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Toward Molecular 4f Single-Ion Magnet Qubits

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Supporting Information

ABSTRACT: Quantum coherence is detected in the 4f single-ion magnet (SIM) Yb(trensal), by isotope selective pulsed EPR spectroscopy on an oriented single crystal. At X-band, the spin−lattice relaxation (T_1) and phase memory (T_m) times are found to be independent of the nuclei bearing, or not, a nuclear spin. The observation of Rabi oscillations of the spin echo demonstrates the possibility to coherently manipulate the system for more than 70 rotations. This renders Yb(trensal), a sublimable and chemically modifiable SIM, an excellent candidate for quantum information processing.

Quantum coherence is a fundamental property of electron spins and has the promise of being at the core of future computation technologies such as quantum computing.[1] Quantum computation protocols exploit the coherent superposition of states in quantum objects, or "qubits", for the processing of information. To date, there have been several proposals for the physical realization of such qubits, including among others: quantum dots in semiconductors, photons, and superconducting nanostructures.[2] With respect to electron-spin-based qubits, several candidates have been proposed,[1,3] the most interesting results in chemistry having been obtained for metal-ion localized spins.[4] These can either be nanoscaled polymetallic clusters[5] or smaller monometallic molecular systems[6] which simultaneously possess the potential to display quantum coherence and are processable by soft-chemical methods. Indeed, some of these molecules are now seriously challenging the quantum coherence properties of highly performing purely inorganic systems.[7] A much less explored class of compounds in the field of quantum information processing are single-molecule and single-ion magnets (SMMs and SIMs, respectively),[8] i.e., molecules exhibiting superparamagnetic behavior.[9] While numerous metal-ion compounds exhibit SMM or SIM behavior, most excitingly, mono- and dinuclear lanthanide (4f) complexes have now dwarfed the performance of the first generations of SMMs in terms of long spin−lattice relaxation times, T_1.[10] This observation is rather interesting for the development of realistic qubit candidates since the phase memory time, T_m, mainly determined by the spin−spin relaxation time T_2, becomes limited by short spin−lattice relaxation times, T_1, via the dependence $T_2 \leq 2T_1$.[2,12] In addition, T_1 should remain short enough to allow an optimal qubit reset time.[13] Despite these promising features of lanthanide complexes, only few studies have reported on the quantum coherence properties of 4f metal centers in complexes[14] or in inorganic lattices.[15] Previous studies investigated lanthanide ions in purely inorganic hosts as potential qubits and speculated about spin-state detection by exploiting the characteristic photoluminescence of lanthanides,[16] a major advantage of lanthanides[17] over other classes of qubit candidates. Herein we report a single-crystal study of the lanthanide SIM, Yb(trensal)[11] (**1**, Figure 1, left), doped into the isostructural diamagnetic host,

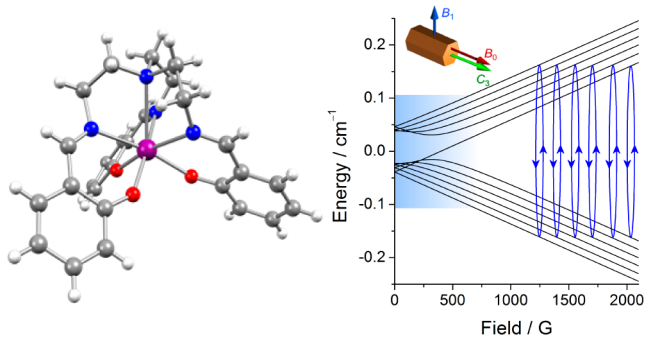

Figure 1. Left: Molecular structure of **1**.[11] Color code: purple, Yb; red, O; blue, N; gray, C; white, H. Right: Zeeman diagram of the $I = 5/2$ isotope of **1** calculated with $B_0 \| C_3$. The observed EPR transitions correspond to individually accessible qubits. The blue-shaded area defines the clock transitions region.

