An NCN-pincer ligand dysprosium single-ion magnet showing magnetic relaxation via the second excited state

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Single-molecule magnets are compounds that exhibit magnetic bistability purely of molecular origin. The control of anisotropy and suppression of quantum tunneling to obtain a comprehensive picture of the relaxation pathway manifold, is of utmost importance with the ultimate goal of slowing the relaxation dynamics within single-molecule magnets to facilitate their potential applications. Combined ab initio calculations and detailed magnetization dynamics studies reveal the unprecedented relaxation mediated via the second excited state within a new DyNCN system comprising a valence-localized carbon coordinated to a single dysprosium(III) ion. The essentially C2v symmetry of the DyIII ion results in a new relaxation mechanism, hitherto unknown for mononuclear DyIII complexes, opening new perspectives for means of enhancing the anisotropy contribution to the spin-relaxation barrier.

Acting as tiny magnets, Single-molecule magnets (SMMs) are chemically and physically interesting compounds as a platform on which to build future spin-based devices. Recently the enormous potential of lanthanide(III) ions and dysprosium in particular, has been recognized as a potential source of both the high spin and high anisotropy required for SMM behavior. The blocking of magnetization for Ln-SMMs arises as a result of strong axiality of ground state, which for ions with odd number of electrons (e.g., DyIII) implies the transversal components gxy, gyz dwarfed by axial components gz, gzz. The spin is then forced to undergo reversal through a thermally activated process giving a relaxation which follows an Arrhenius behavior with a barrier D. This can be likened to a levee that prevents flooding by water even if one side of the levee is lower than the other (Figure 1). For the barrier of the levee in Louisiana, conforming to the laws of classical physics, the water is not breaking through rather than having to go over the top of the barrier. For a SMM, which is a quantum object, it is a question whether the spins can tunnel (break) through the barrier or can be forced to overcome the barrier.

Breaking through such a levee for a SMM is always constrained by the separation between the bistable ground state and the first excited state and arises from the removing the (2J + 1)-fold degeneracy of the ground multiplet provided by the surrounding crystal field (Figure 1, left). The implication to enhance SMM behavior is that we can construct a high levee by elaborating the coordination environment of the lanthanide ions to give suitable constraints to tunneling processes (Figure 1, right). In previous ab initio studies, this scenario was explored by considering an idealized diatomic [DyO]+ complex. As a result of the perfect axiality of all of the Kramers doublets (KDs) the transversal magnetic field induces a tunneling splitting in [DyO]+ only at the highest order of perturbation theory, following a path similar to that of the reversed double-well potential of Mn12-Ac24. The difference is that, for LnII ions, the total multiplet width of CF splittings of the order of 100–1000 cm−1 open huge perspectives for means of enhancing the anisotropy contribution to the magnetic relaxation barrier.

So far a clear-cut example of such a magnetic relaxation via higher excited state energy levels has never been seen before for Ln complexes. Here, we chose to probe the magnetism of a localized Dy-C bond...
containing complex stabilized by an aryldiimino NCN-pincer ligand (Inset of Figure 2), as exists in [2,6-(2,6-C₆H₃R₂N=CH)₂-C₆H₃]-DyCl₂(THF)₂ (DyNCN). More striking still, this unique Dy–C bond occupies the crystallographic C₂ axis in DyNCN. The combination of *ab initio* calculations and detailed magnetization dynamics studies reveals the two lowest Kramers doublets being extremely axial in nature and possessing parallel anisotropy axes along C₂ direction, which results in the unprecedented relaxation going via the second excited state in compound DyNCN.

