Single-Molecule Magnets

Quantum Tunneling of Magnetization in Lanthanide Single-Molecule Magnets: Bis(phthalocyaninato)terbium and Bis(phthalocyaninato)dysprosium Anions**

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Single-molecule magnets (SMMs) are the class of high-spin molecules that exhibit magnetization hysteresis at low temperature, that is, the property of macroscopic magnets.[1–5] Most SMMs are composed of several transition-metal ions, whose spins are coupled by strong exchange interactions to give a large effective spin with a predominant uniaxial anisotropy. The quantum nature of SMMs is manifested by staircase hysteresis loops,[5,6] temperature-independent relaxation,[7–12] and quantum phase interference.[13] The discovery of these phenomena led to potential applications in quantum computing.[14]

The finding of slow magnetization relaxation in lanthanide complexes has opened the possibility of constructing

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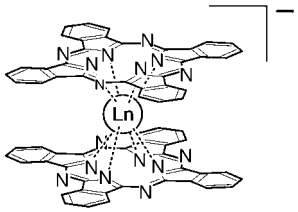
SMMs containing only a single metal ion as a magnetic center.[15] Alternating current (ac) magnetic susceptibility measurements have been reported for the bis(phthalocyaninato)terbium anion $[Pc_2Tb]^-$ (Pc = dianion of phthalocyanine) and an isostructural dysprosium complex $[Pc_2Dy]^-$ above 2 K.[15,16] One of the important results was that slow



magnetization relaxation was observed in temperature ranges that were significantly higher than those of previously known transition-metal SMMs. For example, the peak positions in the χ'' versus T plot (χ_M'' refers to the out-of-phase component of ac susceptibility) of the Tb and Dy complexes are at 40 and 10 K, respectively, for a 1-kHz ac frequency.[15,16] The Arrhenius analysis showed that the dominant relaxation path in the high-temperature range, above 25 K for $[Pc_2Tb]^-$ and 3 K for $[Pc_2Dy]^-$, is a thermally activated Orbach process that involves excited substates in the ground multiplet.[16] Hysteresis loops were measured at 1.7 K; however, no clear evidence of quantum tunneling was observed because of instrumental limitations.[16]

Herein, we report magnetic hysteresis measurements for these lanthanide single-ion SMMs in the subkelvin temperature range. Clear evidence of quantum tunneling of magnetization (QTM) is presented for the first time. We found that the quantum process in these single-ion SMMs is a result of the resonant quantum tunneling between entangled states of electron and nuclear spin systems, which was first reported for the scheelite-structured compound $LiYF_4$ doped with trivalent Ho ions.[17]

The compounds were prepared as reported in the literature[18,19] with certain modifications.[20] The doped single-crystalline samples were prepared by recrystallization from a mixed solution of TBA[Pc_2Ln] (TBA = tetrabutylammonium) and TBA[Pc_2Y] with a [Ln]/[Y] ratio of 1:49 in acetone. All measurements were performed using the micro-SQUID technique (SQUID is a superconducting quantum interference device).[21] The field was aligned parallel to the easy axis of magnetization by the transverse field method.[22]

Figure 1 shows magnetization versus field measurements for the diluted sample of the $[Pc_2Tb]^-$ ions at 0.04 K and several field scan rates. These hysteresis loops present a clear staircase-like structure, which indicates the occurrence of QTM. Such measurements were also performed on less-diluted and undiluted TBA[Pc_2Tb] samples, and revealed similar features that were, however, significantly broadened because of magnetic dipolar interactions among adjacent molecules. Notably, the figure shows no clear step at $\mu_0 H = 0$ T.

