exhibit remnant magnetization in zero field on a longer time scale than a second and at commonly accessible temperature (ca. 2 K and above) are rare.[9] Herein we study the influence of nuclear spins on $[\mathrm{Dy(tta)_3(L)}]\cdot\mathrm{C_6H_{14}}$ $(\mathbf{1})_{\mathrm{solid}}$ (tta$^-$ = 2-thenoyltrifluoroacetonate and L = 4,5-bis(propylthio)-tetrathiafulvalene-2-(2-pyridyl)-benzimidazole methyl-2-pyridine) which display magnetic bistability in both solid and solution states.[3e] We deliberately chose a mononuclear complex to eliminate interactions between magnetic centers, which make the analysis more difficult. The energy barrier of this system was found to be equal to 40 K, in the absence of an external DC field, in the high-temperature regime ($T > 6$ K). For $T < 6$ K the magnetization relaxes through a pure tunneling process. This gives rise to a butterfly shaped hysteresis that is open up to 4 K.

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Initially, **1** is made of the natural Dy^{III} ion, that is, a mixing of the four abundant stable isotopes ^{161}Dy (18.9%) and ^{163}Dy (24.9%) for which I = 5/2, and ^{162}Dy (25.5%) and ^{164}Dy (28.2%) with no nuclear spin.[3e] The present study is focused on the chemical substitution of the natural Dy^{III} ion with ^{161}Dy (I = 5/2) and ^{164}Dy (I = 0) leading to the isotopically enriched ^{161}**1** and ^{164}**1** compounds. Their dynamic magnetic properties in solid state, in solution, and when dispersed in a Y^{III}-based matrix (solid solution) are compared. Finally, we demonstrate that zero-field magnetic memory can be tailored by adjusting both the distance between magnetic centers and the nuclear spins.

Single-crystal structures of $^{161}\mathbf{1}{\cdot}C_6H_{14}$ and $^{164}\mathbf{1}{\cdot}C_6H_{14}$ were obtained (Figure 1 and S1–S4) as described for the natural **1** compound and found to be isostructural (see syntheses in Supporting Information and Table S1). They are abbreviated hereafter $^{161}\mathbf{1}_{solid}$, $^{164}\mathbf{1}_{solid}$, and $\mathbf{1}_{solid}$, respectively. Isostructurality of the solid solutions of formula $[^{161}Dy_{0.03}Y_{0.97}(tta)_3(L)]{\cdot}C_6H_{14}$ ($^{161}\mathbf{1}_{sol\text{-}sol}$) and $[^{164}Dy_{0.04}Y_{0.96}(tta)_3(L)]{\cdot}C_6H_{14}$ ($^{164}\mathbf{1}_{sol\text{-}sol}$), has been evidenced on the basis of X-ray powder diffraction patterns (Figure S5, Table S2). All derivatives are constituted of mononuclear complexes that crystallize in the triclinic $P\bar{1}$ space group (Table S1). The Dy^{III} center is surrounded by three tta^- ions and one bidentate L ligand creating a N_2O_6 antiprism environment (D_{4d} symmetry from SHAPE analysis[10]). The shortest intermolecular Dy–Dy distance is 9.33–9.35 Å in both compounds. UV/Vis absorption spectra in CH_2Cl_2 of ^{161}**1** and ^{164}**1** are identical to the natural derivative (Figure S6).

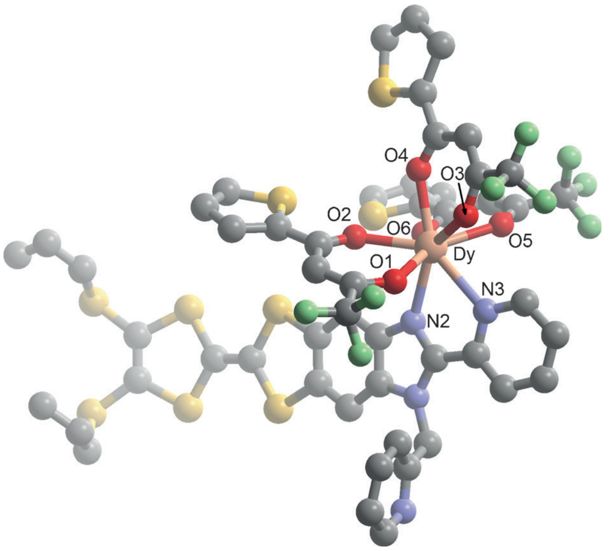

Figure 1. Molecular structure of ^{161}**1** and ^{164}**1** (H atoms and solvent molecules are omitted for clarity). Green F, yellow S, gray C.

