Persistence of slow dynamics in Tb(OETAP)_2 single molecule magnets embedded in conducting polymers

T Orlando¹,², M Filibian¹, S Sanna¹, N Giménez-Agullo³, C Sáenz de Pipaón³, P Ballester³,⁴, J R Galán-Mascarós³ and P Carretta¹

¹ Department of Physics, University of Pavia-CNISM, I-27100 Pavia, Italy
² Max Planck Institute for Biophysical Chemistry, D-37077 Gottingen, Germany
³ Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, E-43007 Tarragona, Spain
⁴ Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluis Companys 23, E-08010, Barcelona, Spain

E-mail: pietro.carretta@unipv.it

Received 6 May 2016, revised 21 June 2016
Accepted for publication 30 June 2016
Published 20 July 2016

Abstract
The spin dynamics of Tb(OETAP)_2 single ion magnets was investigated by means of muon spin relaxation (μSR) both in the bulk material as well as when the molecule is embedded into PEDOT:PSS polymer conductor. The spin fluctuation time is characterized by a high temperature activated trend, with an energy barrier around 320 K, and by a low temperature tunneling regime. When the single ion magnet is embedded into the polymer the energy barrier only slightly decreases and the fluctuation time remains of the same order of magnitude, even at low temperature. This finding shows that these single molecule magnets preserve their characteristics which, if combined with those of the conducting polymer, result in a hybrid material of potential interest for organic spintronics.

Keywords: molecular magnetism, muon spin relaxation, spin dynamics

(Some figures may appear in colour only in the online journal)

1. Introduction
The trend towards ever-smaller electronic devices is driving electronics to its ultimate molecular-scale limit leading to severe drawbacks and to the breakdown of Moore’s law [1] while, on the other hand, it allows for the exploitation of quantum effects both in electronics and in spintronics. Single molecule magnets (SMM) are among the most promising materials to be used in molecular spintronic devices [2–4] or as logic units in quantum computers [5], since they combine the classical macroscopic properties of bulk magnetic materials with the advantages of nanoscale entities, such as quantum coherence. It has already been shown that molecular magnets can be used to build efficient memory devices and, in particular, single crystals can serve as storage units for dynamic random access memories [6]. SMMs can be exploited for all these applications thanks to their bistability and sizeable energy barriers against magnetization reversal [7]. Nevertheless, most of SMMs are characterized by energy barriers in the tens of K range or below, giving rise to sufficiently long spin coherence times only at liquid helium temperature [8]. Accordingly, the study of lanthanide based single ion magnets (SIMs) where the crystal field (CF) splitting among the \( |J,m\rangle \) states gives rise to energy barriers exceeding 700 K have attracted a great interest [9, 10]. These lanthanide-based single-ion magnets (SIMs) were discovered by Ishikawa and co-workers in a series of double-decker phthalocyanine (Pc) complexes [9, 11, 12]. Recently, other double decker (DD) SIMs [13] and triple-deckers [14], have been synthesized, with a variety of ligands [15–17]. However, all of them show energy barriers lower than the ones found in Ln(Pc)_2 DD, in particular than the ones observed in Tb(Pc)_2. Nowadays, one
of the major challenges for the future exploitation of these materials in spintronics is to organize them in monolayers and to address them individually. Tb(Pc)₂ has already been processed on graphite [18], on carbon nanotubes [19] or on gold [20]. However, the poor solubility and stability in the gas phase of these DDs makes it difficult to obtain perfectly organized arrays of these SIMs. Thus, it would be a significant breakthrough if analogous magnetic properties could be found in easy to process single ion magnets.

Tetraazaporphyrins (or porphyrazines) are an attractive alternative for the bulkier Pc ligands. These macrocycles are constituted by four pyrrole rings bridged by azanitrogens, giving an analogous binding mode to Pc but without the extended aromatic skeleton. This, besides reducing the molecular size, causes an increase in the solubility and processability of their corresponding DD complexes. Recently we have reported the synthesis, structure and the basic magnetic properties of lanthanide DD complexes with octaethyltetraazaporphyrin (OETAP) [21]. SIM behavior has been found in the Tb and Dy derivatives. Notably, in this case, the Ln(OETAP)₂ neutral complexes are highly soluble in organic solvents and they can even be sublimed using mild conditions. Preliminary ¹H NMR measurements in Tb(OETAP)₂ have allowed to evidence an energy barrier of a few hundreds of Kelvin degrees [21], smaller than the one of Tb(Pc)₂ but still sizeable and interesting for applications. Nevertheless, the shortening of the NMR relaxation rates lead to the suppression of the NMR signal over a broad temperature range, not allowing for an accurate study of the spin coherence time, one of the most relevant parameters for the technological applicability of SIMs. In order to suitably investigate the temperature dependence of the spin dynamics one can exploit the potential of muon spin relaxation (µSR) technique, which has been successfully used in the past to study molecular magnetism [10, 22–25]. Here we show that the correlation time for the spin fluctuations in Tb(OETAP)₂ SIMs is characterized by a high temperature activated behaviour followed by a low temperature tunneling regime. Moreover, we have investigated the behaviour of these SIMs when they are embedded in PEDOT:PSS conducting polymers, giving rise to an interesting system where the mutual interplay between the polymer transport properties and the SIMs magnetic state can be assessed. We found that the temperature dependence of the correlation time for the spin fluctuations is very similar to the one of bulk Tb(OETAP)₂, although with a slightly lower energy barrier, showing that these materials do preserve their SIM behaviour even when they are embedded into a conducting matrix.