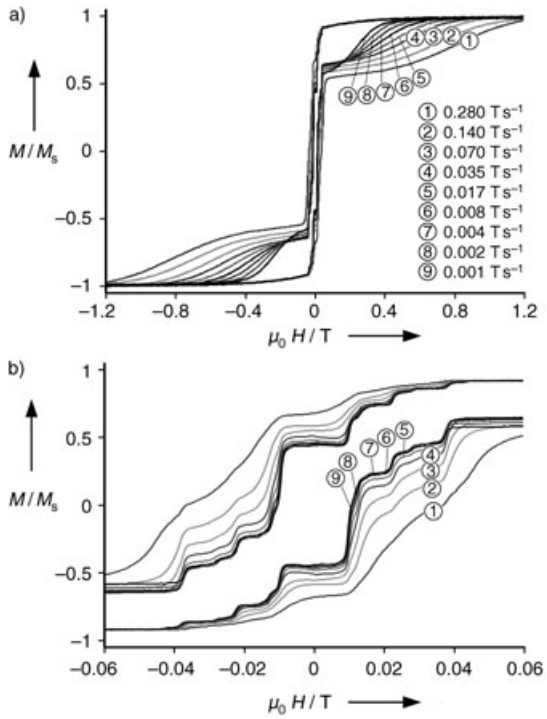


Figure 1. a) Hysteresis loops at 0.04 K for a single crystal of TBA[$(Pc)_2Tb_{0.02}Y_{0.98}$] measured at several field scan rates. The applied magnetic field was aligned along the easy axis of magnetization. b) Enlargement of the hysteresis loops in (a).

In known transition-metal-cluster SMMs, where energy separations between substates with different $|S_z|$ values are of the order of 1–10 cm^{-1}, QTM occurs when energy levels of two substates coincide under an appropriate magnetic field and the states are brought to resonance. In the lanthanide single-ion SMM $[Pc_2Tb]^-$, such level crossings occur only at very high fields because the substates are separated by a few hundred cm^{-1}.[20,23,24] This situation is illustrated in Figure 2a, which shows a Zeeman diagram for the $J = 6$ ground multiplet

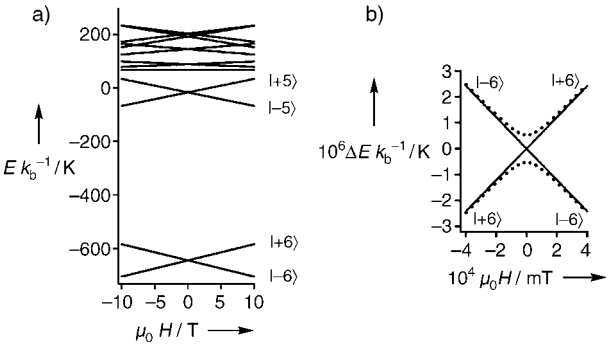


Figure 2. a) Zeeman energy diagrams as a function of longitudinal magnetic field for the $J = 6$ ground multiplet with the ligand-field parameters determined for TBA[Pc_2Tb] in a previous work:[20] $A_2^0\langle r^2\rangle = 414$ cm^{-1}, $A_4^0\langle r^4\rangle = -228$ cm^{-1}, and $A_6^0\langle r^6\rangle = 33$ cm^{-1}. b) Enlargement of the region around the intersection between the lowest substates. The dotted lines are obtained with an additional $A_4^4\langle r^4\rangle O_4^4$ ligand-field term with $A_4^4\langle r^4\rangle = 10$ cm^{-1}. The plot shows a tunnel splitting of 1.05×10^{-6} K.

of TBA[Pc_2Tb] obtained by using the ligand-field (LF) parameters previously determined.[20]

Figure 2b shows the enlargement of the area around zero field for the lowest $J_z = \pm 6$ substates. Under the assumption that all off-diagonal matrix elements of the LF Hamiltonian are negligible,[20] no mixing occurs among the two sublevels at $\mu_0 H = 0$ T (solid lines). In the case of C_4 symmetry, the LF terms $A_4^4\langle r^4\rangle O_4^4$ and $A_6^4\langle r^6\rangle O_6^4$, which comprise the off-diagonal elements that couple $|J_z\rangle$ and $|J_z-4\rangle$ states, can take nonzero values.[25] The plots with dotted lines in the Zeeman diagram are calculated with a small nonzero $A_4^4\langle r^4\rangle$ value. This result illustrates that the $J_z = \pm 6$ substates are brought to resonance at $\mu_0 H = 0$ T, thus giving rise to an "avoided level crossing" which allows QTM to occur.

