PHYSICAL REVIEW B **79**, 220404(R) (2009)

Spin dynamics in the neutral rare-earth single-molecule magnets $[TbPc_2]^0$ and $[DyPc_2]^0$ from μSR and NMR spectroscopies

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(Received 17 April 2009; published 12 June 2009)

The spin dynamics in $[TbPc_2]^0$ and $[DyPc_2]^0$ single-molecule magnets have been investigated by means of muon and nuclear spin-lattice relaxation rate measurements. The correlation time for the spin fluctuations was found to be close to 0.1 ms already at 50 K, about 2 orders of magnitude larger than the one previously found in other lanthanide-based single-molecule magnets. In $[TbPc_2]^0$ two different regimes for the spin fluctuations have been evidenced: a high-temperature activated one involving spin fluctuations across a barrier $\Delta \simeq 880$ K separating the ground and first excited states and a low-temperature regime involving quantum fluctuations within the twofold degenerate ground state. In $[DyPc_2]^0$ a high-temperature activated spin dynamics is also evidenced which, however, cannot be explained in terms of a single spin-phonon coupling constant.

DOI: 10.1103/PhysRevB.79.220404 PACS number(s): 75.50.Xx, 76.75.+i, 76.60.−k

Molecular nanomagnets have attracted major attention in the last decade owing to their possible technological applicability as logic units in computers[1] or in life sciences as contrast agents.[2] So far, the most studied molecular nanomagnets are the ones based on transition-metal ions, which are characterized by a twofold degenerate ground state separated from the first excited states by a barrier induced by the magnetic anisotropy.[3] The stability of the ground state and the applicability of these compounds above liquid helium temperature (T) are nevertheless prevented by the small magnetic anisotropy which characterize transition-metal complexes.[4] In order to increase the anisotropy the synthesis of lanthanide (Ln)-based molecular magnets has been envisaged and recently the double-decker phthalocyaninato lanthanide complexes $[Pc_2Ln]^-$ ($Pc \equiv C_{32}H_{16}N_8$) have been recognized as potential single-molecule magnets (SMMs) which could function above cryogenics temperatures.[5,6] In fact, $[Pc_2Tb]^-$ and $[Pc_2Dy]^-$ complexes are the first mononuclear lanthanide systems exhibiting very slow relaxation and quantum tunneling of magnetization.[5,7,8] It has been recently observed[9] by means of nuclear magnetic resonance (NMR) that in $[TbPc_2]^-TBA^+ \times N[TBA]Br$, where N represents the degree of dilution within the organic tetrabutylammonia (TBA) matrix, the characteristic correlation time (τ_c) for the spin fluctuations becomes on the order of a μs at liquid-nitrogen T,[9] much longer than in any other molecular magnet. These relatively long τ_c originate from the huge barrier separating the twofold degenerate $|J=6, m=\pm 6\rangle$ crystal field (CF) ground state from the first excited $|J=6, m=\pm 5\rangle$ state. In $[TbPc_2]^-TBA^+ \times N[TBA]Br$ compounds, barriers as high as $\Delta \simeq 920$ K have been found.[9] The CF splitting is determined both by $[TbPc_2]^-$ structure and by the arrangement of the other molecules around it. In fact, upon varying N different values for Δ have been estimated. Moreover, it has been observed that at temperatures $T \ll \Delta$ quantum fluctuations, related to the tunneling between $m=\pm 6$ levels, arise.[9]

In order to increase the stability of the ground state the CF splitting has to be enhanced and the tunneling rate lowered. In this work we have considered the effect of the one-electron oxidation of $[Pc_2Ln]^-$. The resulting neutral $[Pc_2Ln]^0$ complex has an unpaired π electron which resonates between the Pc molecules, yielding a compression of the cage around Ln^{3+} ion and possibly to an increase in the CF splitting.[10–12] Hereafter we present an investigation of the spin dynamics in two different neutral compounds, $[TbPc_2]^0$ and $[DyPc_2]^0$, by means of NMR and muon spin relaxation (μSR). The T dependence of τ_c has been derived from the muon and nuclear spin-lattice relaxation rates and in $[TbPc_2]^0$ found to be close to 0.1 ms, already at 50 K, much longer than the one found in $[TbPc_2]^-TBA^+ \times N[TBA]Br$.[9] The T dependence of the relaxation rate is determined by the spin fluctuations induced by spin-phonon coupling. Accordingly, information on the CF level splitting and on the spin-phonon coupling was derived.

