

An Endohedral Single-Molecule Magnet with Long Relaxation Times: DySc₂N@C₈₀

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Supporting Information

ABSTRACT: The magnetism of DySc₂N@C₈₀ endofullerene was studied with X-ray magnetic circular dichroism (XMCD) and a magnetometer with a superconducting quantum interference device (SQUID) down to temperatures of 2 K and in fields up to 7 T. XMCD shows hysteresis of the 4f spin and orbital moment in Dy^{III} ions. SQUID magnetometry indicates hysteresis below 6 K, while thermal and nonthermal relaxation is observed. Dilution of DySc₂N@C₈₀ samples with C₆₀ increases the zero-field 4f electron relaxation time at 2 K to several hours.

Incorporation of magnetic ions in molecular clusters can lead to the formation of so-called single-molecule magnets (SMMs).¹ These molecules are characterized by slow magnetic relaxation, making them candidates for applications in quantum computing, spintronics, and high-density storage devices.²

Double-decker phthalocyanines [Pc₂Ln^{III}]⁻ (Ln^{III} = Tb,^{3a,b} Dy,^{3a,b} or Ho^{3c}) were the first mononuclear complexes shown to exhibit SMM behavior. The class of mononuclear SMMs has since been extended by mononuclear complexes of lanthanides^{4a-j}, actinides^{5a-c} and first-row transition metals.^{5d,e} Dinuclear dysprosium complexes have also been reported to show SMM behavior.^{6a-d} In this Communication we show that the mononuclear dysprosium cluster DySc₂N@C₈₀ exhibits exceptionally long relaxation times.

Magnetism in lanthanide complexes is somewhat different from their transition-metal counterparts. The 4f levels of lanthanide ions have an unquenched orbital moment and a (2J + 1)-fold degenerate ground state. If this degeneracy is lifted in a ligand field (LF), different J_z states can be separated by an energy comparable to the thermal energy at room temperature.^{4f}

Metal nitride cluster fullerenes (NCFs) offer the opportunity to encage up to three paramagnetic ions. Since their first isolation,^{7a} they have received widespread interest in research.^{7b-d} Varying the three metal ions implies a great

diversity of endohedral units: M_xSc_{3-x}N@C₈₀ (x = 1, 2; M = Er,^{8a,b} Gd,^{8c,d} Y,^{8e} Lu^{8f}), TbSc₂N@C₈₀,^{8g} CeSc₂N@C₈₀,^{8h} Lu₂CeN@C₈₀, NdSc₂N@C₈₀,^{8f} DySc₂N@C₇₆,⁸ⁱ DySc₂N@C₆₈,^{8j} Lu_xSc_{3-x}N@C₆₈ (x = 1, 2),^{8j} ScYErN@C₈₀,^{8k} Lu_xY_{3-x}N@C₈₀ (x = 1, 2),^{8l} and TiSc₂N@C₈₀.^{8m}

Investigations on the magnetism of single ions inside fullerenes started with Gd@C₈₂, which turned out to be paramagnetic down to 3 K.^{9a} For Dy@C₈₂, superconducting quantum interference device (SQUID) and X-ray magnetic circular dichroism (XMCD) measurements revealed paramagnetic behavior down to 1.8 K.^{9b-e} The observed magnetic moment is reduced in this system compared to the free trivalent Dy ion, which is attributed to a quenched orbital moment due to the crystal field splitting from the carbon cage and/or electron back-donation from the cage to the Dy ion.^{9c} In contrast, C₈₀ NCFs have a carbon cage with a closed shell, and less coupling between the moments of the metal ions and a diamagnetic cage is expected. SQUID magnetization measurements on Ln₃N@C₈₀ (Ln = Tb and Ho)^{10a,b} are in line with a model where the LF of the N³⁻ ion induces an easy axis for the individual Ln^{III} moments directed along the respective Ln–N bond. In this model the magnetic anisotropy due to the LF is strong enough that the Ln^{III} moments do not align with the external field but instead parallel to the bond directions.^{10a} Nevertheless, the magnetization curves recorded on Ln₃N@C₈₀ (Ln = Tb,^{10a,b} Ho,^{10a,b} Tm,^{10c} Er,^{10d,e} Gd^{10f}) and Er_xSc_{3-x}N@C₈₀^{10d} (x = 1, 2) above 1.8 K showed paramagnetism without hysteresis.

In the present case we have a single Dy^{III} ion in a diamagnetic carbon cage (see Figure 1). Since Sc^{III} ions are not paramagnetic, the LF due to the N³⁻ ion will result in magnetic anisotropy directed along the Dy–N bond. Furthermore, if the LF stabilizes a ground state with a large J_z, the prerequisite for magnetic bistability is fulfilled.