This picture itself, however, provides only an insufficient explanation for the step structures observed at nonzero magnetic fields. Terbium has a nucleus with $I = 3/2$ spin in a natural abundance of 100%. It is therefore necessary to take into account the interaction between the $(4f)^8$ system and the nucleus. Exact numerical diagonalization of a $[(2J+1)(2I+1) \times (2J+1)(2I+1)]$ matrix, which includes the above ligand-field parameters, the hyperfine interaction $A_{hf}\boldsymbol{JI}$, and the nuclear quadrupole interaction term $P\{I_z^2 - 1/3\, I(I+1)\}$, was performed. Figure 3 shows the Zeeman diagram for the eight $|J_z\rangle\,|I_z\rangle$ states created from the combinations of the $J_z = \pm 6$ doublets and $I = 3/2$ quartets. The level intersections are seen at 13 magnetic-field positions. All step positions observed in Figure 1 are reproduced by using $A_{hf} = 0.0173\ cm^{-1}$ and $P = 0.010\ cm^{-1}$. The four largest avoided level crossings are indicated. An important conclusion drawn from this numerical study is that the inclusion of the nuclear quadrupole term is mandatory to explain the seemingly irregularly arranged staircase structures in the hysteresis loops of $[Pc_2Tb]^-$. The hyperfine interaction term alone cannot account for all the steps observed. This finding is in sharp contrast to the situation for Ho ions in a $LiYF_4$ matrix where equidistantly positioned steps were observed which have been fully explained by the hyperfine interaction alone.[17]

Figure 4 shows hysteresis loops for the $[Pc_2Dy]^-$ complex at 0.04 K with varied field scan rates. A steep drop in magnetization is observed near zero field, unlike the in the Tb case. Apart from this zero-field step, only slight indications of steps can be seen at about $\mu_0 H = 7$ and 14 mT. Small remanent magnetization is present at low sweep rates.

The situation for the Dy complex is more complicated than that for the Tb complex. There are seven naturally occurring isotopes of Dy, namely, ^{156}Dy, ^{158}Dy, ^{160}Dy, ^{161}Dy, ^{162}Dy, ^{163}Dy, and ^{164}Dy, with a natural abundance of 0.06, 0.01, 2.34, 18.91, 25.51, 24.90, and 28.18%, respectively. ^{161}Dy and ^{163}Dy have a nuclear spin of $I = 5/2$ while other nuclear species have $I = 0$.

In the cases of $I = 0$, there is only one level crossing at $\mu_0 H = 0$ T. However, no tunneling should occur because of the Kramers theorem of spin parity. This theorem asserts that no matter how unsymmetric the crystal field, an ion possessing an odd number of electrons (that is, a half-integer spin system) must have a ground state that is at least doubly degenerate (that is, no tunnel splitting), even in the presence