The static magnetic measurements ($\chi_M T$ vs. T and M vs. H curves) of $^{161}\mathbf{1}_{solid}$ and $^{164}\mathbf{1}_{solid}$ perfectly superimpose (Figure S7) onto the one of the natural $\mathbf{1}_{solid}$. This is expected since on a long-time-scale magnetism is governed by the electrons and is not affected by the nuclear magnetic moment. For both isotope derivatives, the out-of-phase component of the AC susceptibility (χ_M'') shows frequency dependence below 14 K as in the natural one (Figure 2). However, the shift of the maximum of χ_M'' on the χ_M'' vs. ν curves (where ν is the frequency of the oscillating field) toward low frequencies upon cooling is much more pronounced for $^{164}\mathbf{1}_{solid}$ than for $^{161}\mathbf{1}_{solid}$. At 2 K, the maximum is shifted on the low-frequency side in going from the magnetically (^{161}Dy) to the non-magnetically (^{164}Dy) active dysprosium nucleus. Relaxation times were extracted (Figure S8–S10, Tables S3–S5), and their temperature dependences follow a modified Arrhenius law ($\tau^{-1} = \tau_0^{-1}\exp(-\Delta/T) + \tau_{TI}^{-1}$) in the temperature range 2–15 K to account for the saturation of τ at lower temperatures than 5 K (Figure 3); where τ_0, τ_{TI} and Δ stand for the intrinsic

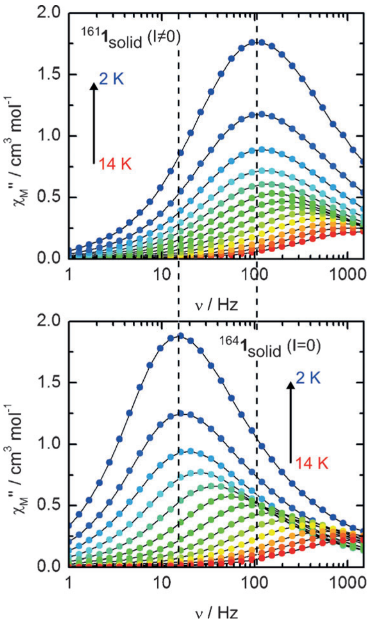

Figure 2. Frequency dependences of χ_M'' of $^{164}\mathbf{1}_{solid}$ and $^{161}\mathbf{1}_{solid}$ in zero field in the temperature range 2–14 K.

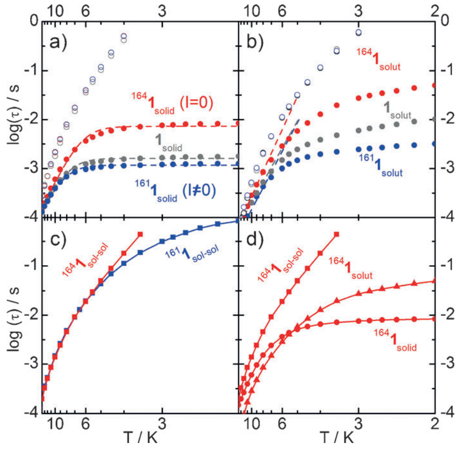

Figure 3. Temperature dependences of the relaxation times (τ) at 0 Oe (solid symbols) and 1 kOe (open symbols) for ^{164}**1** (red) and ^{161}**1** (blue). Data of the natural derivative $\mathbf{1}_{solid}$ are in gray with the best fits (dotted lines). Full lines are eye guides only: a) microcrystalline (solid), b) amorphous diamagnetic matrix (solution), c) isomorphous crystalline matrix (solid-solution), d) all the ^{164}**1** derivatives.

relaxation time, the temperature independent relaxation time and the barrier height, respectively. Thus the thermally activated regime is not affected by the isotopic enrichment and coincides with the natural derivative **1** (Table S5).[3e] In the thermally independent regime, the influence of the isotopic enrichment is drastic; the relaxation time in this temperature region increases by 10-fold when a magnetically active nucleus is replaced by a non-active one. This clearly shows the influence of metal-centered nuclear magnetic moments on slowing down the relaxation of electronic magnetic moments in lanthanide-based SMMs at low temperatures. The experimental relaxation time measured for the natural derivative is an average of the major isotope derivatives. The frequency dependence of the AC susceptibility is the superposition of three Debye functions corresponding to the three different nuclear magnetic moments in natural Dy^{III}.