**Results and discussion**

**X-Ray structure analysis.** Compound DyNCN was synthesized via transmetalation between 2,6-(2,6-C₆H₃R₂N=CH)₂-C₆H₃Li and LnCl₃(THF)₁₂ (Ln=Nd, Dy) and crystallizes in the space group *P*₄/2₂/2, with *Z* = 4. The whole molecule exhibits *C*₂ crystallographic symmetry, in which the Dy–C bond is located on a 2-fold rotation axis $\left[\frac{\sqrt{2}}{2}\frac{\sqrt{2}}{2}0\right]$. The monoanionic NCN-pincer ligand coordinates to the central metal ion in a *κκκ*: *κN*: *κN*’ tridentate mode to form a meridional conformation. The two N-aryl rings dispose the vertical positions against the NCN plane, which are parallel to the two cis-located THF rings, respectively. The chloride groups arrange in trans-positions to form a large Cl–Dy–Cl angle (176.500(23)°) bisected by the NCN plane. Therefore, if one focuses only on the atoms of the first coordination sphere two nearly exactly perpendicular planes (Cl1/N1/O1A/N1A) and (Cl/C1/C1A) are formed. Then the effective CF is of *C*₂ᵥ symmetry.

**Electronic structure calculations.** The interaction of the 4f orbitals involved in the formation of the robust organometallic surroundings seems to play a key role in the LF thereby enhancing the magnetic properties. A few carbon ring coordinated Ln-based SMMs, that include ligands such as cyclopentadienide and cyclooctatetraenide, have generated profound thoughts and enlightenment. The discovery of these bona fide organometallic SMMs underscores the significance of making use of the simple Ln-C bond to design molecules with strong axiality. The title compound with a strong single Dy–C bond combining the huge conjugation effect of a carbanion offers a new paradigm for single ion anisotropy as shown from the *ab initio* calculated electronic structure of lowest eight Kramers doublets of DyNCN in Table 1 (see Experimental Section and the ESI of Figure S1–S7 and Table S1–S8 for details).

Table 1 shows the low lying spin-orbit energy spectrum of the DyNCN molecule in the largest computational model. We notice a large energy separation of the ground and first excited Kramers doublets. As shown in Figure 3, the main anisotropy axis of the complex passes along the main symmetry axis of the complex, i.e. it is parallel to the Dy-C chemical bond. The reason for the strong effect of the ligating C atom is the fact that it holds a negative charge as the ligand is a carbanion. The calculated Mulliken charge on the carbon atom revealed a negative charge of $-1.17$ on the ligating carbon atom. The localized character of the negative charge is probably due to intramolecular electrostatic effects: the negative charge of the carbanion is attracted by positively charged Dy¹¹⁺ ion, and the ligating C atom is the closest point to the Dy¹¹⁺ ion. This is also the reason why the Dy-C bond is unusually short ($≈2.39$ Å) even though the computed Mulliken charges on both chlorine atoms are slightly larger ($≈1.60$). The longer Dy-Cl distances ($≈2.60$ Å) make the cumulative (total) effect of both chlorine atoms less important for the magnetic anisotropy of the two low lying Kramers doublets than the influence of the much closer carbon atom. In fact, we have already seen for other complexes that the main anisotropy axis is mainly oriented by the effect of the closest ligand.

As a result of the above described effects, we notice an interesting fact of collinearity of the main anisotropy axes in the ground (almost pure $±15/2$) and first excited (almost pure $±13/2$) doublets. We will see later that the collinearity of anisotropy axes is a key factor for enhancing the magnetic blocking performance of this compound. Analysing further the magnetic anisotropy of the second excited KD ($262$ cm⁻¹) we notice that it is again very axial, i.e. of $±15/2$ type, but its main magnetic axis is perpendicular to the main symmetry axis of the complex, passing through the two chlorine atoms. The third, fourth and fifth excited KDs are less axial, while the sixth and seventh excited KDs are again highly axial, with their main