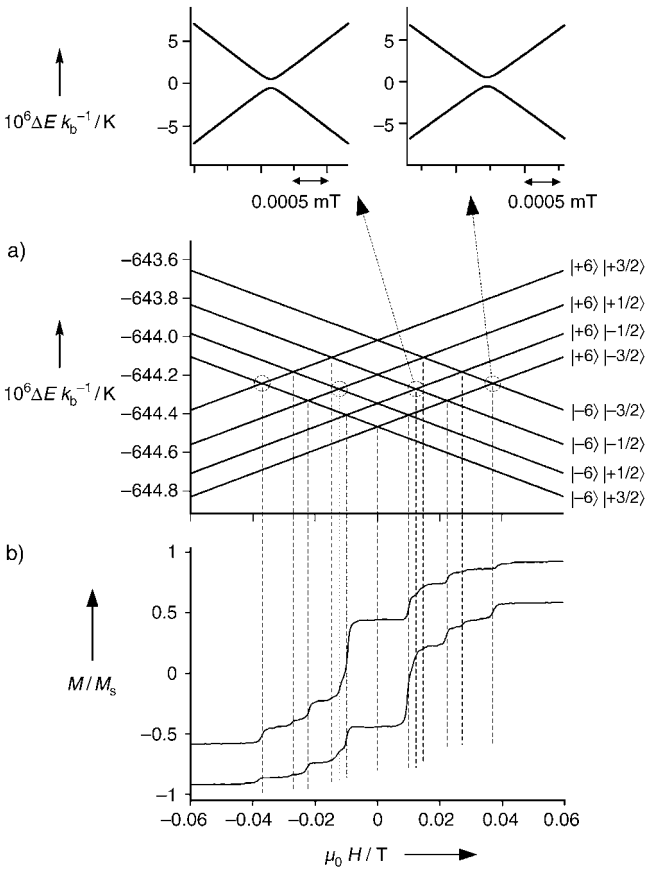


Figure 3. a) Zeeman diagrams for the lowest $J_z = \pm 6$ substates combined with the $I = 3/2$ nucleus state calculated with the LF parameters used in Figure 2b, $A_{hf} = 0.0173\ cm^{-1}$ for the hyperfine interaction term, and $P = 0.010\ cm^{-1}$ for the nuclear quadrupole interaction term. The circles indicate the positions where avoided level crossing occurs. b) Hysteresis loop at 0.04 K for a single crystal of TBA[$(Pc)_2Tb_{0.02}Y_{0.98}$] measured at 0.001 Ts^{-1}.

of crystal fields and spin–orbit interactions.[26] Hence, the Dy complexes with $I = 0$ should not contribute to the step structure. However, the Dy complexes with a nuclear spin $I = 5/2$ have avoided level crossings because two coupled half-integer spins ($J = 13/2$ and $I = 5/2$) lead to an integer total spin. Figure 5 shows the Zeeman diagram for the lowest sublevels calculated for the $I = 5/2$ case, with the same value for $A_4^4\langle r^4\rangle$ as in the above Tb case and the LF parameters determined previously.[20] Five avoided level crossings are seen. The hyperfine constant A_{hf} was assumed to be $0.0042\ cm^{-1}$, so that the avoided level crossings coincide with the positions indicated by the broken lines in Figure 4. A major difference from the Tb case concerns the tunnel splitting: the gaps are smaller by two orders of magnitude. This may be the reason why in the Dy case no clear step structures are observed at $\mu_0 H \neq 0$ T. Generally, a greatly reduced gap leads to significantly smaller tunneling probability according to the Landau–Zener model.[27]

In conclusion, we have shown the occurrence of QTM in the first lanthanide SMMs, $[Pc_2Tb]^-$ and $[Pc_2Dy]^-$ ions, by hysteresis loop measurements of doped single crystals in the subkelvin temperature range. There is a fundamental differ-

