



Slow Relaxation of the Magnetization in a Quasi-Linear Europium(II) Molecule

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Molecules that can retain their magnetic state (magnetization alignment) below a characteristic blocking temperature – so-called Single-Molecule Magnets (SMMs) – have attracted significant attention due to their potential use in molecular-scale data storage applications. SMM properties typically arise from the combination of a large magnetic moment subjected to a uniaxial anisotropy, thus creating an energy barrier separating “up” and “down” magnetization states. Strong spin-orbit coupling (SOC) in the 4f shell can lead to large moments and significant magnetic anisotropy for certain molecular geometries, resulting in some of the best performing SMMs. However, until now, no europium (Eu) SMMs had been reported. This is because trivalent Eu^{3+} ($4f^6$), with spin & orbital moments $S = 3$ & $L = 3$, respectively, has no net moment, i.e., $J = L - S = 0$; meanwhile divalent Eu^{2+} ($4f^7$) has no first-order orbital moment ($L = 0$, $S = 7/2$), leading to an approximately spherical $^8\text{S}_{7/2}$ electronic configuration.

In this work, optimization of the crystal field acting on a Eu^{2+} ion residing in a quasi-linear molecular geometry gives rise to the first europium SMM. This is attributed to a sizeable 2nd-order orbital contribution to the magnetic ground state, resulting in appreciable anisotropy. High-field EPR is the method of choice for characterizing this anisotropy. In particular, measurements at several frequencies, spanning a wide magnetic field range (**Fig. 1**), are essential for constraining the multiple Hamiltonian parameters describing the effective spin $S = 7/2$ ground state. The EPR results are supported by electronic structure calculations, highlighting the importance of 2nd order SOC and the linear geometry in achieving non-negligible uniaxial anisotropy.

The divalent oxidation state is rare for molecular lanthanide complexes. Meanwhile, achieving a linear N–Eu–N coordination geometry (**Fig. 1** inset) is synthetically challenging, underscoring the importance of this work in shining a light on factors that give rise to SMM behavior for the otherwise isotropic $4f^7$ electronic configuration.

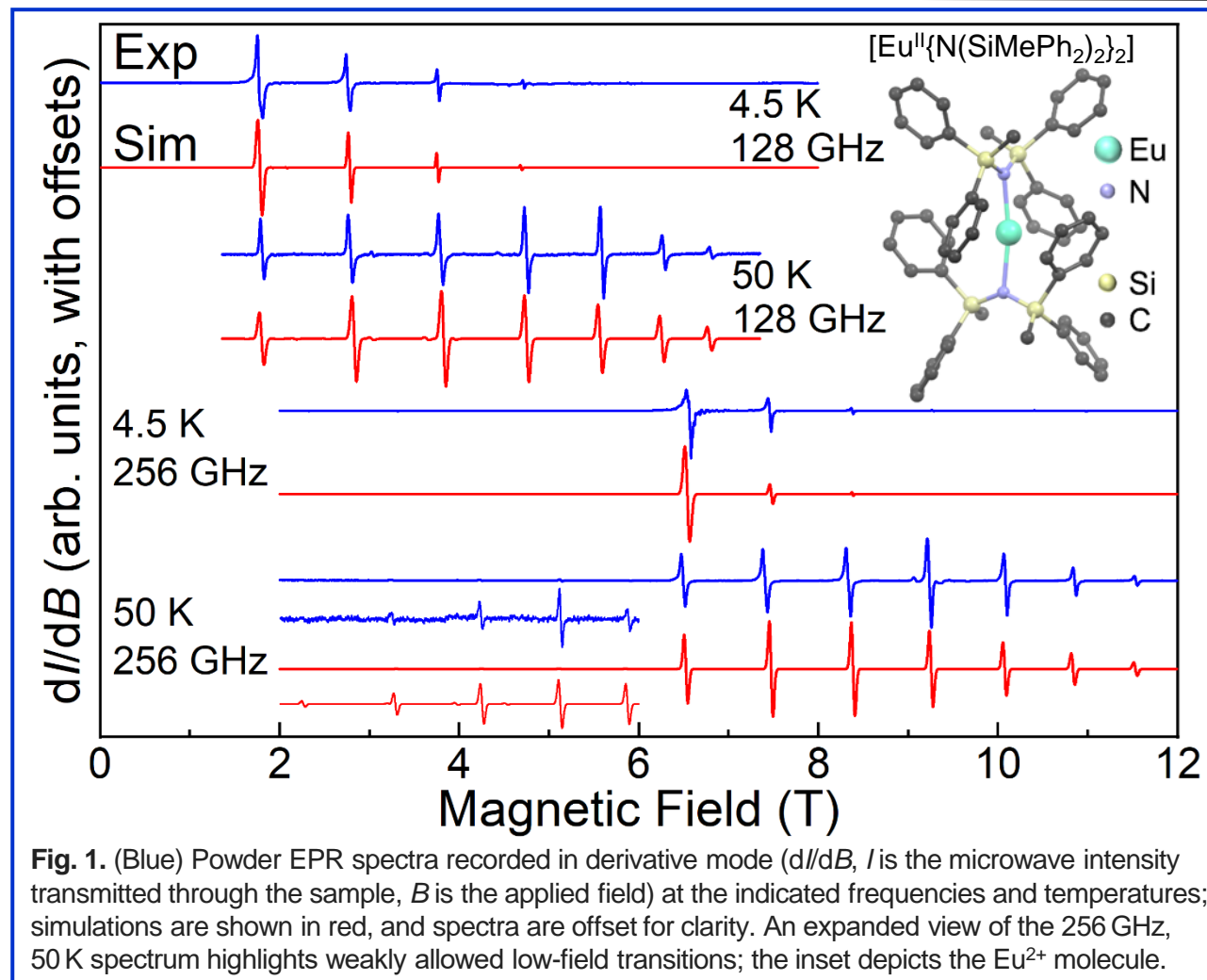


Fig. 1. (Blue) Powder EPR spectra recorded in derivative mode (dI/dB , I is the microwave intensity transmitted through the sample, B is the applied field) at the indicated frequencies and temperatures; simulations are shown in red, and spectra are offset for clarity. An expanded view of the 256 GHz, 50 K spectrum highlights weakly allowed low-field transitions; the inset depicts the Eu^{2+} molecule.

Facilities and instrumentation used: EMR program, 15/17 Tesla Transmission Spectrometer & 12.5T Heterodyne Quasi-Optical Spectrometer.

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