Lu(trensal). **1** possesses desirable properties such as a modifiable periphery, photoluminescence, and sublimability.[11,18] Furthermore, **1** is an interesting qubit candidate due to the very large splitting between the electronic ground doublet and the first excited ligand (crystal) field state, determined by luminescence spectroscopy to 464 cm^{-1}, and its intrinsic slow paramagnetic relaxation (~1 ms at 4 K).[11] These features have two important implications: First, spin−lattice relaxation should not hinder long coherence times, and second, the ground Kramers doublet of the $J = 7/2$ ground term of Yb^{3+} ($^2F_{7/2}$) can be approximated as an effective spin-1/2 system in a wide temperature interval, with the ground state g-factors $g_\| = 4.3$ and $g_\perp = 2.9$.[11] Thus, the simultaneous display of long T_1 and of allowed electron paramagnetic resonance (EPR) transitions makes **1** particularly

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suitable for studies of coherent manipulation of the electron-spin by use of EPR protocols. Furthermore, some proposals for the implementation of quantum computing algorithms on molecular species[19] take advantage of the presence of a number of accessible states of the molecule, resulting for instance from coupling of the electronic spin to nuclear ones via hyperfine interactions. In addition, the study of the effect of hyperfine interactions on quantum coherence is of interest for field-fluctuation protection in qubits, through the so-called clock transitions (Figure 1).[20] Such clock transitions occur in field ranges wherein the relevant eigenstates display vanishing derivatives with respect to the field strength, thereby suppressing the effect of magnetic field fluctuations on coherence. However, when addressing these transitions on polycrystalline samples by EPR, line broadening severely limits the number of hyperfine lines that can be individually addressed. This problem is overcome by use of single crystals where the ordered orientation of molecules facilitates addressing of individual isotope lines in an intrinsically multi-isotopic material. To this purpose, we herein perform a single-crystal pulsed EPR study of **1** which crystallizes in the trigonal $P\bar{3}c1$ space group as large pencil-shaped crystals and in which the Yb^{3+} ion and the apical tertiary amine nitrogen atom (Figure 1, left) both lie on the crystallographic C_3 axis. The natural composition of ytterbium encompasses the isotopes $^{168,170-174,176}$Yb of which the ^{171}Yb (14%) and ^{173}Yb (16%) isotopes possess a nuclear spin of $I = 1/2$ and 5/2, respectively. The remaining isotopes do not bear a nuclear spin. We were unable to observe any Hahn echo in **1**. Dilution in the isostructural diamagnetic host, Lu(trensal), results in the observation of a Hahn echo. The echo-detected field-swept (EDFS) X-band pulsed EPR spectrum of a single-crystal of diamagnetic Lu(trensal) at ~7% Yb doping (**1**′) was obtained by a standard Hahn echo pulse sequence for the field orientations along ($B_0 \| C_3$) and perpendicular ($B_0 \perp C_3$) to the crystallographic 3-fold rotation axis (Figure 2). In both these cases, the microwave field, B_1, is perpendicular to both B_0 and C_3. The observed EDFS spectra of **1**′ can essentially be assigned to transitions between different electronuclear states of single Yb^{3+} centers, in accordance with our previous interpretation of the continuous wave (c.w.) X-band EPR spectra.[11] In addition, the EDFS X-band EPR spectra of **1**′ display additional resonances, marked by "*" in Figure 2, that we assign to minority sites within **1**′, characterized by the presence of neighboring Yb^{3+} centers.[21] The concentration of such sites in **1**′ is low, as evidenced by the low intensity of the relevant lines in the c.w. X-band EPR spectrum of **1**′, (Figure 2, inset). The intensity of these lines is enhanced in the EDFS X-band EPR spectrum of **1**′, likely because of a longer T_m associated with resonances originating from these sites. This interesting counterintuitive feature will be investigated in further studies. The qualitative appearance of the EDFS X-band EPR spectra of **1**′ for $B_0 \| C_3$ and $B_0 \perp C_3$ is similar. For both orientations, the main, central line corresponds to the $I = 0$ isotopes. The attribution of the observed bands to the various isotopes of Yb is given in Figure 2 as stick diagrams. The observed well-resolved lines provide for a rare opportunity to selectively study the qubit potential, and its orientational dependence, of different Yb isotopes. Quantum coherence in molecular qubits, manifested in the phase memory time, T_m, can be directly measured by pulsed EPR spectroscopy. The T_m times of **1**′ (Figure 3) were determined at the field positions indicated in