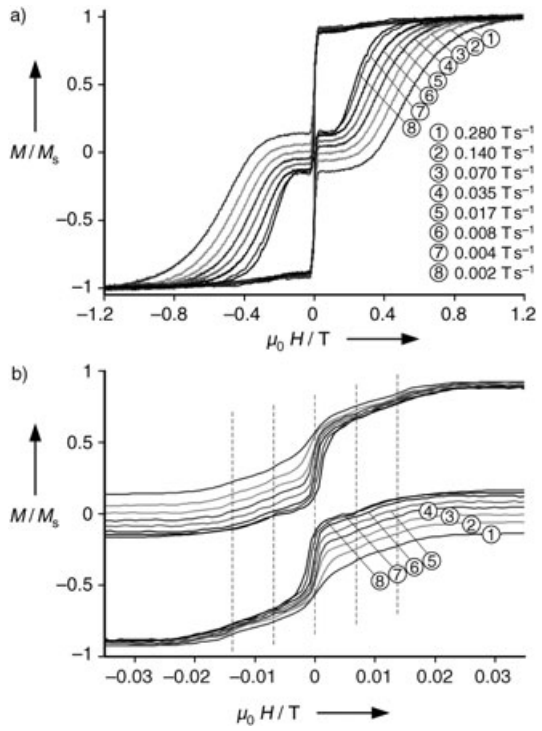


Figure 4. a) Hysteresis loops at 0.04 K for a single-crystalline sample of TBA[$(Pc)_2Dy_{0.02}Y_{0.98}$] measured at several field scan rates. The applied magnetic field was aligned along the easy axis of magnetization. b) Enlargement of the hysteresis loops in (a). The broken lines indicate the expected quantum resonances.

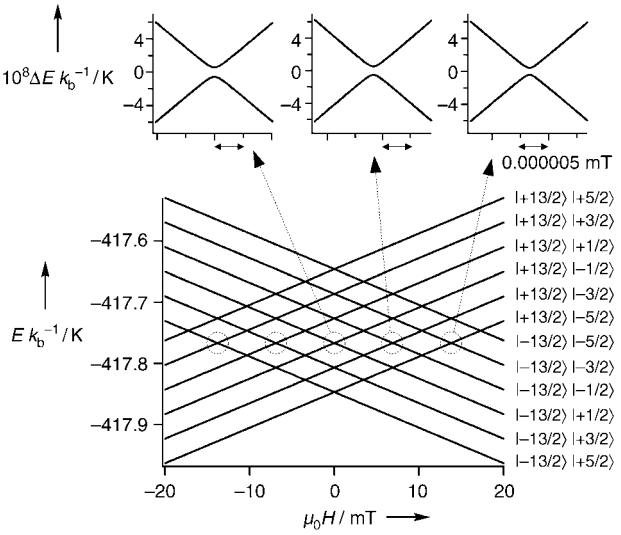


Figure 5. Energy as a function of the longitudinal magnetic field for the lowest $J_z = \pm 13/2$ substates combined with the $I = 5/2$ nucleus state calculated with the LF parameters previously determined[20] and $A_4^4\langle r^4\rangle = 10\ cm^{-1}$. The hyperfine constant is assumed to be $A_{hf} = 0.0042\ cm^{-1}$. The circles indicate the positions where avoided level crossing occurs.

ence in the mechanism of QTM between the lanthanide SMMs and the previously known transition-metal-cluster SMMs. The latter mechanism exhibits QTM between different substates $|S_z|$, whereas the former manifests QTM between the entangled states $|J_z\rangle|I_z\rangle$ of the electron and nuclear spin system.[17] The Tb complex with $J_z = \pm 6$ ground doublet and $I = 3/2$ nuclear spin gives avoided level crossings at the intersection of $|6\rangle|I_z'\rangle$ and $|-6\rangle|I_z\rangle$. In the Dy case, only ^{161}Dy and ^{163}Dy complexes, with a nonzero nuclear spin of $I = 5/2$, can exhibit avoided level crossings at the intersection of $|13/2\rangle|I_z\rangle$ and $|-13/2\rangle|I_z'\rangle$.