| Free-ion Multiplet | Energy (cm⁻¹) | $g_x$ | $g_y$ | $g_z$ |
|-------------------|-------------|------|------|------|
| 1/2               | 0           | 9.69E+04 | 2.12E+03 | 19.8101 |
| 3/2               | 176         | 8.72E+03 | 3.46E+02 | 17.0586 |
| 5/2               | 262         | 0.4261  | 0.4374 | 19.4439 |
| 7/2               | 348         | 1.9619  | 2.5423 | 12.8581 |
| 9/2               | 445         | 8.0980  | 7.2355 | 5.4345 |
| 11/2              | 526         | 0.4681  | 0.6001 | 14.0045 |
| 13/2              | 597         | 0.5562  | 0.6555 | 19.4099 |
| 15/2              | 645         | 5.87E+02 | 0.2346 | 19.3829 |
anisotropy axis lying in the plane perpendicular to the main symmetry axis of the complex.

Table 2 shows the parameters of the crystal field acting on the ground atomic multiplet of the Dy III ion. We notice that, although the ab initio calculation was performed in the C1 point group (i.e. effectively ignoring the symmetry) the departure from the perfect point group symmetry is very small, leading to the fact that only parameters of the even projection on the quantization axis enter in the decomposition of the ab initio energy matrix. The largest parameter, sets the main anisotropy axis of the ground and of the first excited KD, while the significant value of the second largest parameter, is probably responsible for the anisotropy of the second excited KD. In other words, the parameter is the largest in the case when the quantization axis is parallel to the main anisotropy axis of the second excited KD, i.e. passing along the Cl-Cl axis.

Figure 3 | Low-lying electronic structure for DyNCN. (Top) Anisotropy axes in eight lowest Kramers doublets at the Dy site of DyNCN (KD: 1–8 ranked in order of the energy from ground state to the seventh excited state as shown in below scheme). The red dashed line corresponds to the anisotropy axis of KD: 1, 2, 4 and 5; the green dashed line shows the anisotropy axis of the second excited KD (KD 3 lying at 262 cm⁻¹). (Bottom) Magnetization blocking barrier of the DyNCN. The black lines represent the energy levels of the ground multiplet J = 15/2 aligned according their magnetic moment on the C2 symmetry axis. The arrows represent the averaged matrix element of the transversal magnetic moment connecting the corresponding states, given as (|m_x| + |m_y| + |m_z|)/3. The red arrows show the most probable path for the magnetic relaxation at high temperatures.

The ab initio calculated magnetic properties of DyNCN are in good agreement with direct current (dc) magnetic susceptibility measurements (Figure S7) which gives confidence in the anisotropic properties of the low-lying KDs discussed above. In addition, as shown in Figure S8, the preliminary powder INS spectra obtained on DyNCN exhibit two peaks, around 19 and 28 meV, that are also roughly consistent with the state transitions predicted by the ab initio calculation. Unfortunately the strong H background prevents a more detailed statement on the level structure and further investigations will be discussed in a separate publication.
**Static magnetic properties.** The investigation of the magnetic properties of a polycrystalline sample revealed a room temperature $\chi_M T$ value of 13.8 cm$^3$ K mol$^{-1}$ (Figure S7), in agreement with the expected value for $g=4/3$ of the $^4H_{15/2}$ ground state of a single Dy$^{3+}$. A gradual decrease on lowering the temperature is observed above 10 K and attributed to the depopulation of the substates. The lowest Kramers doublet has strong uniaxial magnetic anisotropy along the $C_2$ axis. The next Kramers doublet lies at about 176 cm$^{-1}$. The large energy difference results in a predominant population of the lowest levels up to relatively high temperature: the population ratio remains 99.3% at 50 K. Thus, the static magnetic behavior of the complex below 50 K is almost exclusively described by the ground doublet.

**Dynamic magnetic properties.** However, dynamic magnetic properties will be strongly influenced by the nature of excited substates. To investigate this possibility, variable-frequency alternating current (ac) magnetic susceptibility measurements were performed.

