Enhancing coherence in molecular spin qubits via atomic clock transitions

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Quantum Computing is an emerging area within the information sciences revolving around the concept of quantum bits (or qubits). A major obstacle is the extreme fragility of these qubits due to interactions with their environment that destroy their "quantumness". This phenomenon, known as decoherence, is of immense fundamental interest.[1,2] There are many competing candidates for qubits, including superconducting circuits,[3] quantum optical cavities,[4] ultracold atoms[5] and spin qubits,[6-8] and each one has its strengths and weaknesses. When dealing with spin qubits, the strongest source of decoherence is the magnetic dipolar interaction.[9] To minimize it, spins are typically diluted in a diamagnetic matrix. For example, this dilution can be taken to the extreme of a single phosphorus atom in silicon,[6] while in molecular matrices a typical ratio is one magnetic molecule per 10,000.[10] However, there is a fundamental contradiction between reducing decoherence by dilution, and allowing quantum operations via the interaction between spin qubits. To solve this apparent paradox, the design and engineering of quantum hardware can benefit from a "bottom-up" approach whereby the electronic structure of magnetic molecules is chemically tailored to give the desired physical behavior. Here we present a very effective way of eliminating decoherence in solid-state molecular spin qubits without resorting to extreme dilution. It is based on the design of molecular structures with crystal field ground states possessing large tunneling gaps that give rise to optimal operating points, or atomic clock transitions, at which the quantum spin dynamics become protected against dipolar decoherence. This approach is illustrated with a holmium molecular nanomagnet in which long coherence times (up to 8.4 μs at 5 K) can be obtained at unusually high concentrations. This finding opens new avenues for quantum computing based on molecular spin qubits.

One of the proposed approaches to obtaining spin qubits is that of using magnetic molecules.[8-16] Up to now, coherence has been optimized through dilution and deuteration to minimize dipolar and hyperfine interactions, respectively.[10,16] A class of molecules in which these two sources of decoherence can be minimized by alternative means are the so-called polyoxometalates. In the past, these metal-oxide clusters have been used as model systems in molecular magnetism due to their ability to host magnetic ions in chemically tailored environments of high symmetry and rigidity.[17] Currently, these molecules are seen as potential building blocks in quantum computing architectures.[18-22]

38   In the present study we chose the $[Ho(W_5O_{18})_2]^{9-}$ complex (abbreviated HoW_{10}) which has been subject to

39   extensive structural, magnetic and spectroscopic characterizations that raised the possibility of observing

40   coherent spin dynamics.[23,24] HoW_{10} is formed by two molecular tungsten oxide moieties encapsulating a

41   Ho^{+3} ion (Fig. 1). The geometry around Ho^{+3} exhibits a slightly distorted square-antiprismatic environment,

42   which can be approximated by a D_{4d} "pseudo-axial" symmetry. This results in a splitting of the $J = 8$

43   ground state spin-orbit manifold according to its m_J quantum numbers. Quantitatively this splitting can be

44   described in terms of a crystal-field (CF) Hamiltonian (double summation in eq. 1) which, for D_{4d}

45   symmetry, contains the axial CF terms $B_2^0\hat{O}_2^0$, $B_4^0\hat{O}_4^0$ and $B_6^0\hat{O}_6^0$ (see Methods for definition and discussion

46   of terms in eq. 1).[24]

47

$$\hat{H} = \sum_{k=2,4,6} \sum_{q=0}^{k} B_k^q \hat{O}_k^q + \hat{J}\cdot\ddot{A}\cdot\hat{I} + \mu_B \vec{B}_0 \cdot \ddot{g} \cdot \hat{J} - \mu_N g_N \vec{B}_0 \cdot \hat{I} \qquad (1)$$

49

50   This results in an isolated $m_J = \pm4$ ground doublet, separated from the first excited states ($m_J = \pm5$) by

51   ~20 cm^{-1}. This picture provides a reasonable description of the magnetic properties of this molecule.[23]

52   However, minor deviations from D_{4d} symmetry that are present in the crystal make operative the

53   tetragonal $B_4^4\hat{O}_4^4$ CF interaction. Interestingly, the match between the (±integer) values of the ground state

54   spin projections, $m_J = \pm4$, with the tetragonal (i.e., $q = 4$) order of the main symmetry axis of the molecule,

55   results in the $B_4^4\hat{O}_4^4$ [$\hat{O}_4^4 = \frac{1}{2}(\hat{J}_+^4 + \hat{J}_-^4)$] interaction generating an unusually large quantum tunneling gap,

56     $\Delta \sim 9.18$ GHz (~0.3 cm^{-1}).[24] This gap is a crucial factor for the coherence of electron spin dynamics in

57   molecular spin qubits, and is the main subject of the present study.

58

59   The standard approach for probing coherent spin dynamics involves the use of "electron spin echoes" in

60   pulsed Electron Paramagnetic Resonance (EPR). The HoW_{10} system is attractive in this regard because

61   its predicted tunneling gap (~9.18 GHz, Fig. 1) is close to the X-band frequency associated with the most

62   sophisticated EPR spectrometers. While the magnitude of the gap is set by B_4^4, interesting details of the

63   EPR spectra are determined also by the hyperfine interaction between the Ho electron and nuclear spins

64   (second term in eq. 1). Holmium occurs naturally in only one stable isotope (^{165}Ho) with a nuclear spin of

65     $I = {}^7/_2$. A strong hyperfine coupling ($A_{//} = 830\pm10$ MHz) results in the observation of eight ($2I + 1$) well-

66   resolved transitions via continuous-wave (CW) high-frequency EPR measurements.[24] The energy level

67   scheme that arises from the combination of CF and hyperfine coupling, together with the Zeeman

68   interaction (3rd and 4th terms in eq. 1), gives rise to a series of avoided level crossings between $m_J = \pm4$

69   states (with the same m_I), resulting in multiple gaps in the energy diagram near zero-field (Fig. 1a).