$[TbPc_2]^0$ and $[DyPc_2]^0$ were synthesized according to the templating[13] reaction of the phthalonitrile precursor in boiling amyl alcohol in presence of 1,8-diazabicyclo(5.4.0)-undec-7–ene under inert atmosphere for 24 h. Treatment of $[Ln(acac)_3 \times nH_2O]$ with phthalonitrile gave both the anionic $[Pc_2Ln]^-$ and the neutral $[Pc_2Ln]^0$, as observed in earlier reports.[13] The crude reaction mixture was presorbed on active (H_2O-0%) basic alumina oxide. This treatment helps to convert the unstabilized anionic form to the neutral one. Purification was carried out by column chromatography on basic alumina oxide (deactivated with 4.6% H_2O, level IV) with chloroform-methanol mixture (10:1) as eluent. Analytically pure powder samples were achieved by additional radial chromatography on silica gel followed by recrystallization from chloroform-hexane mixture.

^{1}H NMR measurements have been performed by using standard rf pulse sequences. While above 100 K the full NMR line could be irradiated and the spectra obtained from the Fourier transform of half of the echo, below 40 K the spectra became rather broad [Fig. 1(a)] and they could be derived from the envelope of the echo amplitude upon varying the irradiation frequency. This broadening is clear evidence of the slowing down of the spin dynamics in these SMMs. Further information in this respect can be obtained from the study of the nuclear spin-lattice relaxation rate $1/T_1$. ^{1}H $1/T_1$ was estimated from the recovery of the

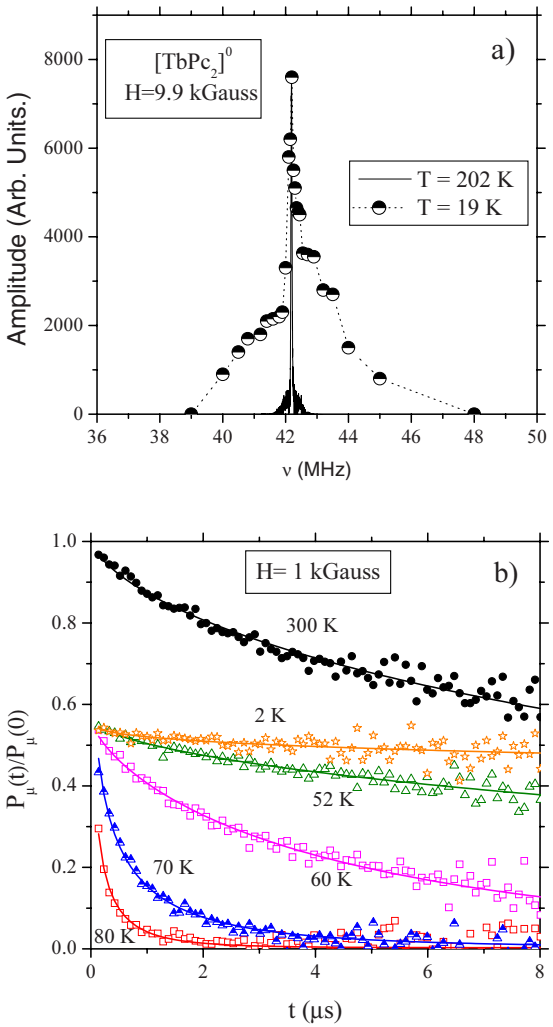

FIG. 1. (Color online) (a) ^{1}H NMR spectrum in $[TbPc_2]^0$ at $T=19$ K (circles) compared to the much narrower spectrum obtained at $T=202$ K (line). The linewidth at half intensity decreases from a few MHz at 19 K to about 37 kHz at 202 K. (b) Time evolution of the muon polarization in $[TbPc_2]^0$ sample normalized to its value for $t\rightarrow 0$ at six selected temperatures.

