Molecular spintronics is interesting for its hybrid character, at the crossroads between spintronics, molecular electronics, and molecular magnetism. In this new field, one tries to exploit the properties of molecules in order to create original features, useful in spintronics and quantum information. In particular, organic semiconductors are promising since they may offer the possibility of transferring spin information on longer distance and time scale than conventional materials. Moreover, molecular material could bring additional functionalities to devices, enabling the control of spin information with different stimuli (e.g., switchability with light, electric field, etc.).

Among the molecular systems, single-molecule magnets (SMMs) have been extensively studied since they behave like quantum magnets and are promising candidates for quantum information processing. On the one hand, they present magnet-like properties such as a large spin in the ground state along with a large and well-defined magnetic anisotropy. On the other hand, their small dimension grants them quantum properties such as quantum tunneling of magnetization (QTM) and interference effects between tunneling paths. Besides, the synthetic chemistry can produce various SMM structures at high yield and low cost, with functionalizing groups that help grafting SMMs on different supports.

One of the most promising SMMs for magnetic storage and quantum computation is the bis(phtalocyaninato)terbium(III) complex, or TbPc2, in the following, depicted in Figure 1. It is a single ion complex, which has the advantage of being magnetically more stable, with regard to mechanical deformations, than other SMMs. The magnetic characterization of the anionic form of TbPc2 diluted in a diamagnetic matrix of YPc2 has revealed the importance of nuclear spin interaction.

Magnetic Interaction Between a Radical Spin and a Single-Molecule Magnet in a Molecular Spin-Valve

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ABSTRACT Molecular spintronics using single molecule magnets (SMMs) is a fast growing field of nanoscience that proposes to manipulate the magnetic and quantum information stored in these molecules. Herein we report evidence of a strong magnetic coupling between a metallic ion and a radical spin in one of the most extensively studied SMMs: the bis(phtalocyaninato)terbium(III) complex (TbPc2). For that we use an original multiterminal device comprising a carbon nanotube laterally coupled to the SMMs. The current through the device, sensitive to magnetic interactions, is used to probe the magnetization of a single Tb ion. Combining this electronic read-out with the transverse field technique has allowed us to measure the interaction between the terbium ion, its nuclear spin, and a single electron located on the phtalocyanine ligands. We show that the coupling between the Tb and this radical is strong enough to give extra resonances in the hysteresis loop that are not observed in the anionic form of the complex. The experimental results are then modeled by diagonalization of a three-spins Hamiltonian. This strong coupling offers perspectives for implementing nuclear and electron spin resonance techniques to perform basic quantum operations in TbPc2.

KEYWORDS: spin–spin interaction · single-molecule magnets · molecular electronic · spintronic · molecular spin-valve

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spin driven transitions in the terbium ion. Recently, the quantum properties of this nuclear spin coupled to the Tb ion has been exploited to demonstrate the first coherent manipulation of an isolated SMM spin. As a result and in order to integrate TbPc₂ in electronic devices, it has been extensively studied under different forms: crystal, thin film, or isolated on substrate or between electrodes. In addition, the structure of TbPc₂ can be modified by the addition of ligands that would improve the grafting to a particular surface. For instance, the hexyl 6-pyrene substituted TbPc₂, used in the present article and labeled TbPc₂, in the following, is known to graft with a very good selectivity onto sp²-type carbon materials such as graphene or carbon nanotubes.

The neutral form of TbPc₂ has the particularity to have an unpaired electron (radical) delocalized over the two phthalocyanine (Pc) ligands. As a result, this complex forms a three-spins system: the Tb nuclear spin, the Tb electronic moment, and the Pc radical spin. Only coherent manipulations of the nuclear spin have been achieved so far since the terbium electronic spin, the Tb electronic moment, and the Pc radical spin.

RESULTS AND DISCUSSION

Magnetic Properties of TbPc₂. In this section, we will first discuss the magnetic properties of the anionic form of TbPc₂ (with no radical spin on the Pc). The +III oxidation state and the strong spin–orbit coupling in Tb give rise to a total angular momentum of J = 6 in the ground state. The influence of the phthalocyanine groups lifts the degeneracy among the Jₜ substates. By using the ligand field parameters of ref 26 and the Stevens operators formalism, we calculate the ground state as a function of the longitudinal magnetic field. The corresponding ligand field and Zeeman Hamiltonians are the following:

\[ \mathbf{H}_y = \alpha A_2^{\alpha}O_2^{\alpha} + \beta (A_2^{\alpha}O_4^{\alpha} + A_4^{\alpha}O_4^{\alpha}) + \gamma A_6^{\alpha}O_6^{\alpha} \]  
\[ \mathbf{H}_{\text{Zeeman}} = g_\beta \mu_B H J \cdot H \]  

where the Oₖ are the Stevens operators, Aₖ the ligand field parameters, α, β, and γ the Stevens constants, g_β the gyromagnetic factor in Tb, and H the magnetic field applied along the quantization axis. The numerical diagonalization of \( \mathbf{H}_{\text{Zeeman}} + \mathbf{H}_y \) gives \( J_z = \pm 6 \) as a ground doublet, isolated from the first excited state, \( J_z = \pm 5 \), by 600 K. Therefore, we can consider the electronic moment as an Ising-like spin within the low-temperature regime. The presence of a transverse anisotropy, A₄⁴O₄⁴ couples the two states \( J_z = \pm 6 \) giving rise to an avoided level crossing at the intersection between those states. The amplitude of the tunnel coupling is about 1 μK. As a result, quantum tunneling of the magnetization (QTM) occurs in such molecule when the magnetic field is swept adiabatically through this anticrossing. In the case of a nonadiabatic evolution, the electronic moment ends up in the excited state and can relax to the ground state by emitting a phonon whose energy matches the Zeeman energy. This mechanism is called a direct transition and implies a strong coupling between the electronic moment and the phonon bath. The two mechanisms of magnetization reversal are depicted in Figure 2a and illustrated with a magnetization curve measured by the micro-SQUID technique, on a single crystal of [TbPc₂]⁻ TBA⁺ (TBA = tetrabutylammonium) diluted in the diamagnetic [YPc₂]⁻ TBA⁺, see Figure 2b. A large amount of molecules reverses their magnetization by QTM since the total magnetization M abruptly changes at zero magnetic field, where \( J_z = \pm 6 \) are brought into resonance. The remaining molecules, that are in the excited state, continuously reverse their electronic moment at higher magnetic field, using the direct transition mechanism.

We now investigate the magnetic properties of the neutral form. Magnetometry of the neutral TbPc₂ diluted in YPc₂ has been achieved on a single crystal in the same conditions as the anionic form. The magnetization curve of Tb₀.₀₂Y₀.₉₈Pc₂ is plotted Figure 2c. For each field sweep direction two steps in the magnetization are visible, one at zero field and one around 70 mT. As sketched in Figure 2d, the compound
is expected to form a 3D network of interacting spins $S = 1/2$ due to the radical nature of the Pc. Indeed, the magnetic characterization of a pure YPc$_2$ crystal has shown a radical–radical interaction of 1 K. One possible interpretation of the magnetization curve is that the transition at zero magnetic field corresponds to the concomitant spin reversal of the Tb ion and the unpaired electron while the transition at finite magnetic field corresponds to the QTM of the Tb ion only followed by a direct transition of the unpaired electron. However, no signature of the hyperfine interaction is visible in contrast with Figure 2b to confirm our assumption.

In order to investigate in more detail the interaction occurring in this molecule, we propose in the following to study the magnetization properties of a single neutral TbPc$_2$ complex thanks to our original carbon-nanotube based detector.

**Molecular Spin-Valve.** The device we use in the present study is made out of a carbon nanotube in a transistor configuration, see Figure 3a. The current is injected and measured thanks to the source and drain electrodes. The side gates are used to control the electric field along the nanotube in order to optimize the detector response. As demonstrated in previous research papers, in the case where two molecules are strongly coupled to the nanotube (see Figure 3b), the device behaves as a spin-valve analogue (see Figure 3c). One of the molecule plays the role of a spin polarizer, while the second one analyzes the spin current. Exploiting this effect allows a complete study of the Tb magnetic moment such as a characterization of its anisotropy, of the Landau–Zener tunnelling, or of the hyperfine interaction. Figure 3d shows the differential conductance as a function of the increasing magnetic field with a 20 mT $s^{-1}$ sweep rate. Those curves present two abrupt conductance changes related to the magnetization reversal of two molecules coupled to the nanotube. Two different behaviors can be observed in this figure, the green curves present both reversals close to zero field, whereas the orange curves show one reversal close to zero field and a second one above 0.2 T. In the first case, both molecules experience QTM at low field, while in the second case one of the two molecules does not reverse by QTM at low field. This behavior is fully consistent with the stochastic nature of QTM. From the occurrence of QTM events, we can estimate the Landau–Zener probability of tunneling of one molecule to be $\sim 0.2$, very close to the theoretical value of 0.25, considering a tunnel splitting of 1 $\mu$K. In the case both molecules experience QTM at low field, it is not possible to discriminate which one tunnels first and which conductance jump corresponds to which molecule. To solve this problem we use the transverse field technique, which applies a constant magnetic field perpendicular to the easy axis of the first molecule.