70

71   Single-crystals of $Na_9[Ho_xY_{(1-x)}(W_5O_{18})_2]\cdot nH_2O$ (where Y is non-magnetic) were prepared with Ho

72   concentrations ranging from $x = 0.25$ to $x = 0.001$, i.e., up to three orders of magnitude away from the

73   usual high-dilution limit,[10] allowing a study of the effects of dilution on electron dipolar spin-spin

74 decoherence. Fig. 2a displays electron-spin-echo- (ESE-) detected EPR spectra recorded at 5 K for a
75 dilute (x = 0.001) sample at frequencies from 9.1 to 9.8 GHz, with θ = 29° (θ is the angle between B_0 and
76 the z-axis of the crystal); ESE signals were generated using a two-pulse Hahn-echo sequence (see
77 Methods).[25] Four broad peaks of equal intensity are observed at the two lowest frequencies (9.11 and
78 9.18 GHz), which were selected to be close to the gap minima in Fig. 1b. With increasing frequency,
79 these peaks split and move symmetrically apart, as expected on the basis of predictions in Fig. 1b. For
80 the most part, the data lie on the simulated curves, with the obvious exception of the two lowest
81 frequencies and some lower field (< 60 mT) data points. The simulations are based on previously
82 determined Hamiltonian parameters,[24] and the spectra are plotted against the re-scaled longitudinal
83 applied field, B_{0z} (= $B_0\cos\theta$), to facilitate comparisons between different samples (see Methods).

84

85 Two-pulse ESE measurements were separately utilized to determine 5 K transverse relaxation times, T_2,
86 at selected points within the spectrum for the x = 0.001 concentration. The longest T_2's are found in the
87 vicinity of the gap minima for the smallest crystals (see Figs. 2b, 3 and Methods), with values ranging
88 from 5.2 to 8.4 μs, whereas the values are substantially shorter away from the minima. In fact, the T_2
89 values exhibit sharp divergences right at B_{min} (Fig. 3). The key to understanding this behavior is the
90 quadratic field dependence of the EPR transition frequencies close to the gap minima (see Methods),

91

$$ f = \Delta + \frac{\gamma_z^2}{2\Delta}(B_{0z} - B_{min})^2, \tag{2} $$

92

93 such that the derivative $df/dB_{0z} \propto (B_{0z} - B_{min}) \to 0$ as $B_{0z} \to B_{min}$. Although not explicitly included in eq. 1,
94 nearly all sources of dipolar decoherence (due, e.g., to dynamics associated with the nuclear bath and
95 collective electron spin excitations, or magnons) can be approximated as a time-dependent magnetic
96 noise, $\delta B_0(t)$, acting on the central spin qubit (the spin being measured) via the Zeeman interaction, i.e.,
97 processes that flip nearby spins cause variations in the local field, δB_0, at the position of the central spin,
98 thereby altering its frequency/phase. Many of these processes involve indirect pairwise spin flip-flops
99 (spin diffusion) that are extremely hard to mitigate, and persist to very low temperatures. The extreme
100 axial anisotropy of HoW$_{10}$ results in an insensitivity to the perpendicular applied field component, $B_{0\perp}$ (see
101 Methods). Meanwhile, sensitivity to $\delta B_{0z}(t)$ vanishes (to first order) as $B_{0z} \to B_{min}$ and $df/dB_{0z} \to 0$,
102 resulting in a vanishing contribution to the dipolar decoherence. This is the concept behind so-called
103 'atomic clock transitions'. Named after atomic clocks, these transitions are protected against
104 environmental noise sources according to the principle described here (i.e., df/dB_0 = 0), resulting in a
105 clock frequency that exhibits exceptional phase stability.[26,27] Indeed, one expects the dephasing time, T_2,
106 to scale as $(B_{0z} - B_{min})^{-n}$ (n > 0, see Extended Data Fig. 1),[28,29] thus explaining the observed divergences
107 at the clock-transitions (CTs). For comparison, T_2 measurements are displayed in the right panel of Fig. 3
108 for several 'normal' EPR transitions, i.e., m_J = −4 to +4 transitions away from the gap minima, where the

109   frequency dependence approaches the linear regime and $df/dB_{0z} \rightarrow \gamma_z$ = 139.9 GHz/T (Fig. 1). Although

110   T_2 is moderately peaked at the centers of these resonances, the sharp divergences seen at the CTs are

111   clearly absent (see Methods for further discussion).

112

113   ESE-detected measurements for an x = 0.01 sample reveal essentially identical divergences in T_2 at the

114   CTs to those seen in Fig. 3, with maximum values ranging from 4 to 8 μs (see Extended Data Figs. 1 and

115   2). However, T_2 values associated with 'normal' EPR transitions well away from the CTs are much shorter

116   (~100 ns, not shown). Because the collection of ESE spectra requires the detection of an echo, the

117   observation of these 'normal' EPR transitions is challenging for $x \geq 0.01$. These findings are consistent

118   with the idea that dipolar 'noise' increases with increasing Ho concentration, resulting in shorter T_2's for

119   the 'normal' EPR transitions, yet an apparent insensitivity to the Ho concentration at the CTs.

