Multi-Frequency Pulsed EPR Studies on a Yb(III) Molecular Nanomagnet

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Introduction

Recently, the development of single-molecule magnets has shifted rapidly away from the use of transition metals in favor of lanthanides due to their large single-ion anisotropy. This is a direct consequence of the relatively strong spin-orbit coupling inherent to lanthanides, which, in the presence of the appropriate crystal field, gives rise to well separated spin-orbit projected states that can permit slow relaxation of the magnetization. The motivation for studying such systems presumes that the so-called Orbach mechanism provides the primary pathway through which the magnetization relaxes. However, previous studies on Yb(trensal) (**1**) have shown that simply having a large zero field energy barrier is not a sufficient criterion to achieve a high blocking temperature [1]. In so doing, it was demonstrated that **1** has the additional potential for use as a molecular spin qubit [2]. To further investigate these properties, we employ multi-frequency pulsed electron paramagnetic resonance (EPR) studies in order to probe the interactions that limit both spin-lattice (T_1) and spin-spin (T_2) relaxation by measuring the dependence on temperature and magnetic field.

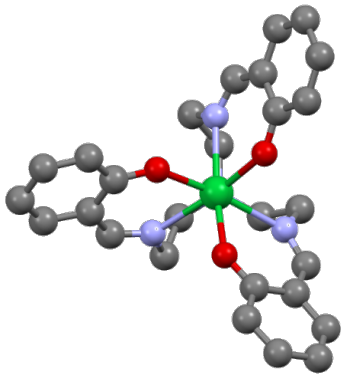

Fig.1 Structure of **1**. The C_3 axis, which coincides with the magnetic easy axis, is directed out of the page.

Experimental

Pulsed EPR studies on a single crystal of both the deuterated and non-deuterated versions of **1** were conducted on the 94 GHz HiPER spectrometer in EMR facility. Results were also obtained at 120 and 240 GHz on the heterodyne quasi-optical spectrometer, but are not presented here.

Results and Discussion

The field-swept echo-detected spectrum in **Fig.2** shows three clearly resolved isotopes of Yb(III), weighted by their natural abundance: ^{171}Yb (14%) and ^{173}Yb (16%) possessing nuclear spin I = 1/2 and 5/2, respectively, with the strong central transition originating from isotopes bearing no nuclear spin. As is consistent with previous X-band EPR measurements, T_2 shows no drastic variation between isotopes [2]. T_2 measurements performed on the central I = 0 transition were then compared to previous temperature dependence data taken at X-band [2], as shown in **Fig.3**. In comparison to the non-deuterated version of **1**, we observe a marginal increase in T_2. This small variation indicates that the spin-spin interactions between the central Yb(III) ion and the hydrogens coordinated to the nitrogen atoms shown in **Fig.1** do not contribute significantly to the decoherence mechanism limiting T_2. However, in comparison to X-band, we see a marked decrease in coherence times for both versions of **1**.

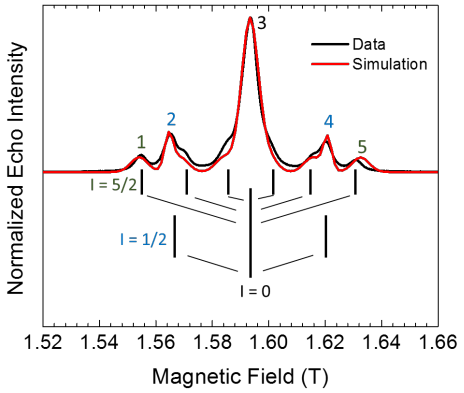

Fig.2 Field-swept echo-detected spectrum of 1 at 3.5 K, with the applied magnetic field oriented along the C_3 axis.

Conclusions

From the comparison shown in **Fig.3**, the decrease in T_2 with respect to resonant field could indicate a strong contribution from the so-called 'direct process', which scales the spin-lattice relaxation time as $1/B^n$ [1]. As such, it is likely that the phase memory time, which ultimately defines the utility of a spin qubit candidate, is limited by T_1. Therefore, further T_1 relaxation measurements will be performed at multiple frequencies in order to identify the decoherence mechanisms leading to the suppression of T_2.

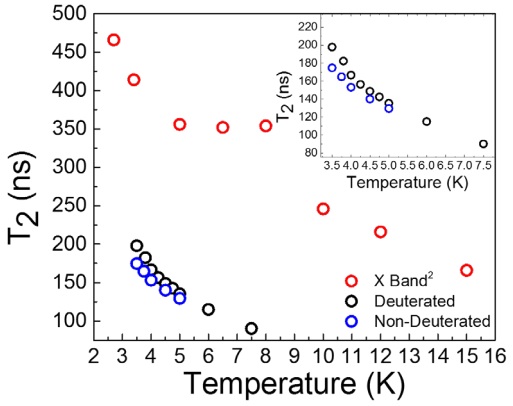

Fig.3 Temperature dependent T_2 measurements of both the deuterated and non-deuterated versions of **1** at 94 GHz, compared to previous X-band measurements [2].

Acknowledgements

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References

[1] Pederson, K.S., *et al.*, Inorg. Chem., **54**, 7600-7606 (2015).
[2] Pederson, K.S., *et al.*, J. Am. Chem. Soc., **138**, 5801-5804 (2016).