nuclear magnetization after a saturating rf pulse sequence. The recovery was found to be a stretched exponential, which evidences a distribution of relaxation rates for the ^{1}H nuclei, likely to be related to differences in the hyperfine coupling between Ln^{3+} and the 16 protons of each Pc molecule. The T dependence of $1/T_1$, reported in the inset of Fig. 2, evidences a progressive increase upon cooling from room temperature down to $T\simeq 140$ K, while for $T\leq 40$ K $1/T_1$ is found to progressively decrease. In the intermediate T range $140\geq T\geq 40$ K the observation of ^{1}H NMR signal is prevented by the short relaxation times.

In order to explore the spin dynamics in these intermediate T ranges we have studied $[TbPc_2]^0$ and $[DyPc_2]^0$ by means of μSR, which allows measurement of much faster relaxation rates and to work at low fields, thus perturbing the SMM only to a minor extent. Zero-field (ZF) and longitudinal field (LF) μSR experiments were carried out at ISIS pulsed muon facility on MUSR beam line. The background

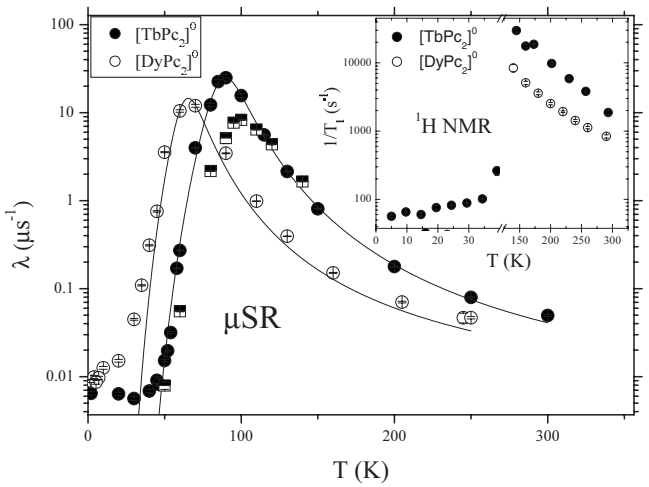

FIG. 2. T dependence of the muon longitudinal relaxation rate in $[TbPc_2]^0$ and $[DyPc_2]^0$ for $H=1000$ G (circles) and for $H=2500$ G (squares). The lines are the best fits according to Eq. (3). In the inset the T dependence of ^{1}H $1/T_1$ is reported for the two compounds, for $H=1$ T.

asymmetry contribution was found to be around 10% out of the 30% total initial asymmetry for both samples. The time decay of the muon polarization $P_\mu(t)$ in the samples shows a different behavior for temperatures above and below $T^*\simeq 90$ K for $[TbPc_2]^0$ and $\simeq 60$ K for $[DyPc_2]^0$ [Fig. 1(b)]. Above T^* the decay follows a stretched exponential behavior $P_\mu(t)=A\exp(-(\lambda t)^\beta)$, with an exponent of $\beta\simeq 0.5$ and $A\simeq 20\%$.

