Observation of Cooperative Electronic Quantum Tunneling: Increasing Accessible Nuclear States in a Molecular Qudit

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ABSTRACT: As an extension of two-level quantum bits (qubits), multilevel systems, so-called qudits, where \( d \) represents the Hilbert space dimension, have been predicted to reduce the number of iterations in quantum-computation algorithms. This has been tested in the well-known \([\text{TbPc}_2]^{10+}\) single-molecule magnet (SMM), which allowed implementation of the Grover algorithm in a single molecular unit. In the quest for molecular systems possessing an increased number of accessible nuclear spin states, we explore herein a dimeric \( \text{Tb}_2 \)-SMM via single-crystal \( \mu \)-SQUID measurements at sub-Kelvin temperatures. We observe ferromagnetic interactions between the \( \text{Tb}^{III} \) ions and cooperative quantum tunneling of the electronic spins with spin ground state \( J_z = \pm 6 \). Strong hyperfine coupling with the \( \text{Tb}^{III} \) nuclear spins leads to a multitude of spin-reversal paths, leading to seven strong hyperfine-driven tunneling steps in the hysteresis loops. Our results show the possibility of reading out the \( \text{Tb}^{III} \) nuclear spin states via cooperative tunneling of the electronic spins, making the dimeric \( \text{Tb}_2 \)-SMM an excellent nuclear spin qudit candidate with \( d = 16 \).

INTRODUCTION

Exploitation of the quantum properties in device applications has boosted numerous studies of molecules exhibiting slow relaxation of magnetization, termed single-molecule magnets (SMMs).

Increasing Accessible Nuclear States in a Molecular Qudit can be described as an effective two-qubit system, also known as qudit (\( d = 4 \), representing the dimensions of the qudit).

The inherent multilevel characteristics, as well as the shielded nature of the nuclear spins against decoherent environmental fluctuations (electronic, magnetic, etc.), have ultimately led to the implementation of Grover’s quantum algorithm on a single \([\text{TbPc}_2]^{10+}\) molecule.

Two main characteristics allow the use of the \([\text{TbPc}_2]^{10+}\) molecule as a qudit: (i) the inherent multilevel properties (qudits where \( d > 2 \)) and (ii) the presence of hf-QTM events. Because of the multiplicity in \([\text{TbPc}_2]^{10+}\), entanglement and superposition of multiple states can be achieved in qudits in large dimensions with smaller clusters of processing units.

In this work, we show how the ferromagnetic interaction between the electronic spins in a dinuclear complex, namely,
dentally, both sets of molecules are nearly parallel, with a small two generated by screw-and-glide-plane symmetries. Coinci- molecules are related by an inversion center, with the other group, with four molecules residing in the unit cell. Two intermolecular interactions are expectedly small.

complex, composed of two Pc and one chromatography.

extremely robust, allowing its puri fi cation via column chromatography.

RESULTS AND DISCUSSION

Synthesis and Crystal Structure. The studied SMM, namely, [Tb₂Pc₁H₈Pc₂] (I), increases the multiplicity of nuclear spin states available for manipulation. Our results show, for the first time (despite a large number of previously reported triple-decker lanthanide complexes), that reversal of the electronic spins occurs via cooperative tunneling (cotunneling) at specific level crossings, induced by the interaction operating between the electronic states of the TbIII ions.

Figure 1. (a) Side view of the crystal structure of I. The red double arrow indicates the Tb···Tb intramolecular distance. (b) Representation of the packing diagram showing a quasi-single orientation of the I units within the crystal lattice (view along the [010] plane). (c and d) Respective skew angles for the TbIII ion sandwiched between two Pc groups and one Pc and H₈Pc groups. Color code: Tb, dark blue; N, cyan; C, gray. H atoms omitted for clarity.

Magnetic Description. Magnetic measurements were conducted by employing the neat sample I and a magnetically diluted sample, i.e., 1% I into 99% [Y₂Pc₁H₈Pc₂] (I₁dil), where intermolecular dipolar fields are strongly reduced. The investigations were conducted in the region of 2 K ≤ T ≤ 300 K using a commercial SQUID magnetometer. The temperature-dependent magnetic susceptibility χM(T) of the powder sample I exhibits a room temperature value in agreement with the expected value for two non-interacting TbIII ions, i.e., 23.5 cm³ mol⁻¹ K compared to 23.6 cm³ mol⁻¹ K (for two TbIII ions with gJ = 3/2, where J = 6). Upon cooling, χM(T) stays practically constant up to ca. 16 K, where it sharply increases to 35.3 cm³ mol⁻¹ K because of ferromagnetic interactions between the TbIII ions, caused probably by a combination of dipolar and exchange interactions (vide infra). The same behavior is observed in I₁dil (Figures 2 and S3). Likewise, magnetization (M) versus applied field (H) studies between 2 and 5 K (from 0 to 7 T) show that the saturation value for I is reached at relatively low fields (ca. 1 T), leading to an M(H) value of 9.2 μB at 7 T. Moreover, alternating magnetic susceptibility studies, conducted at zero direct-current (dc) field for both samples I and I₁dil, show a frequency-dependent magnetic behavior characterized by a single relaxation process. I can, therefore, be described as an SMM (Figures 2b and S4 and S5).