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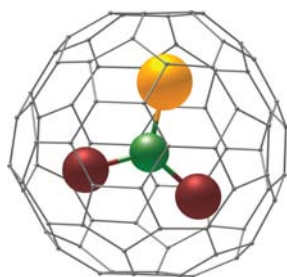


Figure 1. Chemical structure of $\text{DySc}_2\text{N}@C_{80}$ (green, N; purple, Sc; orange, Dy). The C_{80} cage is shown as a wire frame.

The robustness of endofullerene molecules and their ordering on surfaces¹¹ makes them ideal models for studying and possibly exploiting the intrinsic magnetic properties of SMMs deposited on substrates. Here we show that $\text{DySc}_2\text{N}@C_{80}$ exhibits SMM behavior with long relaxation times. By combining element-specific XMCD¹² and SQUID magnetometry on diluted and nondiluted samples, it is demonstrated that the magnetic behavior of $\text{DySc}_2\text{N}@C_{80}$ can be attributed to single Dy^{III} ions.

The synthesis, XMCD¹³ and SQUID measurement details are described in the Supporting Information. The SQUID measurements were performed using undiluted samples (1) and a sample diluted with C_{60} (2).

Figure 2a displays X-ray absorption in the energy range of the Dy $M_{4,5}$ -edges, with data normalized to the maximum $3d \rightarrow 4f$ absorption signal of right and left circular polarized light ($I^+ + I^-$). Spectra were recorded on 1 at 2 K and 6 T. Polarization-dependent X-ray absorption spectra after background subtraction, I^+ and I^- , and the resulting XMCD spectrum, $I^+ - I^-$, are shown in the middle and bottom of Figure 2a. Using sum rules,^{14a,b} the average magnetic moment of the Dy^{III} ions was extracted from the dichroism and the total absorption spectra in Figure 2a. From the calculation we obtain $\langle L_z \rangle / \langle S_z \rangle = 1.75$, in close agreement with the value of 2 derived from a $4f^9$ occupancy and Hund's rules, which predict a ${}^6H_{15/2}$ ground state. The expectation value of the Dy $\langle T_z \rangle$ operator was evaluated according to eq 8 in ref 14b. At saturation, the average Dy^{III} magnetic moment is $m_{\text{sat}} = 4.4 \mu_B$. This value is lower than $(15/2)g_J\mu_B = 10 \mu_B$ expected from the Hund ground state with a Landé factor $g_J = 20/15$, even if it is reduced by a factor of 1/2 due to an isotropic distribution of the easy axes.^{14c} In the present case, the LF could stabilize a ground state different from $J_z = \pm 15/2$, explaining the additional reduction of the observed magnetic moment.

Figure 2b displays the element-specific magnetization curve obtained from XMCD at the Dy M_5 -edge, together with the field dependence of the total magnetic moment measured by SQUID magnetometry. The agreement between the two data sets demonstrates that the magnetic moments measured by our SQUID magnetometer can be attributed to the Dy^{III} ions. From the observed hysteresis loops it is evident that the system exhibits slow magnetic relaxation. The shape of the hysteresis depends on the relaxation rate, so the deviation between the two data sets may be caused by a slightly higher sample temperature during XMCD measurement and different field scan rates for the two experiments, 1.3 (SQUID) and 17 mT s^{-1} (XMCD).

Magnetization loops from 1 at different temperatures using SQUID magnetometry are shown in Figure 3. Below 6 K hysteresis is observed. Hysteresis was also detected in the range