120

121   Fig. 4 displays 5 K ESE-detected spectra for a concentrated x = 0.1 sample which are in stark contrast to

122   those in Fig. 2: narrow resonances are observed at the CTs that do not shift at all with frequency, i.e., the

123   data do not follow the simulations even though CW measurements indicate no measurable variation in

124   the spin Hamiltonian parameters with Ho concentration.[24] The total suppression of 'normal' EPR

125   transitions is attributed to a further reduction of T_2 upon increasing the Ho concentration, to the extent that

126   an echo can no longer be detected. Nevertheless, the T_2 values at the CTs remain long (~0.7 μs),

127   resulting in the narrow ESE-detected resonances. Indeed, because the echo intensity is T_2-weighted, the

128   resonance lineshape is a direct manifestation of the field dependence of T_2 at B_{min}. Analysis of CW EPR

129   spectra suggests that the main contribution to the linewidth is a Gaussian distribution in the B_4^4 parameter

130   (σ_{B44} = 0.63 MHz). This causes significant vertical broadening of the tunneling gap, Δ, and EPR transition

131   frequencies, as illustrated in Fig. 1b, which includes contours at the $\pm\sigma_\Delta$ and $\pm2\sigma_\Delta$ levels (σ_Δ = 123 MHz is

132   the standard deviation in Δ—see Methods). These simulations indicate measurable intensity at the CTs

133   up to at least 9.4 GHz. However, the B_4^4 distribution does not shift the CTs appreciably to lower or higher

134   fields, i.e., all molecules in the distribution have their CTs at essentially the same B_{min} values. This

135   explains the observation of narrow CT peaks spanning a wide frequency range in the x = 0.1 sample

136   (Fig. 4); similar behavior is also discernible at other concentrations (see Extended Data Fig. 3).

137

138   After magnetic 'noise', several other sources of decoherence remain. First and foremost, the CTs do not

139   protect against direct flip-flop processes that involve the central spin qubit.[28,29] These energy-conserving

140   events involve coupling to other spins via the off-diagonal component of the dipolar interaction ($\hat{S}_1^+\hat{S}_2^-$ +

141     $\hat{S}_1^-\hat{S}_2^+$). The inhomogeneous broadening will provide some protection against this source of dephasing,

142   because it requires the central spin to be resonant with other spins. Nevertheless, direct flip-flops likely

143   explain the shorter T_2's at the CTs in the x = 0.1 sample. However, unlike the aforementioned indirect

144   spin diffusion processes, direct flip-flops can be controlled at the stage of device design through the

145   tuning/detuning of individual CT frequencies. Finally, coupling to lattice dynamics (phonons) via the CF is

146 also likely to provide significant decoherence pathways, particularly as the temperature is raised.[16]

147 Indeed, a significant temperature dependence of T_2 is found at the CTs (more than a factor of 2 decrease

148 upon heating the sample to 7 K), suggesting that T_2 may become limited by spin-lattice relaxation

149 ($T_1 \approx 20$ µs at 5 K). This is something that will be the subject of future investigations.

150

151 The critical result from this study is the demonstration that CTs can be employed as a means of

152 enhancing the coherence of molecular spin qubits in concentrated samples. Therefore, instead of

153 attempting to suppress magnetic noise, which can be impractical at the stage of device design, we have

154 shown here that one can fortify the molecular spin qubit itself against this noise through the use of CTs. In

155 terms of design criteria, the molecule of choice should possess a large tunneling gap within the ground

156 magnetic doublet matching the working frequency of the EPR cavity. The key to this strategy is the

157 chemical design of molecular structures with appropriate CF states. In rare earth complexes with integer

158 spin, this goal translates into matching the m_J components of the ground doublet with the rotational order

159 (q) of the main symmetry axis of the molecule (see Methods). While this is not trivial to achieve, the case

160 of HoW_{10} is not an isolated example. For example, within rigid polyoxometalate chemistry, the Terbium

161 derivative of the $[LnP_5W_{30}O_{110}]^{12-}$ series with pentagonal structure (approximate C_{5v} symmetry) has been

162 characterized as having an $m_J = \pm 5$ ground state with an even larger tunneling gap of ~21 GHz that may

163 be suitable for pulsed Q-band EPR.[30] Tunability across this range (10 – 100 GHz) is desirable and

164 practical for quantum information applications, given that it sits at the current high end of the electronics

165 spectrum. Moreover, operation at these CTs requires application of only very moderate magnetic fields

166 (<0.2 T in the present example). Of course, this strategy can and should be combined with other known

167 ideas that are already being applied with great success, such as using rigid lattices with low abundance of

168 nuclear spins.[16] Nevertheless, it is remarkable that working with CTs offers the unique advantage of

169 allowing long coherence times with high concentrations of molecular spin qubits. In fact, for other

170 molecular spin qubit candidates, T_2 values of the order of tens of µs were only observable in deuterated

171 and highly diluted samples of Cr_7Ni molecular wheels[10] and $Cu(mnt)_2$ complexes.[16]

172

173 **References**

1   Schlosshauer, M. A. Decoherence: and the Quantum-To-Classical Transition. Springer (2008)

2   Stamp, P. C. E. Quantum information: Stopping the rot. *Nature* **453**, 167-168 (2008)

2   Stamp, P. C. E. Quantum information: Stopping the rot. *Nature* **453**, 167-168 (2008)

3   Devoret, M. H., Schoelkopf, R. J. Superconducting Circuits for Quantum Information: An Outlook. *Science* **339**, 1169-1174 (2013)

4   Duan, L. Quantum physics: A strong hybrid couple. *Nature* **508**, 195-196 (2014)

5   Weitenberg, C. *et al.* Single-spin addressing in an atomic Mott insulator. *Nature* **471**, 319-324 (2011)

6   Pla, J. J. *et al.* A single-atom electron spin qubit in silicon. *Nature* **489**, 541-545 (2012)

[7] Taminiau, T. H., Cramer, J., van der Sar, T., Dobrovitski, V. V., Hanson, R. Universal control and error correction in multi-qubit spin registers in diamond. *Nature Nanotechnology* **9**, 171-176 (2014)