Single-Crystal Studies. The nuclear spins embodied in the ¹⁹⁵TbIII metal ions, the small interaction between the ions, and the SMM character make I an excellent candidate for investigating hf-QTM. The important question here is whether the observed small ferromagnetic interaction occurring between electronic spins of the TbIII ions allows the coupling of the TbIII nuclear spin, thus increasing the number of accessible nuclear states that could be utilized for testing
quantum algorithms. In order to answer this question, we studied a single crystal of 1 at sub-Kelvin temperatures with the $\mu$-SQUID technique. Employing the transverse field method, the magnetic field was applied along the mean easy axis of magnetization, which lies close to the [101] crystallographic plane. Figure 3 shows open hysteresis loops at different magnetic-field sweep rates and temperatures (Figures 3 and S6), confirming the SMM behavior. In particular, the hysteresis loops in the vicinity of $\mu_B H = 0$ show a staircase-like structure with seven main transitions occurring at $\pm 15.4$, $\pm 30.4$ and $\pm 45.7$ mT (Figures 3 and 4a,b). Furthermore, two additional broad transitions are observed at $\pm 550$ mT (Figures 4b, inset, and S8). This observation of seven transitions is different from but also analogous to the behavior of the parent mononuclear $[\text{TbPc}_2]^-$ complex, which shows only four hf-QTM transitions at $\pm 12$ and $\pm 37$ mT. These correspond to the avoided level crossings that conserve the nuclear spin of the Tb$^{III}$ ion. The tunnel splittings are a result of the transverse ligand-field interactions, which are caused by the transverse crystal-field terms ($A^0_{2g} O^0_{2g}$ and $A^0_{4g} O^0_{4g}$) arising from a small distortion of the $D_{4h}$ symmetry of the molecule. Note that a recently reported fused Pc-bridged Tb dimer, with a relatively long intramolecular Tb…Tb distance of 11.3135(7) Å, exhibits only four hf-QTM transitions, suggesting that the two Tb-containing moieties act as two rather independent SMM units. Furthermore, a mixed heteronuclear Tb$^{III}$–Dy$^{III}$ dimeric SMM with geometrical parameters almost identical with those found in 1 does show only four hf-QTM transitions. The lack of additional QTM transitions in the dimeric Tb$^{III}$–Dy$^{III}$ SMM could be ascribed to the isotopic mixture of nuclear states in the Dy$^{III}$ ions as well as smaller or quenched Tb$^{III}$–Dy$^{III}$ interactions.

In the following, it will be shown that the electronic states of the Tb$^{III}$ ions of 1 are effectively coupled and the observed multitude of hf-QTM steps can be assigned to a cotunneling of the electronic spin $J_e = \pm 6$, while the nuclear spin states are conserved. For this purpose, we choose a ligand-field (lf) Hamiltonian that takes into account the distorted electronic environment of the two Tb$^{III}$ ions in 1, imposing locally an approximate $C_4$ symmetry:

$$\mathcal{H}_l = a A_{2g}^0 O_{2g}^0 + b (A_{4g}^0 O_{4g}^0 + A_{4g}^1 O_{4g}^1) + c (A_{4g}^0 O_{4g}^0 + A_{4g}^4 O_{4g}^4)$$

where $i = 1$ or 2 refers to each Tb$^{III}$ ion, $a$, $b$, and $c$ are the Stevens coefficients, $O_k^f$ are the equivalent Stevens operators, and $A_{4g}^f$ are the ligand-field parameters. In order to account for the effect of the magnetic field and Tb$^{III}$ nuclear spin on the multiplicity of the $m_f$ states, three other terms are included:

$$\mathcal{H}_T = \mathcal{H}_l \mathcal{H}_M - g_\mu_B \mathcal{H}_M \mathcal{J}_z^I + \mathcal{A}_4 \mathcal{I}_z^I$$

where $g = 2$ and $I$ for Tb(1) and $I$ for Tb(2), while the remaining terms are set to zero. Because of the close proximity of the Tb$^{III}$ ions, i.e., an intramolecular Tb…Tb distance of 3.5230(6) Å (vide supra), both ions are connected by a weak dipolar interaction of the form $\mathcal{H}_{dp}$ (see section 3 in the Supporting Information for a more detailed description). Thus, the Hamiltonian for 1 reads

$$\mathcal{H} = -2I_1 J_{2I_{dp}L_z}^I + \mathcal{H}_T$$

(3)