As the hallmark of a SMM, the in-phase ($\chi'$) and out-of-phase ($\chi''$) component, of DyNCN are characterized by the frequency dependence below $\sim$35 K going through a frequency dependent maximum above 100 Hz) on lowering the temperature (Figure 4a, b), signaling the “freezing” of the spins by the anisotropy barrier arising from the split substates. To quantify the thermally activated process, the $\chi''$ curves were divided by the dc susceptibility $\chi_{dc}$, in which the relaxation time $\tau$ matches the inverse of the angular frequency $2\pi\nu$ exactly at the peak temperature of the corresponding curve (Figure S9). As expected for a single-molecule magnet, the relaxation times exhibit an exponential dependence on temperature between 24 and 27.5 K, and an Arrhenius fit to the data gives an effective relaxation barrier of $U_{rel} = 233(4)$ cm$^{-1}$, with a pre-exponential factor of $\tau_0 = 6(1) \times 10^{-10}$ s (Figure 5). The barrier height of DyNCN is more than 50 cm$^{-1}$ above the first excited KD, which strongly supports the assignment that an Orbach process occurs through the second excited state (Figure 3 Bottom). This assignment is consistent with ab initio calculated energy of the second excited KD (266 cm$^{-1}$ in the best approximation (see the ESI)), which fits perfectly the barrier $U_{rel} = 270(5)$ cm$^{-1}$ extracted for the diluted sample (Figure 5).

On cooling, deviations from the Arrhenius law become more and more important, which indicates that the blocking under this barrier is not complete and not even observable at all when $T < 10$ K with a temperature-independent relaxation time $10^{-4}$ s. The observed relaxation rate at this temperature is entirely due to quantum tunneling of magnetization (QTM). In the undiluted sample of DyNCN the QTM is mainly due to the contribution of magnetic dipolar interactions to the transversal component of internal magnetic field $H_{dip}$ at each Dy site. This leads to the tunneling splitting of the ground-state Kramers doublet by the amount $\Delta_{un} = g_{X,Y} \mu_B H_{dip}$ while this tunneling gap contributes directly to the QTM relaxation rate. Given the relatively large value of the latter (Figure 5a), magnetic hysteresis in this compound is only observed without coercivity using the sweep rate accessible with a conventional magnetometer (Figure 6).

In order to reduce the influence of the molecular surrounding on the spin dynamics of the dysprosium ion, magnetic measurements on a sample in which Dy$^{3+}$ is magnetically diluted by the isostructural Lu$^{3+}$ analogue in a molar ratio of 1 : 19 (Dy$_{0.05}$Lu$_{0.95}$NCN) were performed. In contrast to the pure DyNCN, hysteresis is observed with a small coercive field for the diluted sample (inset of Figure 6). As a result of reduction of transversal component of internal field $H_{dip}$ upon dilution, the relaxation times at low temperatures are two orders of magnitude slower than those operating in the undiluted sample. Therefore, as observed also in other crystals containing SMMs, magnetic site dilution effectively chokes the pathway for ground state quantum tunneling. Here, the ac spectra could only be recorded only within a limited frequency range of 0.04 Hz, which prevented observation of the more sluggish real quantum regime at temperatures below 6 K.

**Table 2 | Ab initio calculated parameters of the crystal field acting on the ground J = 15/2 multiplet on the basis of the ab initio results presented in Table 1 (in units of cm$^{-1}$). The parameters are given for the coordinate system employed in the ab initio calculations (given in the SI)**

| k | q | $B_k^{i}$ |
|---|---|---|
| 2 | -2 | -0.8223285E + 00 |
| 2 | 0 | -0.2952967E + 01 |
| 2 | 2 | 0.2085183E + 01 |
| 4 | -4 | 0.5765483E + 02 |
| 4 | -2 | -0.9592991E - 03 |
| 4 | 0 | 0.4952142E - 02 |
| 4 | 2 | 0.2436407E - 01 |
| 4 | 4 | -0.3230413E - 01 |
| 6 | -6 | 0.3422239E - 04 |
| 6 | -4 | 0.1810159E - 04 |
| 6 | -2 | 0.4855725E - 04 |
| 6 | 0 | 0.2270114E - 04 |
| 6 | 2 | -0.1666892E - 04 |
| 6 | 4 | 0.6830792E - 04 |
| 6 | 6 | -0.6617125E - 04 |