[8] Ardavan, A. *et al*. Will Spin-Relaxation Times in Molecular Magnets Permit Quantum Information Processing? *Phys. Rev. Lett*. **98**, 057201 (2007)

[9] Takahashi, S. *et al*. Decoherence in crystals of quantum molecular magnets. *Nature* **476**, 76-79 (2011)

[10] Kaminski, D. *et al*. Quantum spin coherence in halogen-modified Cr_7Ni molecular nanomagnets. *Phys. Rev. B* **90**, 184419 (2014)

[11] Wedge, C. J. *et al*. Chemical Engineering of Molecular Qubits. Phys. Rev. Lett. **108**, 107204 (2012)

[12] Leuenberger, M. N., Loss, D. Quantum computing in molecular magnets. *Nature* **410**, 789-793 (2001)

[13] Warner, M. *et al*. Potential for spin-based information processing in a thin-film molecular semiconductor. *Nature* **503**, 504-508 (2013)

[14] Graham, M. *et al*. Influence of electronic spin and spin-orbit coupling on decoherence in mononuclear transition metal complexes. *J. Am. Chem. Soc.* **136**, 7623-7626 (2014)

[15] Thiele, S. *et al*. Electrically driven nuclear spin resonance in single-molecule magnets. *Science* **344**, 1135-1138 (2014)

[16] Bader, K. *et al*. Room temperature quantum coherence in a potential molecular qubit. *Nature Comms.* **5**, 5304 (2014)

[17] Clemente-Juan, J. M., Coronado, E. Magnetic clusters from polyoxometalate complexes. *Coord. Chem. Rev.* **193-195**, 361-394 (1999)

[18] Clemente-Juan, J. M., Coronado, E., Gaita-Ariño, A. Magnetic polyoxometalates: from molecular magnetism to molecular spintronics and quantum computing. *Chem. Soc. Rev.* **41**, 7464-7478 (2012)

[19] Lehmann, L., Gaita-Ariño, A., Coronado, E., Loss, D. Spin qubits with electrically gated polyoxometalate molecules. *Nature Nanotechnology* **2**, 312-317 (2007)

[20] van Hoogdalem, K, Stepanenko, D., Loss, D. Molecular Magnets for Quantum Information Processing. J. Bartolomé et al. (eds.), Molecular Magnets, NanoScience and Technology, Springer-Verlag (2014)

[21] AlDamen, M. A., Clemente-Juan, J. M., Coronado, E., Martí-Gastaldo, C., Gaita-Ariño, A. Mononuclear lanthanide single-molecule magnets based on polyoxometalates. *J. Am. Chem. Soc.*, **130**, 8874-8875 (2008)

[22] Martínez-Pérez, M. J. *et al*. Gd-based single-ion magnets with tunable magnetic anisotropy: molecular design of spin qubits. *Phys. Rev. Lett.* **108,** 247213 (2012)

[23] AlDamen, M. A. *et al*. Mononuclear lanthanide single molecule magnets based on the polyoxometalates $[Ln(W_5O_{18})_2]^{9-}$ and $[Ln(\beta-SiW_{11}O_{39})_2]^{13-}$ (Ln^{III} = Tb, Dy, Ho, Er, Tm, and Yb). *Inorg. Chem. Soc.* **48**, 3467-3479 (2008)

[24] Ghosh, S. *et al*. Multi-frequency EPR studies of a mononuclear holmium single-molecule magnet based on the polyoxometalate $[Ho^{III}(W_5O_{18})_2]^{9-}$. *Dalton Trans.* **41**, 13697-13704 (2012)

[25] Schweiger, A., Jeschke, G. Principles of Pulse Electron Paramagnetic Resonance, Oxford University Press (2001)

26   Bollinger, J. J. *et al*. Laser-Cooled-Atomic Frequency Standard. *Phys. Rev. Lett.* **54**, 1000-1003 (1985)

27   Vion, D. *et al*. Manipulating the Quantum State of an Electrical Circuit. *Science* **296**, 886-889 (2002)

28   Wolfowicz, G. *et al*. Atomic clock transitions in silicon-based spin qubits. *Nature Nanotechnology* **8**, 561-564 (2013)

29   Balian, S. J, Wolfowicz, G., Morton, J. J. L., Monteiro, T. S. Quantum bath-driven decoherence of mixed spin systems. *Phys. Rev. B.* **89**, 045403 (2014)

30   Cardona-Serra, S. *et al*. Lanthanoid single-ion magnets based on polyoxometalates with a 5-fold Symmetry: The Series $[LnP_5W_{30}O_{110}]^{12-}$ (Ln^{3+} = Tb, Dy, Ho, Er, Tm, and Yb). *J. Am. Chem. Soc.* **134**, 14982-14990 (2012)

174

175   **Supplementary Information** is linked to the online version of the paper at www.nature.com/nature.

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184

185   **Author Contributions** S.H., E.C. and A.G. conceived the research and wrote the paper. Y.D. prepared
186   the samples. S.H., M.S. and D.K. designed the experiments, while M.S. and D.K. performed the
187   measurements. S.H., M.S. and D.K. analyzed the results.