![Figure 2. (a) Zeeman diagram of the ground electronic doublet in Tb. Quantum tunnelling of the magnetization (QTM) occurs at the intersection between the states $|J_z = \pm 6\rangle$. A second mechanism occurs at higher magnetic field, enabling the relaxation from the excited state to the ground state by emission of a phonon. (b) Magnetization curve at 40 mK measured with the micro-SQUID technique on a single crystal made of 2% of [TbPc$_2$]$^+ \text{TBA}^-$ diluted in [YPc$_2$]$^- \text{TBA}^-$. Steps around zero magnetic field are attributed to QTM and the continuous reversal at higher magnetic field to direct transition. (c) Magnetization curve of a Tb$_{0.02}$Y$_{0.98}$Pc$_2$ single crystal. When the magnetic field is swept from negative to positive value, two steps are visible, the first one occurs at zero magnetic field and the second one at 70 mT. (d) Magnetic structure of the neutral form of TbPc$_2$ diluted in YPc$_2$ crystal. The Pc ligands are sketched in blue color, the Y atom in yellow, and the Tb atom in purple. Tb$_{0.02}$Y$_{0.98}$Pc$_2$ forms a 3D arrangement of spin 1/2 (blue arrows) interacting together. The Tb ion (purple arrow) is locally coupled to a single electron located in the Pc.](image-url)
As a result, the transverse field shifts the QTM position of the second molecule, which is misaligned, and allows us to unambiguously study the QTM position of the first molecule.

Analysis of Spin Reversals. To analyze the electronic moment reversal of one of the molecules, we apply a constant transverse field of 0.5 T, while the longitudinal field is swept and we store the exact position of the corresponding conductance changes in a histogram. Figure 4a presents the result of 2500 traces in red, i.e., magnetic field going from $-0.4$ to $+0.4$ T and the same number of retraces in blue, i.e., magnetic field going from $+0.4$ to $-0.4$ T. Three sets of four peaks emerge from the statistics. One is centered around zero field and is present in both trace and retrace. Another appears only in the trace at $0.25$ T, mirrored by another set of peaks in the retrace at $-0.25$ T. Three sets of four peaks emerge from the statistics. One is centered around zero field and is present in both trace and retrace. Another appears only in the trace at $0.25$ T, mirrored by another set of peaks in the retrace at $-0.25$ T. To compare with the single crystal hysteresis loop of the anionic form, we integrate the histogram and report the normalized hysteresis loop for a single TbPc$_2$ in Figure 4b. The four steps around zero magnetic field are visible on both hysteresis loops (Figures 2b and 4b) and are attributed to the strong hyperfine coupling between the $J = 6$ electronic moment and the $I = 3/2$ nuclear spin in Tb. To take into account this interaction we use the following Hamiltonian:

$$H_{\text{Tb}} = H_{\text{lf}} + H_{\text{Zeeman}} + A I \cdot J + P \left( \frac{I_z^2}{3} - \frac{1}{3} |I + 1| \right)$$

where $J$ and $I$ are, respectively, the Tb electronic moment and nuclear spin, $A$ the hyperfine constant, and $P$ the quadrupolar term. The hyperfine interaction splits the electronic ground doublet $|J_z = \pm 6\rangle$ in an octuplet $|J_z = \pm 6, I_z\rangle$ with $I_z = \pm 3/2, \pm 1/2, -1/2, -3/2$. Among the 16 intersections within the ground octuplet, only four are avoided level crossing: the ones conserving the nuclear spin state. As a consequence, the four peaks/steps around zero-field in Figure 4a,b correspond to QTMs at these particular anticrossings, which reverse the electronic moment but conserve the nuclear spin.

The transitions appearing at higher magnetic field cannot be explained neither with this model nor with a direct transition picture. In order to study these high field transitions, we increase the sweep rate to reach a regime where only reversal at high magnetic field can be observed. Figure 5a shows the spin-valve features we observe in this regime, at 50 mT s$^{-1}$, similar to the orange curves in Figure 3d. By contrast with the previous measurement, the hyperfine structure is only visible at high field. We measure the conductance as a function of the longitudinal magnetic field, back and forth, while the transverse field is incremented. The position of reversal is reported on the 2D plot ($H_l, H_t$), and then we increment the transverse field by 0.1 mT. Figure 5b presents the evolution of the high field transitions as a function of the transverse field amplitude.