2. Technical aspects and experimental results

Tb(OETAP)₂ powders were grown and characterized as described in [21]. In order to embed the SIMs into the polymer the following synthesis procedure was adopted. Solid anhydrous 307 mg of PEDOT:PSS were added to 25 ml of HPLC grade dichloromethane and the resulting mixture was stirred for 4 d. Then 15.42 mg of Tb(OETAP)₂ were added to the homogeneous suspension and stirred for 10 min. This solution was dropcast onto a Petri dish open to air and the film formed through slow evaporation.

Zero field (ZF) and longitudinal field (LF) µSR measurements were carried out at the Paul Scherrer Institut (PSI)—Villigen (CH) by using Dolly and GPS instruments of the SµS facility. In a µSR experiment a 100% spin-polarized beam of positive muons (µ⁺) is implanted into the sample. The 1/2 muon spin acts as a local magnetic probe and when a magnetic field \( \mu_B \) perpendicular to the initial polarization is present, the muon spin precesses with an angular frequency \( \omega_L = \gamma_\mu \mu_B \), where \( \gamma_\mu = 2\pi \times 135.53 \text{ Mrad s}^{-1} \text{T}^{-1} \) is the muon gyromagnetic ratio [26, 27]. When the muon decays it emits a positron preferentially along its spin direction, allowing one to reconstruct the time evolution of the muon spin polarization or, equivalently, of the positron emission asymmetry \( A(t) \). On the other hand, when a longitudinal field (LF) is applied along the initial muon polarization, no precession occurs and the time evolution of \( A(t) \) is driven by static or dynamic relaxation mechanisms which are sensitive to the SIMs spin dynamics [26, 27].
In order to derive the asymmetry one has to take into account the different efficiency of the forward and backward positron detectors and correct the raw backward positron counting by a factor $\alpha$ [26], which in our experiments ranged between 1.025 and 1.099. Figure 1 shows the typical time evolution of the muon asymmetry in Tb(OETAP)$_2$ in LF geometry. One observes a very fast initial decay followed by a slow relaxation which indicates a distribution of relaxation rates. The very fast initial decay causes a loss in the initial asymmetry, particularly in ZF (see figure 2), an effect observed in other Tb-based SIM [10, 23]. As the temperature is lowered the relaxation gets faster and then, below about 80 K, the decay becomes significantly more stretched and the average rate decreases again. Accordingly, the asymmetry decay in Tb(OETAP)$_2$ can suitably be fit as the sum of two components

$$A(t) = A_1 e^{-(\lambda_F t)^\beta} + A_2 e^{-\lambda t} + Bck,$$

(1)

with $\lambda_F \gg \lambda$ the corresponding relaxation rates, $\beta$ a stretching exponent and $Bck$ a small constant term ($\approx 2\%$) accounting for the sample environment background. The stretching exponent $\beta$ indicates the presence of more than two muon implantation sites, characterized by different hyperfine couplings with Tb$^{3+}$. In Tb(OETAP)$_2$ $\beta$ was found to be weakly field dependent and to progressively decrease on cooling from $\beta \approx 0.65$ to 0.2. Owing to the very fast initial relaxation the estimate of $\lambda_F$ is characterized by large errors, even by fixing the amplitude of $A_1$ and $A_2$ as temperature independent. For this reason we have rather concentrated on the temperature dependence of the relaxation rate $\lambda$ for the slow relaxing component. One notices a clear maximum around 80 K for the measurements performed at different magnetic fields (see figure 3). Moreover, it is observed that upon increasing the field intensity the asymmetry decay gets progressively slower. Although this behaviour is considered often as an evidence of a static field distribution [26, 27], here it is not the case. In fact, relaxation rates of the order of a few $\mu s^{-1}$ arising from a static field distribution should be completely quenched in a magnetic field of 1 kGauss, while they are not (see figure 1). This indicates that the LF relaxation is determined by the
spectral density of the spin fluctuations at \( \omega_L \), which is varied by changing the magnetic field intensity \([27]\).