To check if the observed behavior is only due to the coupling between electrons and nucleus we applied an external field to suppress the residual tunneling of the electronic magnetic moment through the barrier. For all the derivatives the relaxation times under an external DC field of 1 kOe (optimum DC field)[3e] extracted from the AC data for all temperatures merge onto the same curve (Figure 3, S11–12, Tables S6–S7). The data set shows that the isotopic enrichment only influences the temperature-independent regime observed in zero field and does not affect the thermally activated regime and the intrinsic relaxation time (τ_0). Ab initio calculations supported by single-crystal magnetometry have shown that the ground state of the Dy^{III} ion in such a N_2O_6 environment is well separated in energy from the first excited state ($126\ cm^{-1}$).[3e] The analysis of the computed ground state wave function reveals that the ground state Kramer's doublet is a linear combination of different M_J values with however a large majority of the components $M_J = \pm 15/2$ revealing the magnetic uniaxiality of the system.

Considering Kramer's theorem, the degeneracy of the ground state cannot be removed in the absence of an external field. However in the frame of ligand-field theory $|J_z = \pm 15/2\rangle$ and $|J_z = \pm 13/2\rangle$ components can be mixed by combination of different Stevens operators (such as $\boldsymbol{O}_{66}$, $\boldsymbol{O}_{44}$ and $\boldsymbol{O}_{22}$) acting in low symmetry.[11] Then the coupling between electrons and nucleus, which takes place through the hyperfine coupling $H_{hf} = A_{hf}\, \boldsymbol{I}{\cdot}\boldsymbol{J}$ ($\boldsymbol{I}$ and $\boldsymbol{J}$ are the nuclear spin and electronic angular moment, and A_{hf} the coupling constant), can mix $|J_z = \pm 13/2\rangle$ with $|J_z = \pm 15/2\rangle$ through the transverse component and give rise to quantum tunneling of the magnetization (QTM).[4b,c] In a single molecule of **1**, 54 atoms show magnetically active nuclei but at this stage only the nucleus of the metal ion is modified. For instance, nuclear spins of two nitrogen atoms of the first coordination sphere could couple with the single electrons of Dy^{III} and speed up the relaxation.

Despite the important increase of the relaxation time when the hyperfine coupling is suppressed, the quantum regime still persists in the crystalline phase. In fact, if it is commonly accepted that an intermolecular distance of 10 Å is large enough to consider that the molecules are fairly well isolated, the internal field generated at low temperature by surrounding molecules can still be relatively large. Thus in the Ising approximation the dipolar field generated by the closest neighbor molecule at 9.45 Å is close to 90 Oe. Nevertheless, the local field is the sum of the dipolar fields created by the magnetic moments around Dy^{III}. In the $P\bar{1}$ space group, and even if the magnetic moment is purely axial, the internal field contains a transverse component (a component perpendicular to the easy magnetization axis) which will mix $|J_z = \pm 13/2\rangle$ with $|J_z = \pm 15/2\rangle$ like hyperfine coupling (see Supporting Information). This creates additional relaxation pathways that are not unique because the magnetic poles of the neighboring molecules fluctuate. We decided to combine this successful "Dy^{III}-centered isotopic substitution strategy" with the more common dilution techniques detailed in introduction to cancel this internal field.

The first test has been made using CH_2Cl_2 solutions of $^{164}\mathbf{1}$ and $^{161}\mathbf{1}$ ($^{164}\mathbf{1}_{solut}$ and $^{161}\mathbf{1}_{solut}$). AC magnetic properties have been recorded at zero field and analyzed in the frame of the extended Debye model (Tables S8–S9). Solutions and the solid state behave similarly in the thermally activated regime except τ_0 which is five-times faster in solution with comparable energy barriers (Figure 3, S13–S14, Table S5). Again, the magnetically active nucleus relaxes faster in the quantum regime (below 6 K) than the magnetically inactive one with relaxation times at 2 K equal to 50 ms and 3 ms, respectively. As for solid-state measurements the quantum regime of the natural derivative in solution stands between those of the two enriched compounds and molecules in frozen solution relax slower than in the crystal. Application of an external DC field (1 kOe) dramatically increases the relaxation times, which merge into the same curve (Figure 3, S15–16, Tables S10–S11). It is remarkable that the combination of isotopic substitution and dissolution in a solvent increases the relaxation time by a factor of 50. This can be explained by the distance of approximately 60 Å between the metal centers in these solutions, which leads to the cancellation of the dipolar field generated by the neighboring molecules. Additionally, a five-times dilution does not significantly increase the relaxation time, which means the conditions are adequate to provide the longest relaxation times with this method (Figure S17). This demonstrates that dissolving isotopically selected molecules is an efficient way to diminish QTM. However, it is clear that the thermally independent regime in zero field is not completely suppressed, which at this stage prevents the molecule from operating as a data storage unit in zero field.