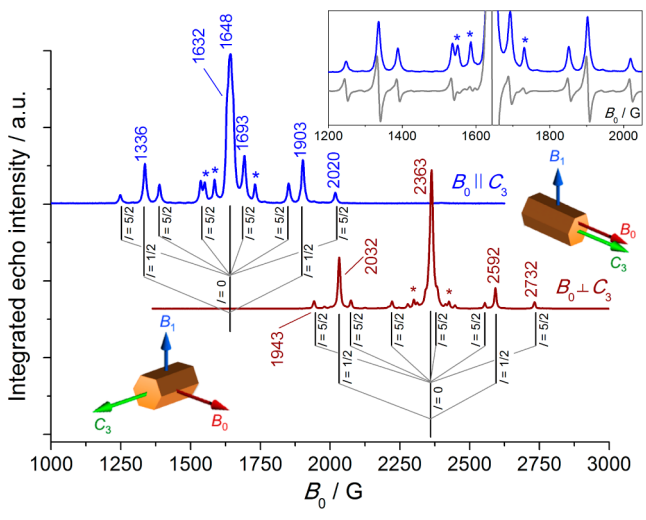

Figure 2. Field-swept echo-detected EPR spectra (9.7 GHz) of an oriented ($B_0 \| C_3$ = blue; $B_0 \perp C_3$ = red) single-crystal of **1**′ at 5 K. Inset: c.w. (gray) and EDFS EPR spectra of **1**′ for $B_0 \| C_3$ at 5 K.

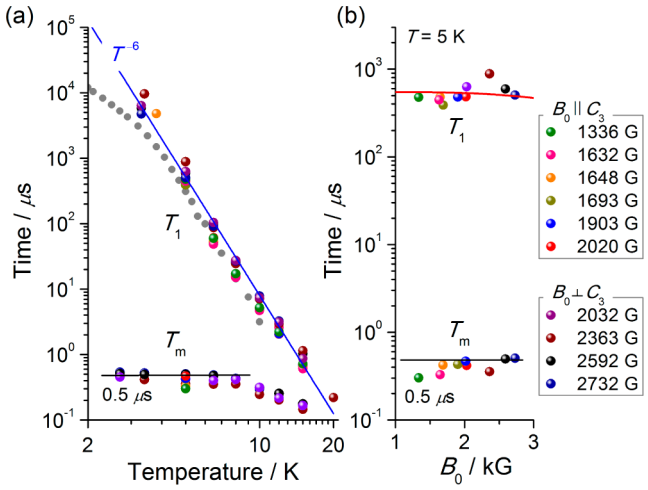

Figure 3. (a) Temperature dependence of T_1 and T_m times for **1**′ as determined by pulsed EPR. The gray points represent the spin−lattice relaxation times obtained on a single-crystal of **1** by ac susceptibility measurements.[11] The solid blue line is calculated as the Raman-like temperature dependence, $T_1 \propto T^{-6}$. The horizontal black line is a guide for the eye. (b) Corresponding field dependence of T_1 and T_m. The red line is the calculated field dependence of T_1 using the model derived from ac susceptibility studies on bulk **1**.[11]

Figure 2, from fitting the timely decay of the Hahn echo (Figures S1−2) induced by the standard $\pi/2-\tau-\pi-\tau-$echo pulse sequence. As shown in Figure 3, T_m is essentially isotope independent and only weakly temperature dependent and maximizes around 0.5 μs at the lowest temperatures. Although this value is significantly shorter than that found in some nuclear-spin-free transition-metal-ion-based systems, it is comparable to those found for lanthanides in molecular and purely inorganic lattices.[14a,b] The spin−lattice relaxation times, T_1, were obtained through the fitting of inversion recovery sequence traces (Figures S3−4). Above 3 K, T_1 of **1**′ exhibits strong temperature dependence described by a power law, $T_1 \propto T^{-n}$ with $n \approx 6$. The extracted T_1 relaxation times are shown in Figure 3, together with the relaxation times, τ, obtained by ac susceptibility measurements on bulk **1**,[11] where a close resemblance between the results obtained by the two techniques is observed. In our case T_1 can be