188

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190   authors declare no competing financial interests. Correspondence and requests for materials should be
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192

193   <u>**Figure Legends**</u>

194

195   **Figure 1: HoW$_{10}$ tunneling gap.** (a) Zeeman diagrams for the m_J = ±4, $I = {}^{7}/_{2}$ ground state, with $B_0//z$: the
196   thin gray lines assume exact D_{4d} symmetry, while the thick black curves assume an 'axial + $B_4^4 \hat{O}_4^4$'
197   parameterization.[24] (Inset) The corresponding 9.64 GHz CW EPR spectrum (from Ref. [24]) is observed
198   well below the D_{4d} prediction (gray arrow denotes expected highest field resonance), providing evidence
199   for the tunneling gap. Indeed, the 'axial + $B_4^4 \hat{O}_4^4$' parameterization gives excellent agreement with the data,
200   both in terms of resonance positions (blue arrows) and intensity (arrow thickness). The red vertical lines,
201   meanwhile, indicate the locations of CTs. (b) 3D EPR intensity map including inhomogeneous broadening

202   due to a Gaussian distribution in B_4^4 (σ_{B44} = 2.1 × 10^{-5} cm^{-1}); darker shading represents stronger intensity,

203   with contours at the $\pm\sigma_\Delta$ (red) and $\pm2\sigma_\Delta$ (blue) levels (σ_Δ = 123 MHz, the s.d. in Δ). Red arrows denote

204   CTs, dashed lines denote locations of 9.64 GHz resonances, and the inset shows the HoW_{10} molecule.

205

206   **Figure 2: ESE-detected spectra for a dilute sample.** (a) Variable frequency measurements at 5.0 K for

207   an x = 0.001 crystal, with θ = 29°; the frequencies are indicated in GHz above each trace. (b) Frequency

208   versus field plot of the resonances in (a). The data are in good agreement with simulations (solid curves)

209   based on the 'axial + $B_4^4\hat{O}_4^4$' parameterization [24]. Selected T_2 values (in µs) determined from the

210   measurements in Fig. 3 are indicated close to some of the data points in (b). Vertical error bars in (b)

211   denote pulse excitation bandwidths ($\pm1/2\tau_{\pi/2}$, where $\tau_{\pi/2}$ is the duration of the π/2 pulse), while horizontal

212   error bars represent standard deviations ($\pm$s.d.) deduced from Gaussian fits to the resonances in (a).

213

214   **Figure 3: T_2 divergence at the CTs.** Field-swept T_2 measurements recorded at 5.0 K for a small x =

215   0.001 crystal at θ = 22° and various frequencies indicated in the right panel. The first four panels illustrate

216   the divergences in T_2 at the CTs, referenced to the left-hand ordinate; the data are plotted in an expanded

217   view as a function of ($B_{0z} - B_{min}$), with best-fit B_{min} values given in each panel. The right-hand panel,

218   meanwhile, displays T_2 values well away from the CTs (see Fig. 1b), referenced to the right-hand

219   ordinate. Error bars denote the standard error in T_2.

220

221   **Figure 4: ESE-detected spectra for a concentrated sample.** (a) Variable frequency measurements at

222   5.0 K for an x = 0.10 crystal, with θ = 20°; the frequencies are indicated in GHz above each trace. The

223   ESE resonances are attributed to CTs. (b) Frequency versus field plot of the CTs in (a). Optimum T_2

224   values (in µs) are indicated next to the 9.11 GHz data. Meanwhile, the curves correspond to predictions

225   based on the CW EPR parameterization [24]. (c) Field-swept T_2 measurements recorded at 5.0 K for a

226   separate x = 0.10 crystal at θ = 25° and frequencies of 9.12 (blue squares) and 9.20 GHz (red circles).

227   Vertical error bars in (b) denote pulse excitation bandwidths ($\pm1/2\tau_{\pi/2}$, where $\tau_{\pi/2}$ is the duration of the π/2

228   pulse), while horizontal error bars represent standard deviations ($\pm$s.d.) deduced from Gaussian fits to the

229   resonances in (a). Error bars in (c) denote the standard error in T_2.

230

231   **Extended Data Figure 1: T_2 scaling.** Field-swept T_2 measurements for the x = 0.001 (a) and x = 0.01 (b)

232   concentrations at 5 K; the data are plotted as a function of ($B_{0z} - B_{min}$) on both log-log (main panels) and

233   linear (insets) scales. The blue lines are power-law fits to the positive ($B_{0z} - B_{min}$) data (green points), with

234   the obtained exponents given in the figures. Error bars denote the standard error in T_2.

235

236   **Extended Data Figure 2: T_2 divergence at the x = 0.01 concentration.** Field-swept T_2 measurements

237   recorded at 5.0 K for two separate crystals at frequencies of 9.12 GHz (blue squares) and 9.20 GHz (red

238   circles). Error bars denote the standard error in T_2.