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[1] R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1993**, *115*, 1804.
[2] R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature* **1993**, *365*, 141.
[3] G. Christou, D. Gatteschi, D. N. Hendrickson, R. Sessoli, *MRS Bull.* **2000**, *25*, 66.
[4] S. M. J. Aubin, M. W. Wemple, D. M. Adams, H.-L. Tsai, G. Christou, D. H. Hendrickson, *J. Am. Chem. Soc.* **1996**, *118*, 7746.
[5] J. R. Friedman, M. P. Sarachik, J. Tejada, R. Ziolo, *Phys. Rev. Lett.* **1996**, *76*, 3830.
[6] L. Thomas, F. Lionti, R. Ballou, D. Gatteschi, R. Sessoli, B. Barbara, *Nature* **1996**, *383*, 145.
[7] S. M. J. Aubin, N. R. Dilley, M. W. Wemple, M. B. Maple, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1998**, *120*, 839.
[8] S. M. J. Aubin, N. R. Dilley, L. Pardi, J. Krzystek, M. W. Wemple, L.-C. Brunel, M. B. Maple, G. Christou, D. N. Hendrickson, *J. Am. Chem. Soc.* **1998**, *120*, 4991.
[9] C. Sangregorio, T. Ohm, C. Paulsen, R. Sessoli, D. Gatteschi, *Phys. Rev. Lett.* **1997**, *78*, 4645.
[10] E. K. Brechin, C. Boskovic, W. Wernsdorfer, J. Yoo, A. Yamaguchi, E. C. SaVudo, T. R. Concolino, A. L. Rheingold, H. Ishimoto, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.* **2002**, *124*, 9710.
[11] a) M. Soler, W. Wernsdorfer, K. Folting, M. Pink, G. Christou, *J. Am. Chem. Soc.*, **2004**, *126*, 2156; b) M. Soler, E. Rumberger, K. Folting, D. N. Hendrickson, G. Christou, *Polyhedron* **2001**, *20*, 1365.
[12] H. Andres, R. Basler, A. J. Blake, C. Cadiou, G. Chaboussant, C. M. Grant, H.-U. Güdel, M. Murrie, S. Parsons, C. Paulsen, F. Semadini, V. Villar, W. Wernsdorfer, R. E. P. Winpenny, *Chem. Eur. J.* **2002**, *8*, 4867.
[13] W. Wernsdorfer, R. Sessoli, *Science* **1999**, *284*, 133.
[14] M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789.
[15] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694.
[16] N. Ishikawa, M. Sugita, T. Ishikawa, S. Koshihara, Y. Kaizu, *J. Phys. Chem. B* **2004**, *108*, 11265.
[17] R. Giraud, W. Wernsdorfer, A. M. Tkachuk, D. Mailly, B. Barbara, *Phys. Rev. Lett.* **2001**, *87*, 057203.
[18] A. De Cian, M. Moussavi, J. Fischer, R. Weiss, *Inorg. Chem.* **1985**, *24*, 3162.
[19] H. Konami, M. Hatano, A. Tajiri, *Chem. Phys. Lett.* **1989**, *160*, 163.
[20] N. Ishikawa, M. Sugita, T. Okubo, N. Tanaka, T. Iino, Y. Kaizu, *Inorg. Chem.* **2003**, *42*, 2440.
[21] W. Wernsdorfer, *Adv. Chem. Phys.* **2001**, *118*, 99.
[22] W. Wernsdorfer, N. E. Chakov, G. Christou, *Phys. Rev. B* **2004**, *70*, 132413.
[23] N. Ishikawa, *J. Phys. Chem. A* **2003**, *107*, 9543.

[24] N. Ishikawa, T. Iino, Y. Kaizu, *J. Phys. Chem. A* **2002**, *106*, 9543.
[25] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance*, Clarendon, Oxford, **1970**, chap. 18.
[26] H. A. Kramers, *Proc. K. Ned. Akad. Wet.* **1930**, *33*, 959.
[27] a) L. Landau, *Phys. Z. Sowjetunion* **1932**, *2*, 46; b) C. Zener, *Proc. R. Soc. London Ser. A* **1932**, *137*, 696; c) S. Miyashita, *J. Phys. Soc. Jpn.* **1995**, *64*, 3207.