The energy diagram of 1 can be calculated by the exact diagonalization of the $(2I + 1)^2(2I + 1)^2(2I + 1)^2(2I + 1)^2$ Hamiltonian (3). For simplicity, we assume $P$ and $A_{hf}$ for both sites to be equal. Employing $A_{hf}$ and $P$ as parameters, we are able to reproduce the seven QTM events observed in the $\mu$-SQUID data with $P = +0.010$ cm$^{-1}$ and $A_{hf} = +0.0215$ cm$^{-1}$ (Figure 4c) provided that $\mathcal{H}_{dp}$ is larger than the hyperfine coupling (vide infra). We find a $P$ parameter equal to the one found for $[\text{TbPc}_2]^-$, while a slightly larger $A_{hf}$ than in the mononuclear case is obtained (cf. $P = +0.010$ cm$^{-1}$ and $A_{hf} = +0.0173$ cm$^{-1}$ for $[\text{TbPc}_2]^-$). Note that the effect of the $6^\circ$ tilting angle between the two differently oriented molecules in

**Figure 2.** (a) $\chi(T) = M$ versus $T$ (inset) data for compound 1 and simulation (solid lines) using the Hamiltonian (3) and parameters described in the text. (b) $\chi(T)$ experimental data for 1 at $H_{dc} = 0$ and an oscillating field of 3.5 Oe. Solid lines are fits to a single Debye process. (c) $\chi(T) = M$ versus 1/$T$ for complex 1 (blue ●) and 1 (red ●) and Arrhenius analysis (solid lines).
the unit cell causes only a small broadening of each crossing point and does not account for additional QTM events.

Numerical diagonalization of the Hamiltonian given by eq 3 results in 100 level crossings close to zero field and for the \(|J_z = \pm 6\rangle\) states (Figure 4c). However, out of these, only 10 have large tunnel splittings, leading to a high probability of electronic spin reversal (only seven are observed because, for some crossings, tunneling occurs at the same resonance field). The tunnel splittings are induced by off-diagonal terms in the Hamiltonian, which couple the \(|J_z = \pm 6\rangle\) states. In the Tb dimer, both \(^{159}\text{Tb}^{III}\) ions are coupled by ferromagnetic interaction (vide infra), and the eigenstates can be expressed as \(|J_{za}, I_{za}\rangle|J_{zb}, I_{zb}\rangle\). At very low temperatures, solely the \(|-\pm 6, \pm 3/2\rangle\) states are populated (for positive fields). Before each field sweep, the nuclear spins are thermalized. For this, a waiting time of more than 1000 s at \(\pm 1\) T was used to thermally equilibrate the nuclear spin system with the thermal bath. The electronic spin reversal occurs at level crossings with large tunnel splittings when the field is swept from a high negative field to a positive one.

The seven events observed in Figure 4b can be rationalized as follows: upon sweeping of the field between \(\pm 1\) T, tunneling occurs while conserving the nuclear states. At zero field, two tunneling events occur between the \(|-6, \pm 1/2\rangle|6, \mp 1/2\rangle\) and \(|6, \pm 1/2\rangle|6, \mp 1/2\rangle\) states and also between the \(|-6, \pm 1/2\rangle|6, \mp 1/2\rangle\) and \(|+6, \pm 3/2\rangle|+6, \mp 3/2\rangle\) states (red circle in Figure 4c). Two other allowed tunneling events occur at \(\pm 15.4\) mT, where the reversal occurs via the states \(|-6, \pm 1/2\rangle\) to \(|+6, \pm 3/2\rangle\) and \(|-6, \pm 1/2\rangle\) to \(|+6, \pm 3/2\rangle\) (orange circles in Figure 4c). At \(\pm 30.4\) mT, the reversal is permitted via \(|-6, \pm 1/2\rangle\) to \(|+6, \pm 1/2\rangle\) and \(|+6, \mp 1/2\rangle\) (blue circles in Figure 4c), while the last event at \(\pm 45.7\) mT is ascribed to the electronic spin flip via the \(|-6, \pm 1/2\rangle\) to \(|+6, \pm 1/2\rangle\) states (purple circles in Figure 4c; see Figure S7 for a detailed description of all states). Therefore, we conclude that simultaneous spin reversals at specific avoided crossings are observed, as long as the nuclear spin states are strictly conserved. As observed in Figure 4b, the cotunnel probability depends not only on the tunnel splittings but also on the thermal population of the levels, yielding a strong temperature dependence of the step height of each transition. Additionally, at \(\mu_0H_z = \pm 550\) mT, two broader transitions are observed (inset in Figure 4b), which are in agreement with...