239 **Extended Data Figure 3: ESE-detected spectra for the *x* = 0.01 concentration.** (a) Variable frequency
240 measurements at 5.0 K, with θ = 30°; the frequencies are indicated above each trace. Similar to spectra
241 for the *x* = 0.001 sample, the broad 9.2 GHz CT peak splits into two upon moving away from the tunneling
242 gap minimum (see also Fig. 1). However, weak ESE intensity can still be detected at B_{0z} = 165 mT at all
243 four frequencies. This is due to vertical broadening of the CT, caused by a Gaussian distribution in B_4^4.
244
245 **Methods**
246
247 **Experimental Details**
248 Pulsed EPR measurements were performed on a commercial Bruker E680 X-band spectrometer
249 equipped with a cylindrical TE$_{011}$ dielectric resonator (model ER 4118 X-MD5) with a center frequency
250 f_0 = 9.75 GHz. Single-crystals of Na$_9$[Ho$_x$Y$_{(1-x)}$(W$_5$O$_{18}$)$_2$]·nH$_2$O (*x* = 0.001 to 0.25) were prepared according
251 to the method described in Ref. [23]. Samples were re-crystallized prior to study, then transferred to the
252 spectrometer directly from the mother liquor and cooled rapidly in order to prevent loss of crystallinity due
253 to evaporation of lattice solvent. The sample temperature was controlled using an Oxford Instruments
254 CF935 helium flow cryostat and ITC503 temperature controller. A strong temperature dependence of T$_2$
255 at the CTs required operation of the cryostat at a base temperature of 5.0 K in order to ensure good
256 thermal stability and sample-to-sample reproducibility.
257
258 For each series of measurements, a single crystal was mounted on a 4 mm diameter quartz rod and
259 positioned at the center of the cylindrical resonator for perpendicular mode excitation. The tendency for
260 samples to rapidly lose solvent, and the low symmetry $P\bar{1}$ space group of the HoW$_{10}$ compound, made it
261 impossible to index and align crystals prior to mounting. However, the Bruker E680 and ER 4118X-MD5
262 dielectric resonator combination allows for *in situ* sample rotation about a single axis. Each crystal was
263 therefore aligned as best as possible on the basis of angle-dependent CW EPR measurements
264 performed at 9.75 GHz and 5.0 K. The remaining misalignment, θ, between B_0 and *z* was determined by
265 scaling the applied field to match the simulations in Fig. 1 (see below). A θ < 30° criterion was then
266 applied; crystals not meeting this condition were discarded and a new sample selected for study.
267
268 When overcoupled for ESE measurements, the bandwidth of the resonator, $\Delta f = f_0/Q \approx 250$ MHz, where
269 the loaded quality factor $Q \approx 40$. This is sufficient to allow variable-frequency measurements with
270 reasonable microwave B$_1$ fields down to a lower limit of ~9.1 GHz. The B$_1$ fields were independently
271 measured under the same conditions via the Rabi oscillation frequency (Ω_R) of a spin-½ EPR standard
272 (the organic radical bisdiphenylene-2-phenylallyl dissolved in polystyrene); B$_1$ values varied from ~4 G at
273 9.1 GHz, to 9 G at 9.75 GHz (Ω_R = 11–25 MHz for *s* = ½). A two-pulse sequence (T/2 − τ − T − τ − echo,
274 where T characterizes the pulse durations and τ the delay time between pulses) was employed for all
275 ESE measurements reported in this work. The values of T, τ and the source power were optimized at

276 each frequency, with the assumption that the optimum conditions correspond approximately to the Hahn-
277 echo sequence, $\pi/2 - \tau - \pi - \tau - $ echo, where π refers to the tipping angle. For T_2 measurements, τ was
278 varied and the resultant echo amplitude then fit to a single exponential decay.
279

280 **Pulse Sequences**
281 Because the ESE measurements were performed well below the center frequency of the cavity, and due
282 to the lack of *a priori* knowledge of the matrix elements associated with the observed transitions, pulse
283 sequences were adjusted at each frequency by one of two methods: (1) the $\pi/2$ pulse length (T/2) and
284 source attenuation were adjusted to maximize the echo intensity relative to the spectrometer noise for the
285 ESE-detected spectra in Figs. 2a and 4a, thereby explaining the variability of the vertical error bars
286 denoting excitation bandwidth (defined as 2/T, or $1/\tau_{\pi/2}$, where $\tau_{\pi/2}$ is the duration of the $\pi/2$ pulse in the
287 Hahn-echo sequence); and (2) Rabi oscillation measurements were used to determine the optimum $\pi/2$
288 pulse length for the detailed T_2 measurements displayed in Figs. 3, 4(c), and Extended Data Figs. 1 and 2
289 [the Rabi pulse sequence was optimized via method (1)]. On this basis, a Rabi frequency,
290 Ω_R = 98 Mrad·s^{-1} (15.6 MHz), was determined for 0 dB attenuation at the CTs, resulting in a minimum $\pi/2$
291 pulse length of 16 ns for the employed spectrometer. This corresponds to an optimum dephasing factor
292 Q_φ = 820, defined here as $Q_\varphi = \Omega_R \cdot T_2$, a figure of merit for qubit operation. We note, however, that this
293 does not preclude shorter pulses using a more powerful microwave source, suggesting the possibility of
294 Q_φ values up to 1.5×10^6 using the modified definition in Ref. [9]. Interestingly, this value is identical to the
295 one reported in Ref. [9] for an Fe_8 nanomagnet, in spite of the vastly different frequencies employed in the
296 two measurements, primarily because of the much longer coherence in the HoW_{10} system. Based on
297 knowledge of the spectrometer used for the Fe_8 study, we estimate a $Q_\varphi = \Omega_R \cdot T_2$ of just 50 for Fe_8; of
298 course, the same arguments concerning limited source power apply in that case. The HoW_{10} Q_φ value
299 compares favorably with other candidate molecular spin qubits using both definitions, e.g., the optimum
300 Q_φ (= $\Omega_R \cdot T_2$) varies from ≈ 2,000 for the Cr_7Ni wheel [7], up to ≈ 10,000 obtained recently for a Cu^{II}
301 coordination complex [16]. However, one should bear in mind that extreme dilution/deuteration was
302 employed in these cases.
303

304 **The Spin Hamiltonian**
305 The energy spectrum associated with the Hund's rule spin-orbit coupled ground state of the Ho^{+3} ion, with
306 L = 6, S = 2, and $J = |L + S| = 8$, can be described by the following effective Hamiltonian (eq. 3):
307

308 $$\hat{H} = \sum_{k=2,4,6} \sum_{q=0}^{k} B_k^q \hat{O}_k^q + \hat{J} \cdot \vec{\text{A}} \cdot \hat{I} + \mu_B \vec{B}_0 \cdot \vec{g} \cdot \hat{J} - \mu_N g_N \vec{B}_0 \cdot \hat{I} \qquad (3)$$