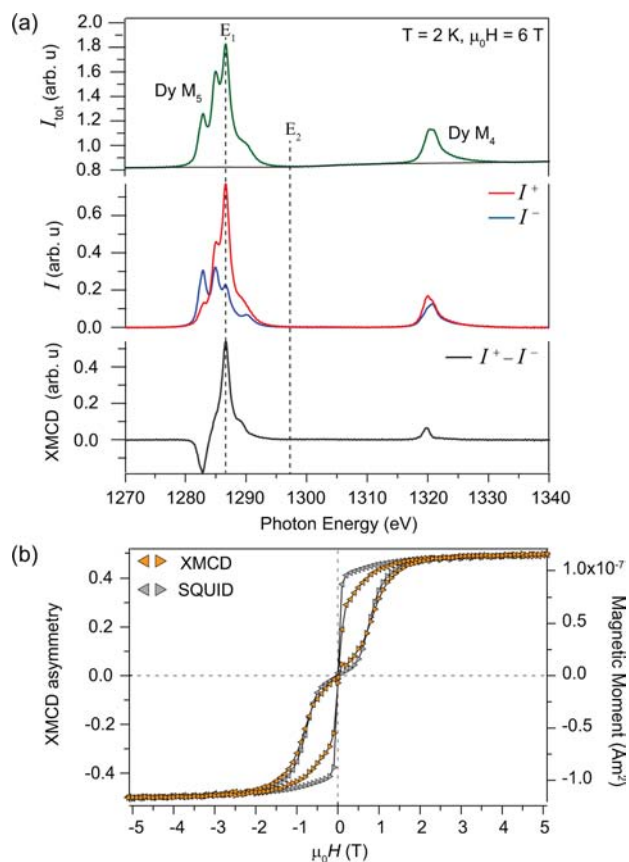


Figure 2. Results for sample 1. (a) Top: Sum of X-ray absorption spectra of both X-ray helicities, I_{tot} recorded at the Dy $M_{4,5}$ -edge at 6 T. Middle: Polarization-dependent X-ray absorption spectra after subtraction of the background, I^+ (red) and I^- (blue). Bottom: XMCD spectrum, $I^+ - I^-$. (b) Magnetization curves recorded by XMCD and SQUID magnetometry at 2 K. The element-specific magnetization curve was constructed from the asymmetry $[(I_{E_1}^+ - I_{E_2}^+) - (I_{E_1}^- - I_{E_2}^-)] / [(I_{E_1}^+ - I_{E_2}^+) + (I_{E_1}^- - I_{E_2}^-)]$ where E_1 and E_2 are the photon energies in panel (a).

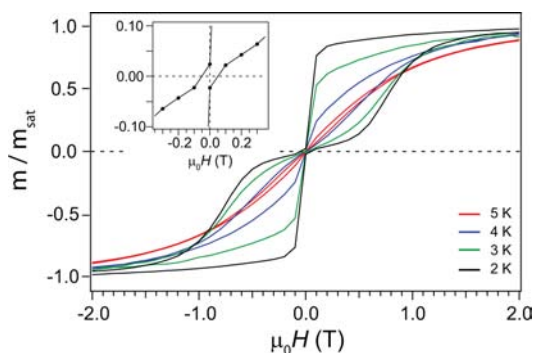


Figure 3. Temperature-dependent magnetization curves for 1 recorded using SQUID magnetometry. Inset: enlargement of the 2 K signal at small fields. m_{sat} is the saturated magnetization at 7 T.

$2 \leq T < 5$ K for sample 2 diluted with 10–20 times C_{60} , indicating that magnetic bistability is a property of single Dy^{III} ions rather than due to intermolecular magnetic interactions.

Hysteresis curves with sharp drops at low fields have been reported for other SMMs such as $[\text{Pc}_2\text{Dy}]^{-15}$ or $(\text{Cp}^*)\text{Er}(\text{COT})$.^{4f} They depend not only on temperature but also on scan time, which indicates that we deal here with slow

magnetization dynamics rather than hysteresis of a ferromagnet: The magnetization relaxes to an equilibrium that depends on field and temperature. This was further investigated by time-dependent SQUID measurements. Figure 4a shows three

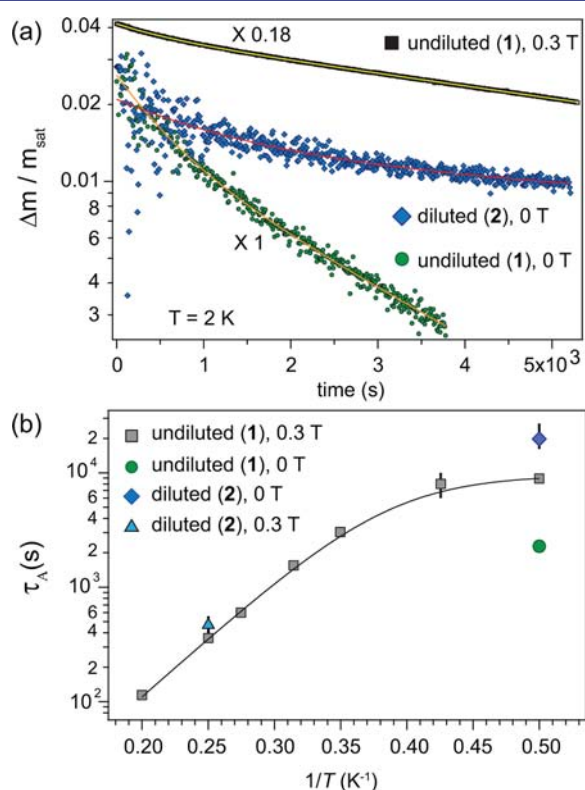


Figure 4. (a) Relaxation of the magnetization for sample 1 and 2 at $T = 2$ K, with $\Delta m(t) = m(t) - m(t \rightarrow \infty)$. m_{sat} is the saturation magnetization. The lines correspond to the best fit of double-exponential eq 1. (b) Magnetic relaxation times τ_A as a function of inverse temperature. Decay times at 0.3 T for the undiluted sample were fitted to eq 2 (solid line).