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assimilated to τ as magnetization relaxation occurs via a single quantum step. The isotope independence of T_1 expresses the fact that in the presence of an external magnetic field dominating the hyperfine coupling, the spin dynamics of **1′** is not determined by the interaction of the electron and nuclear spins. This is in accordance with our previous studies of the bulk spin−lattice relaxation time of concentrated **1** by ac magnetometry.[11] In these previous studies we showed that the spin dynamics in this complex is determined by Raman-like processes, in the presence of an external static magnetic field of the same magnitude as these pulsed EPR studies. Herein, the magnetic field required to study the EDFS EPR spectrum of **1′**, leads to the masking of possible differences in tunneling rates between the various isotopes of Yb, by removing the energy degeneracy of the zero-field eigenstates. Such tunneling rate differences between various Dy isotopes in a SIM were recently observed by Pointillart et al. by magnetometry.[22] The ability to generate arbitrary coherent superposition states in **1′** was probed by transient nutation experiments. The resulting Rabi oscillations are shown in Figure 4, for $B_0 \perp C_3$, at 5 K and at different field positions. Additional data are provided in the Supporting Information. Clear oscillatory behavior is observed at all peak positions, demonstrating the possibility to coherently manipulate any electronuclear state of the Yb isotopes. The same conclusion applies to the $B_0 \| C_3$ orientation (Supporting Information). Interestingly, the Rabi oscillations at the "I = 0 lines" (Figures 4 and S10) appear to exhibit a much stronger damping than the remaining electronuclear lines of the I = 1/2 and 5/2 bearing isotopes. The Fourier transforms of these Rabi oscillations are shown in the right panel of Figure 4 (cf. Supporting Information). The prominent peak observed at each field position is a Rabi frequency, Ω_R, as demonstrated by the linear field dependence of Ω_R on the microwave field strength, B_1 (Figures S12a and S20a). The peak widths are comparable (fwhm ∼2 MHz) for all but the "I = 0" line (fwhm ∼6 MHz, B_0 = 2363 G), reflecting the much faster damping of the latter. The weaker, sharp peak below 10 MHz coincides with the expected Larmor frequencies of the ^{1}H nucleus at the indicated field values, arising from coherence transfer from the electronic spin of Yb to the nuclear spin of ^{1}H (Figures S12b and S20b).[23] It has previously been argued that this coherence transfer induces Rabi oscillations at time scales extending into the microsecond region.[6d,24] In those studies, Rabi oscillations in the microsecond region have only been observed when Ω_R was tuned to coincide with the proton Larmor frequency. In our studies, we observe Rabi oscillations that extend to several microseconds at Ω_R frequencies not related to the proton Larmor frequency. We observe more than 70 Rabi oscillations (Figures S11 and S19) extending to 4 μs. When the magnitude of B_1 is decreased for Ω_R to approach the B_1-independent ^{1}H frequency, a strong damping[25] and a deviation of $\Omega_R(B_1)$ from linearity is observed (Figures S12a and S20a). The qubit figure of merit, Q_M, defined by $2\Omega_R T_2$,[16a] reaches up to 40 in **1′**. These values are low compared to those obtained for transition-metal complexes in rigorously nuclear spin-free surroundings.[7a,b] Nevertheless, the very high number of observed coherent rotations is a promising feature of this SIM, which, to the best of our knowledge, is only the second molecular 4f system that can be brought into an arbitrary coherent superposition of states, the other being a Gd(III) containing polyoxometallate.[6d] Further studies of 4f SIMs with much longer T_1 times would be an interesting extension of this work. In addition, another important factor toward use of molecular systems as qubits is the need to organize these molecules in ordered arrays on surfaces. Very recently, the first sublimable molecular qubit was reported.[26] Based on the previous work by some of us,[18a,27] the possibility to prepare and study, by surface EPR,[28] oriented 2D crystals of **1** on surfaces would be an interesting approach toward qubit entanglement in SIM assemblies.

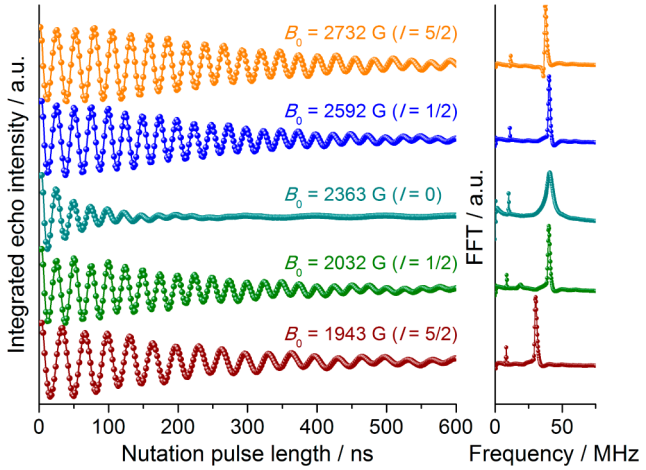

Figure 4. Echo intensity, proportional to the expectation value $\langle S_z \rangle$, as a function of the length of the nutation pulse (t_p) at selected field positions [$B_0 \perp C_3$, T = 5 K, microwave attenuation = 3 dB] (left) and its corresponding Fourier transforms (right). Solid lines are a guide for the eye.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b02702.

Experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

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