Figure 3. (a) Temperature dependence of magnetization of \(1^{\text{st}}\) at a field sweep rate of 0.140 T/s. (b) Field dependence of magnetization at \(T = 30\) mK. The field was applied parallel to the easy axis of magnetization. Before each field sweep, a waiting time of more than 1000 s at \(\pm 1\) T was used to thermally equilibrate the nuclear spin system with the thermal bath.
a ferromagnetic interaction between the Tb III ions, where single spin flips occur between the electronic ground states, i.e., $|±_n J_z, I_z⟩ \leftrightarrow |±_n J_z, I_z⟩$, or $|±_n J_z, I_z⟩ \leftrightarrow |±_n J_z, I_z⟩$, or $|±_n J_z, I_z⟩ \leftrightarrow |±_n J_z, I_z⟩$ (see Figure S8). The hyperfine structure is not experimentally resolved probably because of small distributions of ligand-field parameters and misalignment. As can be seen in Figure S8, these transitions at $\mu_B H_z = ±550$ mT cannot be reproduced by employing a purely dipolar coupling between the Ising $|J_z⟩ = 0$ states, which places the first excited state at $+3.21$ cm$^{-1}$ from the ground state [calculated for a Tb...Tb distance of 3.5230(8) Å using a point-dipole approximation]. Experimentally, the first excited state lies at about $+4.6$ cm$^{-1}$, which is larger than the calculated dipolar value; therefore, it is possible that, in addition, a small contribution of exchange interaction is present. To assess this possibility, we add an isotropic Heisenberg interaction ($J_m$) to the dipolar matrix. The Hamiltonian has the following form:

$$\mathcal{H} = -2 J_m \langle \mathcal{H}_{\text{dd}} + J_{\text{ex}} \rangle I_z + \mathcal{H}_{\text{tb}} + \mathcal{H}_{\text{tb}}$$

(4)

The simulations were adjusted so that the crossing point between the ground state and first excited state observed through μ-SQUID data at $±500$ mT is reproduced. Employing eq 4, we are able to reproduce the crossing point between the first excited state and ground state with $J_m = +0.0097$ cm$^{-1}$. Note that solely from the magnetic data it is impossible to accurately assess the possibility of exchange interactions occurring in I given that both $\mathcal{H}_{\text{dd}}$ and $\mathcal{H}_{\text{dd}} + J_{\text{ex}}$ equally reproduce the data. Our results show that the possibility of exchange interactions occurring between the Tb III ions is highly probable and requires further studies.

### CONCLUSIONS

Hf-driven QTM has been previously observed in several lanthanide complexes; however, what makes I really unique is the collective behavior triggered by the small interaction between the two Tb III ions. This interaction leads to a coupling of the nuclear spins of the two $^{159}$Tb III metal ions, not just causing hf-QTM occurrences, as observed in $[^{159}\text{TbPc}_2]^-$, but additionally increasing the multiplicity of the nuclear spin states and, as a consequence, allowing hf-QTM at additional resonance field positions. Moreover, the results reported here differ from those of exchange bias QTM, where the resonance fields are shifted as a result of exchange with adjacent nuclei.

In conclusion, the resonant QTM has been investigated in a dimeric Tb III-based SMM via μ-SQUID measurements, allowing determination of the hyperfine and quadrupolar parameters. The hf-QTM events are ascribed to the simultaneous reversal (cotunneling) of the electronic spin, while the nuclear spins are conserved. As in the $[^{159}\text{TbPc}_2]^-$ case, the QTM transitions corresponding to each nuclear spin state could be used to read out the nuclear spins in I in a qudit scheme as an enlarged quantum register. Note that in the archetypal $[^{159}\text{TbPc}_2]^-$, just four states are accessible (corresponding to the $m_I = ±1/2$ and $±3/2$ states), limiting the applicability of multilevel quantum algorithms. However, in I, the observation of an enlarged multiplicity of states by cooperative electronic coupling would open a general avenue to the creation of larger quantum directories, thus allowing the realization of a molecular spin qudit with a exploitable dimension of $d = 16$ [with $d = (2I + 1)^n$, where $n = 2$ and $I = 3/2$].

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00823.

Further synthetic details and structural and magnetic plots (PDF)

#### Accession Codes

CCDC 1567148–1567149 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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Notes
The authors declare no competing financial interest.
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