At \( H = 3 \) kGauss the asymmetry decay could also be fit reasonably well, even if with a slightly lower accuracy, with a single stretched exponential decay

\[
A(t) = A_0 e^{-\lambda(t)^\beta} + Bc_k. \tag{2}
\]

Even if \( \lambda_e > \lambda \), their temperature dependence is rather similar, as well as the temperature dependence of the characteristic spin fluctuation time derived from them (figure 4), as we shall see in the following.

The asymmetry decay in Tb(OETAP)\(_2\)PEDOT:PSS shows a clearly different behaviour in zero-field. In fact, as it is shown in figure 2 in ZF, the asymmetry is characterized by a very fast initial decay followed by a gaussian-like relaxation. This second contribution is likely due to the dipolar fields generated by \(^1\)H nuclei in the PEDOT:PSS polymer. In fact, this second term is quenched in a 100 Gauss magnetic field. At those field magnitude or at larger field intensities the data could be fit by equation (2) with \( Bc_k \approx 3\% \) and \( \beta \) decreasing from 0.5 to 0.2 on cooling. The temperature dependence of \( \lambda_e \) for Tb(OETAP)\(_2\)PEDOT:PSS is shown in figure 3. Similarly to Tb(OETAP)\(_2\), also here one notices a maximum around 80 K.

\section{Discussion}

In Ln-based SIMs the degeneracy among \( |J, m| \) states is lifted by the crystal field, which in the case of Tb\(^{3+}\) SIMs causes a splitting of hundreds of Kelvin degrees between the two-fold degenerate \( |J = 6, m = \pm 6\rangle \) ground-state and the first excited states. This CF splitting yields a huge anisotropy barrier, several orders of magnitude larger than the energy difference between the muon hyperfine levels. Accordingly the muon longitudinal relaxation cannot occur through direct relaxation processes, where a transition between CF levels causes a flip of the muon spin, but it rather has to be driven by an indirect relaxation mechanism involving a muon spin flip without a change in \( m \) \([10]\). This process can occur only if the muon hyperfine tensor involves off-diagonal terms coupling the transverse components of the local field \( h_{\tau} \) at the muon with \( I_z \), as is the case for the dipolar coupling. Thus, denoting with \( \tau_m \) the finite life-time of the crystal field levels induced mainly by spin-phonon scattering processes, \( \lambda \) can be written in the form \([28]\)

\[
\lambda = \frac{\gamma^2_\mu \langle \Delta h_{\tau}^2 \rangle}{Z} \sum_{m = -6}^{+6} \frac{\tau_m e^{-E_m/T}}{1 + \omega_L^2 \tau_m^2}. \tag{3}
\]

\( E_m \) being the eigenvalues of the CF levels and \( Z \) the corresponding partition function. It is noted that the low magnetic field (of the order of 1000 Gauss) applied during \( \mu\)SR experiments causes a negligible correction to \( E_m \) and, hence, its effect can be disregarded for \( k_B T \gg \mu_B H J \approx 1 \) K. The life-time for the \( m \) is determined by the transition probabilities \( \tau_{m,m\pm 1} \) between \( m \) and \( m \pm 1 \) levels, which depend on the CF eigenvalues as well as on the spin-phonon coupling constant \( C \) \([29]\):

\[
\frac{1}{\tau_m} = p_{m,m-1} + p_{m,m+1}, \tag{4}
\]

\[
p_{m,m\pm 1} = C (E_{m\pm 1} - E_m)^3 \frac{1}{e^{(E_{m\pm 1} - E_m)/T} - 1}. \tag{5}
\]

Since the CF splitting between the lowest levels of Tb\(^{3+}\) is likely larger than the thermal energy, as it will be confirmed in the following, one can to a first approximation cut the summation in equation (3) to the first term and write

\[
\lambda = \gamma^2_\mu \langle \Delta h_{\tau}^2 \rangle \frac{\tau_e}{1 + \omega_L^2 \tau_e^2}. \tag{6}
\]