relaxation curves at 2 K. At $t = 0$ the field was switched from 0.4 to 0.3 T (0.5 to 0 T), after being ramped down from 7 T at an average speed of 5.4 mT s^{-1} (4.5 mT s^{-1}). Below 3.5 K relaxation data do not exhibit a single-exponential decay, indicating more than one relaxation process. In this temperature range, a double exponential,

$$m(t) = m(t \rightarrow \infty) + \alpha \exp(-t/\tau_A) + \beta \exp(-t/\tau_B) \quad (1)$$

was fitted to magnetization curves $m(t)$, where data were weighted with the noise. α and β are the magnetization of relaxation processes A and B at $t = 0$, and τ_A and τ_B the corresponding relaxation times ($\tau_A > \tau_B$). Above 3.5 K, a single exponential, $\alpha \exp(-t/\tau_A)$, was used to fit the $m(t)$ curves.

The resulting decay times for the slower process, τ_A , are displayed as a function of inverse temperature in Figure 4b. As expected for a thermally activated process, the relaxation times decrease with temperature.

Thermal relaxation mechanisms are generally attributed to higher order phonon processes, such as the Orbach process between the J_z levels. To estimate the effective barrier for thermally driven relaxation, Δ_{eff} the function

$$\tau(T) = \frac{\tau_c \tau_0 \exp(\Delta_{\text{eff}}/k_B T)}{\tau_c + \tau_0 \exp(\Delta_{\text{eff}}/k_B T)} \quad (2)$$

was fitted to the relaxation times. τ_c is the temperature-independent decay time and τ_0 the exponential prefactor for the temperature-dependent part. For 1 at 0.3 T we obtain $\Delta_{\text{eff}}/k_B = 24 \pm 0.5$ K, which compares to 44 K of $[\text{Pc}_2\text{Dy}]^-$ (at $350 \mu\text{T}$ ac field).^{3b} On the other hand, the exponential prefactor has an exceptionally large value, $\tau_0 = 1 \pm 0.1$ s, more than 4 orders of magnitude larger than that of $[\text{Pc}_2\text{Dy}]^-$.^{3b} This indicates peculiar magnetization dynamics in the present system. In contrast to molecules such as $[\text{Pc}_2\text{Dy}]^-$, magnetic moments in the $\text{DySc}_2\text{N}@C_{80}$ endofullerene are protected by a diamagnetic cage, and low phonon density may inhibit thermal relaxation.

The temperature-independent decay times τ_c^A and τ_c^B , ascribed to magnetization decay through quantum tunneling between the $\pm J_z$ states, are $\sim 10^4$ and $\sim 8 \times 10^2$ s, respectively. Since the Dy^{III} ion contains an odd number of electrons, all states have double degeneracy according to Kramer's theorem, so quantum tunneling is only possible in the presence of a perturbation that lifts the degeneracy and allows the doublets to mix. In the present system, Zeeman splitting or intermolecular dipole–dipole or hyperfine interactions with the nuclear spin may give rise to such a perturbation.

The relaxation time in zero field is of particular interest since it is the “remanence time” for a given sample. In zero field there is no Zeeman splitting, and intermolecular dipole–dipole interactions, which must be small due to protection of Dy by the C_{80} cage, can be further weakened by increasing the distance between the Dy atoms. This was achieved by diluting the sample with C_{60} . The data points for 2 in Figure 4 show that dilution leads to a significant increase of the relaxation time >5 h, about 9 times longer than for undiluted samples (~ 40 min). The ratios $\tau_B/\tau_A \approx 0.2$ and $\alpha/\beta \approx 1$ for both 1 and 2. If relaxation processes A and B are affected equally by intermolecular dipole–dipole interactions, this could hint that the difference between A and B is due to different Dy isotopes, i.e., hyperfine interactions between the J_z level and the corresponding nuclear spin.

At 4 K and 0.3 T, 1 and 2 exhibit the same relaxation times (within 10%), as expected for thermally driven magnetic relaxation of individual molecules.

In summary, $\text{DySc}_2\text{N}@C_{80}$ has been shown to be a mononuclear single-molecule magnet with hysteresis below 6 K. The magnetic moment is attributed to the Dy^{III} ion in the diamagnetic carbon cage, and the 4f electrons display exceptionally long relaxation times. If the sample is diluted, relaxation of the magnetization at 2 K increases by a factor of 9.

■ ASSOCIATED CONTENT

📄 Supporting Information

Full author list of ref 14c. Synthesis and details on the measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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