Below T^* a marked decrease in the initial asymmetry is found. This decrease has to be associated with the onset of very low frequency fluctuations. In particular, if the hyperfine field at the muon fluctuates with a characteristic correlation time $\tau_c \gg 1/\gamma_\mu\sqrt{\langle\Delta h^2\rangle}$, with γ_μ as the muon gyromagnetic ratio and $\sqrt{\langle\Delta h^2\rangle}$ as the root-mean-squared static field distribution probed by the muons, the decay of $P_\mu(t)$ is given by the static Kubo-Toyabe function,[14] which in zero field is characterized by a fast initial decay and by the subsequent recovery of the muon polarization to $A/3$. At ISIS the initial fast decay cannot be detected, owing to the pulsed nature of the muon source, and accordingly a loss in the initial polarization is observed and only the longtime tail is detected. At longitudinal fields $H\sim\sqrt{\langle\Delta h^2\rangle}$ an increase in the tail amplitude is expected. Since a LF of 1 kG [Fig. 1(b)] is found to cause an increase in $P_\mu(t\rightarrow 0)/P_\mu(0)$ to $\alpha(H)\simeq 0.55$ for $[TbPc_2]^0$, one can estimate $\sqrt{\langle\Delta h^2\rangle}\simeq 650$ G.[14] Thus, one has to expect that below T^* Ln^{3+} moments are frozen over a time scale $(1/\gamma_\mu\sqrt{\langle\Delta h^2\rangle})\sim 10$ ns. Still, even within this frozen configuration low-energy excitations are present and drive muon spin-lattice relaxation. Hence, for $T<80$ K, one has that $P_\mu(t)=\alpha(H)A\exp(-(\lambda t)^\beta)$.

The T dependence of λ, derived by fitting the decay of the muon polarization according to the procedure reported above, is reported in Fig. 2. One notices a peak around 90 K for $[TbPc_2]^0$ and around 60 K for $[DyPc_2]^0$, in agreement with the NMR findings. The intensity of the peak is observed to scale with the inverse of the field intensity, a situation found when the frequency of the fluctuations is close to Larmor frequency ω_L.

From the T dependence of the spin-lattice relaxation rates it is possible to obtain information on the characteristic correlation time for the spin fluctuations, on the energy barrier between the CF ground state and the first excited states, and on the spin-phonon coupling. In view of the energy difference between the muon (nuclear) hyperfine levels and the m levels of Ln^{3+}, direct muon (nuclear) relaxation processes involving an electron spin excitation are forbidden. The effective relaxation processes are indirect ones, involving a muon (nuclear) spin flip without change in $|m|$. This is possible as the dipolar hyperfine Hamiltonian contains terms coupling the transverse components of the hyperfine field $h_{x,y}$ to J_z. Owing to spin-phonon scattering processes each CF level is characterized by a finite lifetime (τ_m) which yields a Lorentzian broadening and λ (or $1/T_1$) can be written as[15]

$$\lambda \quad \text{or} \quad \frac{1}{T_1} = \frac{\gamma^2 \langle \Delta h_\perp^2 \rangle}{Z} \sum_m \frac{e^{-E_m/T} \tau_m}{1 + \omega_L^2 \tau_m^2}, \tag{1}$$

with $\langle \Delta h_\perp^2 \rangle$ as the mean-square amplitude of the hyperfine field fluctuations, E_m as the eigenvalues of the CF levels, and Z as the corresponding partition function. The lifetime for the m levels can also be expressed in terms of the transition probabilities $p_{m,m\pm1}$ between m and $m \pm 1$ in the form $1/\tau_m = p_{m,m+1} + p_{m,m-1}$. Since the lifetimes are mainly determined by spin-phonon scattering processes those can be expressed in terms of the CF eigenvalues[16]

$$p_{m,m\pm1} = C \frac{(E_{m\pm1} - E_m)^3}{e^{(E_{m\pm1} - E_m)/T} - 1} \tag{2}$$

with C as spin spin-phonon coupling constant. Since in $[TbPc_2]^0$ $\Delta = E_{m=\pm5} - E_{m=\pm6} \gg T$ over all the explored T range, Eq. (2) can be simplified in the form

$$\lambda \quad \text{or} \quad \frac{1}{T_1} = \frac{\gamma^2 \langle \Delta h_\perp^2 \rangle}{2} \frac{2\tau_c}{1 + \omega_L^2 \tau_c^2}, \tag{3}$$