with \( \tau_e = (1/C\Delta E^3) \exp(\Delta E/T) \), where \( \Delta E \) is the CF splitting between the lowest \( m = 6 \) and \( m = 5 \) levels. Notice that although a large crystal field splitting yields a decrease in the fluctuations owing to the Boltzmann exponential factor, it also implies a large spin-phonon coupling so that at the end one finds a non-exponential dependence of the dynamics on the anisotropy barrier. If now one fits \( \lambda \) data of Tb(OETAP)\(_2\) in figure 3 with equation (6), taking for \( \tau_e \) the activated \( T \)-dependence reported above, one observes that the data follow reasonably well the expected trend down to 60–50 K while clear deviations are found at lower temperature. Hence, at least down to 60 K \( \tau_e \) shows an activated behaviour with an energy barrier determined by the crystal field splitting. The failure of the fit at low temperature clearly indicates a deviation of \( \tau_e \) from the activated trend. In order to derive the temperature dependence of \( \tau_e \) from \( \lambda(T) \) data, we inverted equation (6) obtaining

\[
\tau_e = \frac{1}{\lambda \omega_L} \left( \lambda_{\text{max}} \pm \sqrt{\lambda_{\text{max}}^2 - \lambda^2} \right), \tag{7}
\]

with \( \lambda_{\text{max}} \) the maximum value of \( \lambda(T) \), achieved for \( \omega_L \tau_e = 1 \).

Notice that out of the two solutions just one is physically meaningful, i.e. the one yielding \( \tau_e \) increasing on decreasing temperature. The temperature dependence of \( \tau_e \) derived from equation (7) is shown in figure 4.

By plotting \( \tau_e \) versus 1000/T in a semi-log scale one notices a high temperature linear trend, namely an activated trend of \( \tau_e \) and then a low temperature flattening which should be associated with the tunneling among the low-lying energy levels. In particular, one can write that

\[
\frac{1}{\tau_e} = \frac{1}{\tau_{\text{tunn}}} + \frac{e^{-\Delta E/T}}{C \Delta E^3}, \tag{8}
\]

with \( 1/\tau_{\text{tunn}} \) the tunneling rate. The high temperature data for the different magnetic fields can be fit with the same activation energy \( \Delta E = 320 \pm 20 \) K and spin-phonon coupling constant \( C = 250 \pm 30 \) Hz K\(^{-3}\), a value somewhat smaller than the one found in LnPc\(_2\) compounds \([10]\). It is noticed (see figure 4) that at 3 kGauss, for \( T > 25 \) K, \( \tau_e(T) \) derived by fitting the asymmetry with equation (1) or with equation (2) give very close results. Hence, above 25 K the results do not depend on the fitting procedure. On the other hand, the low temperature behaviour depends on the magnetic field and on the asymmetry fitting procedure. The dependence on the fitting law stems from the fact that at low temperature the very fast initial
The dashed line shows the behaviour according to equation (8), as described in the text. The correlation time for the spin fluctuations in Tb(OETAP)$_2$, for different magnetic field intensities, is reported as a function of 1000/T. For $H = 3$ kGauss data obtained starting from the fit of the asymmetry both with equation (1) (squares) and with equation (1) (hexagons) are reported. (right) Comparison of the correlation times of bulk Tb(OETAP)$_2$ with that of Tb(OETAP)$_2$ embedded in the polymeric matrix as a function of 1000/T. The dashed line shows the behaviour according to equation (8), as described in the text.

decay gives rise to a large uncertainty in the relaxation rate when it is fit with the stretched exponential law.

If now we turn to the behaviour of the correlation time for the Tb(OETAP)$_2$ spin fluctuations when it is embedded in the PEDOT:PSS conducting polymers, one notices that the correlation time shows a behaviour very similar to the one found in bulk Tb(OETAP)$_2$, with a slightly lower activation energy $\Delta E = 260 \pm 30$ K and with a spin phonon coupling constant $C = 180 \pm 30$ Hz K$^{-1}$. Remarkably in both materials the fluctuation time becomes longer than a $\mu$s at temperatures of the order of a few tens of Kelvin degree, making those materials potentially interesting for future applications.

4. Conclusion

From a series of LF $\mu$SR experiments we have shown that Tb(OETAP)$_2$ is characterized by a high temperature activated dynamics with a correlation time increasing above the $\mu$s already at temperatures of a few tens of K. At low temperature the tunneling processes among the two fold degenerate ground-state dominate the spin fluctuations and a clear flattening of the correlation time is noticed. $\mu$SR measurements performed in Tb(OETAP)$_2$ molecules show that the spin dynamics is only weakly affected by the conducting polymers suggesting that these hybrid materials are potentially interesting for the development of organic spintronics.

Acknowledgments

Hubertus Luetkens and Alex Amato are gratefully acknowledged for their help during the $\mu$SR measurements at PSI. We acknowledge financial support from the European Union EU (ERC Stg grant 279313, CHEMCOMP), the Spanish Ministerio de Economía y Competitividad (MINECO, project CTQ2015-71287-R and the Severo Ochoa Excellence Accreditation 2014–2018 (SEV-2013-0319), the Generalitat de Catalunya (2014 SGR 797) and the ICIQ Foundation.