309

310 The double summation describes the CF interaction in terms of extended Stevens Operators $\hat{O}_k^q$ (k = 2, 4,
311 6, and $|q| \leq k$), with associated coefficients B_k^q,[31,32] and with $\hat{O}_k^q$ expressed in terms of the total electronic

312   angular momentum operators $\hat{J}$ and $\hat{J}_i$ ($i = x$, y, z). Using this convention, the axial ($q = 0$) coefficients

313   determined from magnetic and continuous-wave (CW) EPR measurements are:[23,24] $B_2^0 = 0.601$ cm^{-1}, $B_4^0 =$

314   6.96×10^{-3} cm^{-1}, and $B_6^0 = -5.10 \times 10^{-5}$ cm^{-1}. This parameterization results in the $m_J = \pm 4$ CF states lying

315   lowest in energy (Fig. 1), separated from the $m_J = \pm 5$ excited states by ~20 cm^{-1}.[23] The 2nd term in eq. 3

316   describes the hyperfine coupling between the Ho^{+3} electron and $I = {}^{7}\!/_{2}$ nuclear spin, resulting in the

317   observation of eight ($2I + 1$) well-resolved electro-nuclear transitions via high-field CW EPR

318   measurements; here, $\hat{I}$ denotes the total nuclear angular momentum operator, and $\overleftrightarrow{A}$ the hyperfine

319   coupling tensor, for which the parallel component, $A_{//} = 830 \pm 10$ MHz, has been determined from the high-

320   field CW EPR spectrum.[24] The final two terms in eq. 3 respectively parameterize the electron and nuclear

321   Zeeman interactions with the local magnetic induction, $\vec{B}_0$, in terms of a Landé g-tensor ($\overleftrightarrow{g}$) and isotropic

322   nuclear g-factor (g_N); μ_B and μ_N represent the Bohr (electron) and nuclear magneton, respectively. The

323   parallel component of the Landé g-tensor, $g_z = 1.25(1)$, has been determined from CW EPR studies.[22]

324

325   In addition to the axial ($q = 0$) CF parameters, CW EPR measurements at X-band frequencies can only be

326   accounted for by including a sizeable tetragonal $B_4^4 \hat{O}_4^4$ $[\hat{O}_4^4 = \frac{1}{2}(\hat{J}_+^4 + \hat{J}_-^4)]$ interaction, with B_4^4

327    $= 3.14 \times 10^{-3}$ cm^{-1} (see Fig. 1a and Ref. [24] for detailed explanation). It is this term (which is allowed

328   because of a small distortion of the HoW$_{10}$ molecule away from exact D_{4d} symmetry) that generates

329   avoided level crossings between $m_J = \pm 4$ states, as seen in Fig. 1a. In principle, the sixth order tetragonal

330    $B_6^4 \hat{O}_6^4$ interaction is also symmetry allowed. However, $\hat{O}_6^4$ contains the commutator $[\hat{J}_z^2, (\hat{J}_+^4 + \hat{J}_-^4)]$ and is,

331   thus, indistinguishable from $\hat{O}_4^4$ within the truncated $m_J = \pm 4$ ground doublet. Therefore, we employ only

332   the $B_4^4 \hat{O}_4^4$ term to capture the effects of the distortion away from exact D_{4d} symmetry. The key point is that

333    $\hat{O}_4^4$ connects the $m_J = \pm 4$ states in 2nd-order, resulting in unusually large (~9 GHz) quantum tunneling

334   gaps. For $B_0 // z$, the frequencies of the resultant weakly allowed EPR transitions between these states

335   then follow a field-dependence of the form (see Fig. 1b),

336

$$f = \sqrt{\Delta^2 + \gamma_z^2 (B_{0z} - B_{\min})^2} \approx \Delta + \frac{\gamma_z^2}{2\Delta}(B_{0z} - B_{\min})^2, \qquad (4)$$

337

338   where the approximate quadratic expression applies for fields close to the gap minima, $B_{\min}$. Indeed,

339   because $\hat{O}_4^4$ represents the only off-diagonal CF interaction in eq. 3, an almost exact mapping of the first

340   expression of eq. 4 onto curves generated via exact diagonalization of eq. 3 is possible, yielding the

341   following parameters: $\Delta = 9.18$ GHz, $\gamma_z = 139.9$ GHz/T (= $1.25 \times 8 \times \mu_B/h$, i.e., $g_z = 1.25$), and $B_{\min} = 23.6$,

342   70.9, 118.1 & 165.4 mT. This analysis assumes $B_0 // z$, while the experiments are typically performed with

343   a small field misalignment ($\theta \neq 0$), as noted above. However, due to the extreme uniaxial symmetry of the

344   HoW$_{10}$ molecule, the perpendicular component of the effective gyromagnetic tensor associated with the

345    $m_J = \pm 4$ doublet, $\gamma_{\perp,\text{eff}} < 0.1$ GHz/T ($g_{\perp,\text{eff}} < 0.01$), resulting in a virtual insensitivity to the perpendicular

346   component of the applied field ($B_{0\perp}$) over the range explored in this investigation; for comparison, note

347   that $\gamma_{proton} \approx 0.04$ GHz/T. For this reason, one can approximate the electronic Zeeman term in eq. 3 using

348   a scalar interaction of the form, $g_z \mu_B B_{0z} \hat{J}_z$ (where $B_{0z} = B_0 \cos\theta$). Eq. 4 then applies quite generally at the

349   gap minima, provided the applied field is rescaled to account for any misalignment. For this reason, all

350   EPR spectra are plotted as a function of the longitudinal applied field component, B_{0z}. Importantly, the

351   derivative $df/dB_{0z} \rightarrow 0$ (i.e. $\gamma_{z,eff} \rightarrow 0$) as $B_{0z} \rightarrow B_{min}$, resulting in an almost complete insensitivity of the