Figure 4 | ac susceptibility. Temperature dependence of the in-phase ($\chi'$, a) and out-of-phase ($\chi''$, b) components of the ac magnetic susceptibility for DyNCN under zero applied dc field.
Figure S11 shows that in the presence of an external dc field $H$ the relaxation rate $\tau^{-1}$ increases in the pure DyNCN compound and decreases in the diluted Dy$_{0.05}$Lu$_{0.95}$NCN sample. The applied magnetic field is known to suppress the QTM and to enhance the direct relaxation process. We may conclude from Figure S11 that the variation of the two contributions do not cancel each other completely, so that the total relaxation rate increases in the former and decreases in the second compound with applied magnetic field.

Upon increasing the temperature to the thermally activated regime (23.6–28.4 K), the relaxation time is hardly affected by magnetic dilution, and from this we can extract the slightly larger energy barrier of $U_{\text{eff}}$ (DyNCN) = 233(4) cm$^{-1}$ and $U_{\text{eff}}$ (Dy$_{0.05}$Lu$_{0.95}$NCN) = 270(5) cm$^{-1}$.

**Conclusions**

In summary, a new carbon coordinated dysprosium single ion magnet, DyNCN, in which the Dy$^{III}$ ion possesses an effective $C_{2v}$ crystal field symmetry has been investigated. The presence of the $C_{2}$ symmetry axis requires that several low-lying KDs of the magnetic anisotropy axes coincide with it, as corroborated by ab initio calculations, resulting in the two lowest Kramers doublet having strong axial and possessing parallel anisotropy axes. This explains the observed thermally activated relaxation via the second excited KD. This new relaxation mechanism, offers a means to exploit single ion effects of lanthanide possessing perfect axial symmetry in order to facilitate magnetic relaxation climbing up to a higher energy levels, and to further open up a broader space for enhancing the anisotropy barrier. Furthermore, our findings should stimulate interest for the synthesis and characterization of organometallic lanthanide-based compounds.

**Methods**

**Synthesis.** The synthesis of the compound DyNCN and the Lu analogue are described in literature.

**Magnetic measurements.** Magnetic susceptibility measurements were performed in the temperature range 2–300 K, using a Quantum Design MPMS XL-7 SQUID magnetometer equipped with a 7 T magnet. The dc measurements were collected from 2 to 300 K and the ac measurements were carried out in a 3.0 Oe ac field oscillating at various frequencies from 1 to 1500 Hz and with a zero dc field. The diamagnetic corrections for the compounds were estimated using Pascal’s constants, and magnetic data were corrected for diamagnetic contributions of the sample holder.

**Inelastic neutron scattering.** The neutron spectroscopy measurements were performed on the SEQUOIA spectrometer at the Spallation Neutron Source of
Oak Ridge National Laboratory. The coarse resolution chopper was phased for and incident energy of 70 meV and spun at 240 Hz. A 1.71 g sample was sealed in an He atmosphere in a flat can to fully cover the 5 cm × 5 cm beam. The sample was designed to minimize the amount of time needed to see a signal above the H background. The sample was cooled to ~5 K using a closed cycle He refrigerator. The raw time of flight data were converted to instrument independent units of Q and energy transfer and is normalized by V to remove detector efficiency differences.

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Author contributions
J.T. designed and supervised the research. C.W. and D.C. carried out the synthesis and characterization studies. Y.-N.G. and J.T. planned and executed the magnetic measurements and analysed the resulting data. G.E.G. and S.E.N. performed the INS measurements. L.U. and L.F.C. performed the ab initio calculations and proposed the interpretation. Y.-N.G., J.T. and A.K.P. wrote the manuscript, with contributions from all the co-authors.

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