References

[1] Waldrop M M 2016 Nature 530 144
[2] Gatteschi D, Sessoli R and Villain J 2007 Molecular Nanomagnets (Oxford: Oxford University Press)
[3] Bogani L and Wernsdorfer W 2008 Nat. Mater. 7 179
[4] Ardavan A, Rival O, Morton J J L, Blundell S J, Tyryshkin A M, Timco G A and Winpenny R E P 2007 Phys. Rev. Lett. 98 057201
[5] Leuenberger M N and Loss D 2001 Nature 410 789
[6] Ekert A K and Jozsa R 1996 Rev. Mod. Phys. 68 733
[7] Branzoli F, Carretta P, Filibian M, Zoppellaro G, Graf M J, Galan-Mascarós J R, Fuhr O, Brink S and Ruben M 2009 J. Am. Chem. Soc. 131 4387
[8] Milios C J, Vinslava A, Wernsdorfer W, Moggach S, Parsons S, Perlepes S P, Christou G and Brechin E K 2007 J. Am. Chem. Soc. 129 2754
[9] Ishikawa N, Sugita M, Ishikawa T, Koshihara S and Kaizu Y 2005 J. Phys. Chem. B 109 11265
[10] Branzoli F, Carretta P, Filibian M, Graf M J, Klyatskaya S, Ruben M, Coneri F and Dhakal P 2010 Phys. Rev. B 82 134401
[11] Ishikawa N, Sugita M, Tanaka T, Ishikawa T, Koshihara S and Kaizu Y 2004 Inorg. Chem. 43 5498
[12] Ishikawa N, Mizuno Y, Takamatsu S, Ishikawa T and Koshihara S 2008 Inorg. Chem. 47 10217
[13] Wang H, Qian K, Wang K, Bian Y, Jiang J and Gao S 2011 Chem. Commun. 47 9624
[14] Katoh K, Kajiwara T, Nakano M, Nakazawa Y, Wernsdorfer W, Ishikawa N, Breedlove B K and Yamashita M 2011 Chem. Eur. J. 17 117
[15] Aldamen M A, Clemente-Juan J M, Coronado E, Martí-Gastaldo C and Gaita-Arino A 2008 J. Am. Chem. Soc. 130 8874
[16] Tuna F, Smith C A, Bodenstein M, Ungur L, Chibotaru L F, McInnes E J L, Winpenny R E P, Collison D and Layfield R A 2012 Angew. Chem., Int. Ed. 51 6976
[17] Lopez N, Prosvirin A V, Zhao H, Wernsdorfer W and Dunbar K R 2009 Chem. Eur. J. 15 11390
[18] Gonidec M et al 2011 J. Am. Chem. Soc. 133 6603
[19] Klyatskaya S, Galán-Mascarós J R, Bogani L, Henrich F, Kappes M, Wernsdorfer W and Ruben M 2009 J. Am. Chem. Soc. 131 15143
[20] Katoh K et al 2009 J. Am. Chem. Soc. 131 9967
[21] Giménez-Agulló N, Sáenz de Pipaón C, Adriaenssens L, Filibian M, Martínez-Belmonte M, Escudero-Adán E C, Carretta P, Ballester P and Galán-Mascarós J R 2014 Chem. Eur. J. 20 12817

[22] Blundell S J, Lancaster T, Brooks M L, Pratt F L, Coronado E, Galán-Mascarós J R, Manson J L, Cadiou C and Winpenny R E P 2005 Synth. Met. 152 481

[23] Branzoli F, Filibian M, Carretta P, Klyatskaya S and Ruben M 2009 Phys. Rev. B 79 220404

[24] Gatteschi D, Carretta P and Lascialfari A 2000 Physica B 289–90 94

[25] Procissi D, Lascialfari A, Micotti E, Bertassi M, Carretta P, Furukawa Y and Kögerler P 2006 Phys. Rev. B 73 184417

[26] Blundell S J 1999 Contemp. Phys. 40 175

[27] Yaouanc A and Dalmas de Réotier P 2011 Muon Spin Rotation, Relaxation, and Resonance: Applications to Condensed Matter (Oxford: Oxford University Press)

[28] Lascialfari A, Jang Z H, Borsa F, Carretta P and Gatteschi D 1998 Phys. Rev. Lett. 81 3773

[29] Villain J, Hartmann-Boutron F, Sessoli R and Rettori A 1994 Europhys. Lett. 27 159