with $\tau_c = \exp(\Delta/T)/(C\Delta^3)$. From the amplitude of λ at T^* one can estimate a root-mean-square amplitude for the fluctuating field at the muon in $[TbPc_2]^0$ $\sqrt{\langle \Delta h_\perp^2 \rangle} \simeq 770$ G. This value is close to the one of the static field distribution giving rise to the fast initial relaxation of the muon polarization, described by Kubo-Toyabe function. By fitting the data with Eq. (3) it is possible to estimate a spin-phonon coupling constant $C \simeq 3000$ Hz/K^3 of the same order of magnitude of that found in other SMM.[9,15] It is noticed that for $T > 100$ K, $\tau_c \omega_L \ll 1$ and from Eq. (3) one has $\lambda \propto \exp(\Delta/T)$. In fact, by plotting either $1/T_1$ or λ vs $1/T$ in a semilogarithmic scale (Fig. 3), one finds a nice linear behavior, consistent with $\Delta \simeq 880$ K.

On the basis of Eq. (3), in light of the data reported in Fig. 2, it is possible to derive the T dependence of τ_c for $[TbPc_2]^0$. In $[TbPc_2]^0$ τ_c shows two regimes (Fig. 4): a high-T activated one and a low-T one, for $T < 50$ K, where the correlation time is constant. The high-T behavior describes spin fluctuations among $m = \pm 6$ and $m = \pm 5$ levels, while the low-T trend rather signals tunneling processes

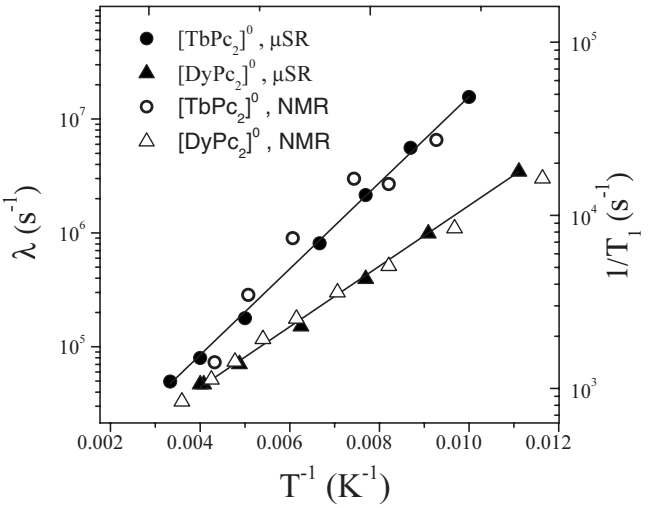

FIG. 3. Muon and ^{1}H spin-lattice relaxation rates are reported as a function of inverse T in a semilogarithmic plot in order to evidence the activated behavior for $T > T^*$. The lines are the best fits yielding $\Delta = 881$ K for $[TbPc_2]^0$ and $\Delta = 610$ K for $[DyPc_2]^0$.

among $m = +6$ and $m = -6$ levels. The total fluctuation rate is given by the sum of the fluctuation rates associated with each process and accordingly one has

$$\frac{1}{\tau_c} = \left(\frac{1}{\tau_c}\right)_{\text{act}} + \left(\frac{1}{\tau_c}\right)_t = C\Delta^3 e^{-\Delta/T} + \left(\frac{1}{\tau_c}\right)_t, \tag{4}$$

with a tunneling rate $(1/\tau_c)_t \simeq 11$ ms^{-1}. It is noticed (Fig. 4) that the T dependence of τ_c can be reproduced very well with the above equation.

It is now useful to compare NMR and μSR results in $[TbPc_2]^0$ with ac susceptibility ones.[5,10–12] In fact, also these measurements evidence a high-T activated behavior with energy barriers which appear to be only slightly smaller than the ones found here. On the other hand, the role of tunneling