We have then dispersed $^{161}\mathbf{1}$ and $^{164}\mathbf{1}$ in an isomorphous crystalline matrix made of the Y^{III} analogue. In the time and temperature windows investigated, these "solid-solutions" ($^{161}\mathbf{1}_{sol\text{-}sol}$ and $^{164}\mathbf{1}_{sol\text{-}sol}$) clearly relax slower than their corresponding solutions, or the pure Dy^{III} analogue ($^{161/164}\mathbf{1}_{solid}$) (Figure 3, S18–S19, Tables S12–S13). The application of an external DC field of 1 kOe does not greatly influence the relaxation process even if it remains slower, S20–S21, Tables S14–S15). We can conclude that at higher temperatures ($T > 3$ K) we have been able to almost suppress quantum tunneling whereas at liquid helium temperature (4.2 K) the Dy^{III} relaxes 100 times slower in solid solution ($^{164}\mathbf{1}_{sol\text{-}sol}$) than in the solid state ($^{161}\mathbf{1}_{solid}$).

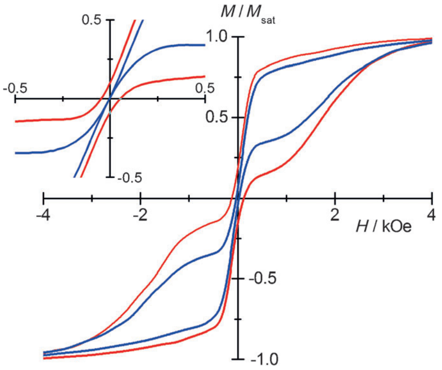

Figure 4. Normalized magnetic hysteresis loops measured at 0.46 K on $^{161}\mathbf{1}_{\text{sol–sol}}$ (blue) and $^{164}\mathbf{1}_{\text{sol–sol}}$ (red). Inset: expended view.

All these findings are confirmed by hysteresis measurements at ^{3}He temperature (0.46 K). For each of the sample preparations (solid, dilution in amorphous or isomorphous diamagnetic matrix), hysteresis loops show typical butterfly shape (Figure 4, S22–S31) but the ^{161}Dy derivatives always show a constriction at zero field that is more important than for the ^{164}Dy ones. This confirms that isotopic substitution is an efficient tool to enhance remnant magnetization, to improve SMMs performances. For a given isotope, whatever the applied field, the loops are narrower for the dispersion in amorphous diamagnetic matrix (frozen solution; Figure S30–S31). On the contrary, dilution in an isomorphous diamagnetic matrix, where there is no distribution of the molecular geometry and where dipolar coupling is suppressed, is by far the best optimization. In fact, hysteresis at 0.46 K of $^{164}\mathbf{1}_{\text{sol–sol}}$ is clearly wider at zero field and bigger than for any of the other investigated systems (Figure 4, S26–S31). Last, despite our efforts, quantum tunneling is not fully suppressed. This could be related to the persistence of nuclear spins close to Dy$^{\text{III}}$, such as those of nitrogen nuclei.

Starting from a chemical object, that is, a mononuclear lanthanide-based complex, which already behaves as a SMM, we have been able to drastically reduce quantum tunneling of the magnetic moments and therefore dramatically improve the capability of the molecule to store magnetic information. We have successively applied three different strategies, one acting on the Dy$^{\text{III}}$ nucleus and the other two acting on the molecule's environment. The first one consisted of the selection of isotopes of Dy$^{\text{III}}$ without nuclear magnetic moment to suppress the hyperfine interaction. This strategy is applicable to any Dy$^{\text{III}}$-based SMM and could lead to dramatic modifications of the magnetic properties because the relaxation time is increased in zero field. The second and third strategies attempt to cancel the internal field by dilution of molecules in an amorphous or an isomorphous diamagnetic matrix. When the methods are combined, these strategies lead to the opening of the hysteresis loop in zero field and the relaxation time ($T = 2$ K) is increased by a factor of nearly 10000, between $\mathbf{1}_{\text{solid}}$ and $^{164}\mathbf{1}_{\text{sol–sol}}$. Moreover, as far as insertion of single-molecules into devices is concerned, the properties of the molecular object are not only a consequence of its interaction with a substrate or with possible neighbors but also result from its isotopic nature.

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