EPR Studies of the Anisotropy of a Mononuclear Terbium Single-Molecule Magnet

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Introduction

Extensive studies of single-molecule magnets (SMMs) have contributed to many fundamental discoveries such as quantum tunneling of the magnetic moment of a molecule through a magnetic anisotropy barrier. The strong spin-orbit coupling associated with *f* shell electrons has recently been exploited in the development of highly anisotropic mononuclear SMMs. One successful strategy involves the encapsulation of lanthanide ions in symmetric polyoxometalate (POM) cages [1]. This encapsulation has the potential to preserve intrinsic SMM properties outside of a crystal, which may prove important in molecular spintronics applications [2]. Multi-frequency continuous wave (cw) high-field EPR measurements offer an in-depth understanding of anisotropies in SMMs. Following similarly detailed studies of a Holmium POM SMM [3], we report here studies of a Terbium POM of the formula $K_{12}[Tb_{1-x}Y_xP_5W_{30}O_{110}]\cdot 54H_2O$ (**1**), for $x = 0.5$.

Experimental

Extensive angle dependent cw EPR measurements were performed at frequency of 134 GHz in order to map the effective magnetic anisotropy of the Tb^{III} POM SMM. Field rotation was achieved using a 9-5-1 T vector magnet in which three orthogonal superconducting coils may be independently driven by separate supplies. The measurements were performed at temperature of 2 K, and EPR spectra were then recorded for many different field orientations: 10° increments in the polar angle, for different azimuthal planes of rotation separated by 15°.

Results and Discussion

Tb^{III} (f^8) has a Hund's rule coupled total angular momentum ground state of **J** = **L** + **S** = 6 (**L** = **S** = 3). The axial nature of the POM ligand field in **1** gives rise to a low-lying doublet state; field-swept EPR measurements at frequencies above ~50 GHz then give rise to a single EPR peak corresponding to the transition within this doublet. The angle-dependence of the resonance field is represented in the polar plot in Fig. 1, confirming the significant magnetic anisotropy. Moreover, the expected axial symmetry is clearly apparent from the polar plot, with low *g* values (red/yellow) at the poles and around the equator; note that, in the figure, the axial *g*-tensor is tilted with respect to the experimental coordinate frame. It is also apparent that higher (>2nd) order multipole terms are needed to reproduce the observed *g*-anisotropy; the effective *g*-values span from 11.2 to 19.1.

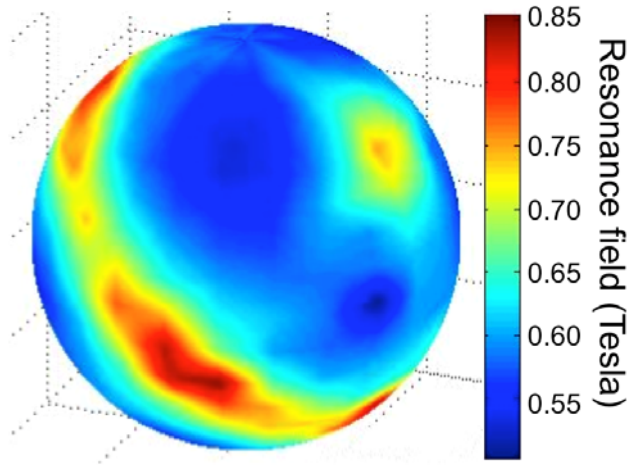

Figure 1. Polar plot of the resonance magnetic field for **1** at a frequency of 134 GHz and a temperature of 2 K.

Conclusions

Comprehensive cw high-frequency EPR studies on the Tb POM SMM offer a reliable determination of the magnetic anisotropy in this strongly anisotropic system. The crystals used for these studies are available in diluted form (x = 1.00, 0.25, 0.1, 0.05, 0.01). Further cw EPR measurements will be performed on multiple compositions of this family, along with pulsed EPR studies at high frequencies (>50 GHz).

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References

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