Interpretation of the Magnetic Interactions. The position of the high field transitions moves toward higher...
longitudinal field when the transverse field is increased. As a consequence, these transitions cannot be interpreted in terms of phonon assisted relaxation since the phonon bath or vibron energies are insensitive to magnetic field.\textsuperscript{33} We can also exclude any intersection with the higher excited state since the latter is expected to lay at 600 K above the ground state, as calculated in the first section, vide supra. As a result, the transverse field evolution implies that the Tb ion couples with another spin system that may be the radical located in the Pc. In order to verify this assumption, we use the following Hamiltonian:

$$\mathcal{H}_{\text{Tb} - \text{Pc}} = \mathcal{H}_{\text{Tb}} + \mu_B \mu_0 (g_J J + g_S S) \cdot \mathbf{H} + \gamma S \cdot \mathbf{J} \quad (4)$$

where $J$ and $S$ are, respectively, the Tb electronic moment and the Pc electron spin, $g_J$ and $g_S$ the corresponding gyromagnetic factors, and $\gamma$ the interaction constant between the Tb electronic moment and the Pc radical. The latter is the only fitting parameter in the Hamiltonian. By diagonalizing $\mathcal{H}_{\text{Tb} - \text{Pc}}$ for a constant 0.5 T transverse field and an interaction of 0.4 K, we obtain the Zeeman diagram in Figure 5c. Both sets of peaks in Figure 5d, obtained at low sweep rate 20 mT s$^{-1}$, are in agreement with the avoided level-crossings of this diagram. We conclude that the first set is the signature of QTM between the states $|J_z = \pm 6, I_z, S_z = \pm 1/2 \rangle$ and the second set of QTM between the states $|J_z = \pm 6, I_z, S_z = \pm 1/2 \rangle$ followed by the relaxation to a ground state $|J_z = \pm 6, I_z, S_z = \pm 1/2 \rangle$.

The assumption of a radical interacting with the Tb ion is supported by combining experiment and simulation with a single fitting parameter: the interaction

Figure 4. (a) Histogram of the magnetization reversal events of a single TbPc$_2$ complex obtained for 2500 field sweeps at 20 mT s$^{-1}$ and under a constant 0.5 T transverse field. Each trace (red) and retrace (blue) histogram shows two series of four peaks, one around zero magnetic field and a second one at higher value. (b) Hysteresis loop of a single TbPc$_2$ complex.

Figure 5. (a) Spin-valve feature at 50 mT s$^{-1}$, exhibiting resonant transitions at high magnetic field. (b) Evolution of transitions at high magnetic field as a function of the transverse field. Each dot corresponds to a measurement of a magnetization reversal for a constant transverse field with red dots for traces and blue dots for retraces. For clarity, the transitions of the second molecule are not reported. (c) Zeeman diagram of the Tb ion coupled to an unpaired spin. Among the 16 intersections between the $|J_z = \pm 6, S_z = \pm 1/2 \rangle$ and $|J_z = \pm 6, S_z = \pm 1/2 \rangle$, four are avoided level-crossings with a tunnel splitting of 1 $\mu$K, idem for the intersections between $|J_z = \pm 6, S_z = \pm 1/2 \rangle$ and $|J_z = \pm 6, S_z = \pm 1/2 \rangle$. (d) The experimental histogram is identical to the one presented in Figure 4a, measured at 20 mT s$^{-1}$ sweep rate and under 0.5 T transverse field.
EXPERIMENTAL SECTION
Our magnetic sensor is composed of a carbon nanotube transistor laterally coupled to the molecules through π-π interactions. The carbon nanotube is grown by chemical vapor deposition on a 300 nm thick SiO2 surface supported by a highly doped silicon back-gate. Nanotubes are contacted by standard e-beam lithography followed by evaporation of a 40 nm thick Pd layer, see Figure 3a. Once the device is fabricated, the surface is cleaned under Ar flow at 300 °C and a solution containing the neutral TbPC2 complexes at 10−3 mol L−1 is dropcasted onto the device and then dried under N2 gas flow. The sample is mounted in a dilution refrigerator and cooled down to 40 mK. A 2D vectorial magnet allows to apply an inplane magnetic field up to 1.2 T.

Conflict of Interest: The authors declare no competing financial interest.

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