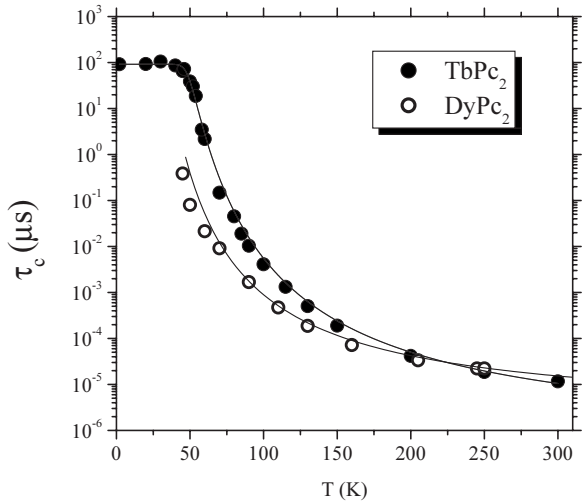

FIG. 4. T dependence of the correlation time for the spin fluctuations in $[TbPc_2]^0$ and $[DyPc_2]^0$ (for $T \geq T^*$) derived from λ data reported in Fig. 2 on the basis of Eq. (3). The solid lines are the best fits according to Eq. (4).

processes in the ac susceptibility measurements has not been addressed for the Pc_2Ln complexes and just the frequency dependence of the ac susceptibility peak was discussed.[10,11] Nevertheless, we remark that also the imaginary part of the ac susceptibility is characterized by a low-T flattening which might originate from tunneling processes.[10,11] Still, in comparing these techniques one should consider that local techniques as NMR and μSR are sensitive to the spin fluctuations of each molecule even if they do not yield a net variation in the macroscopic magnetization, namely, are silent in the ac susceptibility.[17]

Now, if one considers the T dependence of λ in $[DyPc_2]^0$ (Fig. 2), one notices a behavior quite similar to the one found in $[TbPc_2]^0$, with a maximum around 60 K characterized by a slightly lower amplitude. This decrease in the amplitude has to be associated with a lower hyperfine coupling, corresponding to a root-mean-square amplitude for the fluctuating field at the muon $\sqrt{\langle \Delta h_\perp^2 \rangle} \simeq 590$ G. Since Dy^{3+} magnetic moment is slightly larger than Tb^{3+} one, this decrease rather indicates a slightly larger average distance between the rare-earth ion and the muon in $[DyPc_2]^0$. In view of the similarity with $[TbPc_2]^0$ one could try to fit also $[DyPc_2]^0$ $\lambda(T)$ data with Eq. (3). One finds a good fit only for $T > 40$ K, and one can estimate a barrier for the spin fluctuations around 610 K (Fig. 3) and a spin-phonon coupling constant $C \simeq 1780$ Hz/K^3. However, one notices that for $T < 40$ K the data are not so well reproduced. In fact, for $[DyPc_2]^0$ it is likely that the two lowest doublets are separated by an energy barrier in the tens of K range[5] and that the high barrier derived from $\lambda(T)$ corresponds to the one between the first and second excited doublets $|J, \pm m\rangle$. Hence, in order to appropriately fit the data one should resort to Eq. (1). However, even by allowing different possible values for the CF splitting a poor fit of $[DyPc_2]^0$ data is obtained. It is likely that one should consider that the spin-phonon coupling constant is not the same for the scattering processes yielding high- and low-energy transitions.

In conclusion, by means of μSR and NMR spin-lattice relaxation rates we have derived the T dependence of the characteristic correlation time for the spin fluctuations in $[TbPc_2]^0$ and $[DyPc_2]^0$ SMM. In $[TbPc_2]^0$, although the barrier between the ground and first excited states is close to the one of $[TbPc_2]^-$ SMM diluted in a TBA matrix,[9] τ_c is found to be almost 2 orders of magnitude larger for $T < 50$ K. This suggests that in the neutral SMM the structural arrangement around the SMM itself[18] leads to an enhancement of the CF symmetry and to a decrease in the quantum fluctuations within the twofold degenerate ground state. Thus, it appears to be of major relevance, in order to enhance τ_c and to be able to employ SMM at economically affordable temperatures, to carefully investigate the effect of the modifications in the SMM coordination on the spin dynamics.

Useful discussions with F. Borsa and the technical support of S. R. Giblin and P. Ghigna are gratefully acknowledged. The research activity in Pavia was supported by Fondazione Cariplo (Grant No. 2008–2229) research funds.

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