352   EPR transition frequencies at the gap minima to magnetic noise associated with the environment, thus

353   giving rise to the strong T_2 divergences at the CTs. However, the small yet finite $\gamma_{\perp,eff}$ (< 0.1 GHz/T) likely

354   limits T_2 right at the CTs (within ±0.5 G of B_{min}) in these studies due to the field misalignment. In fact,

355      $\gamma_{\perp,eff} \rightarrow 0$ as $B_0 \sin\theta \rightarrow 0$, which may explain the longer T_2 values observed at the lowest field CTs in

356   Fig. 3, and also suggests that longer T_2's may be achievable in precisely aligned samples.

357

358   **T_2 Scaling**

359   The data displayed in Fig. 3 were obtained for a small crystal of the most dilute sample ($x = 0.001$). It is

360   the high quality of this crystal that results in the sharp T_2 peaks at all four CTs (all four B_{min} locations).

361   However, it gives weak ESE signals, making it challenging to perform a detailed analysis of the scaling of

362   T_2 with B_{0z}. Careful T_2 measurements were therefore repeated for larger samples. Unfortunately, the

363   larger crystals are susceptible to twinning that manifests as a broadening of spectral peaks and T_2

364   divergences, with the effect being most pronounced at the higher field CTs (see Fig. 2a). However, the

365   first CT at $B_{min} = 23.6$ mT often remains sharp (see below for explanation). Extended Data Fig. 1 displays

366   T_2 measurements for the $x = 0.001$ and 0.01 concentrations, plotted against $(B_{0z} - B_{min})$ on both

367   logarithmic (main panels) and linear (insets) scales. Similar to the data in Fig. 3, the T_2 peaks exhibit

368   broad tails, with an apparent kink at $|B_{0z} - B_{min}| \approx 2$ mT for the more dilute sample. However, when

369   plotted on a log-log scale, the data follow a power-law (to within the experimental uncertainty) spanning

370   an order of magnitude in $(B_{0z} - B_{min})$ for $x = 0.001$, and almost two orders of magnitude for $x = 0.01$,

371   particularly on the high-field sides of the T_2 peaks. This apparent monotonic behavior of the form

372      $T_2 \propto (B_{0z} - B_{min})^{-n}$ supports our assertion that the decoherence is dominated by dipolar field fluctuations

373   that vanish as $df/dB_{0z} \rightarrow 0$. However, the exponent, n, is both sample-dependent ($n = 0.33$ and 0.46,

374   respectively, for $x = 0.001$ and 0.01), and different from previous predictions:[28,29] $n = 1$ for indirect flip-flop

375   processes (spin diffusion), and $n = 2$ for instantaneous diffusion.[25] We believe that sample inhomogeneity

376   is responsible for these differences in HoW_{10}, thus masking the intrinsic T_2 dependence on B_{0z}, causing

377   obvious sample-to-sample variability. It is nevertheless interesting that a power-law scaling still holds, as

378   opposed, e.g., to Gaussian behavior. This clearly merits further theoretical investigation.

379

380   Reduced ESE intensity and faster T_2 decay curves are part of the reason for the increased error bars and

381   apparent broad tails seen in Fig. 3 and Extended Data Fig. 1. In addition, ESE-Envelope-Modulation

382   (ESEEM)[25] is detectable in the decay curves recorded in these tails (not shown). However, only one to

383   two heavily damped periods of oscillation can be seen, thus adding to the error in T_2 (not to mention a

384   potential systematic error that is not taken into account in our analysis). It is these combined factors that
385   likely explain the apparent kink in some of the data at $|B_{0z} - B_{\min}| \approx 2$ mT, as well as the weak variation
386   in T_2 across the 'normal' transitions seen in the right-hand panel of Fig. 3. Interestingly, enough ESEEM
387   periods can be detected to confirm that it is due to coupling to protons in the sample. Importantly, the
388   ESEEM vanishes at the CTs, providing further strong evidence that the Ho^{+3} spin becomes decoupled
389   from the surrounding dipolar spin bath as both $(B_{0z} - B_{\min})$ and $df/d\,B_{0z} \to 0$.
390

391   **Spectral Broadening**
392   The EPR spectra of HoW$_{10}$ are inhomogeneously broadened,[24] with the two main contributions originating
393   from (i) crystal twinning and (ii) strain in the off-diagonal B_4^4 CF parameter.
394

395   (i) Crystals of HoW$_{10}$ form as long thin needles that tend to aggregate into aligned bundles. Separating
396   single crystals from these bundles can be challenging, particularly given that removal of the samples from
397   their mother liquor for periods of more than a few minutes leads to sample degradation. Even after
398   separation, our measurements suggest varying degrees of mosaic spread, particularly for the larger
399   crystals. Indeed, simulations of high-field CW EPR spectra (where the effects of the mosaicity are more
400   pronounced than at X-band) employed a Gaussian orientational distribution with a full-width-at-half-
401   maximum (FWHM) of 1°, albeit for a small crystal;[24] the distribution is considerably broader for many of
402   the samples employed for ESE measurements. Within the context of eq. 2, this mode of disorder
403   produces a spread in γ_z and the $B_{\min}$ values, resulting in horizontal smearing of the energy levels in Fig. 1,
404   as opposed to a vertical smearing produced by a distribution in B_4^4 (see below). The horizontal smearing
405   becomes more pronounced at higher fields, akin to g-strain. Consequently, the EPR spectra often
406   become broader with increasing field, as is clearly evident in Fig. 2, and less so in Fig. 4.
407

408   Although subtle, the effects of sample mosaicity are most pronounced at the CTs. The horizontal spread
409   in the CTs results in a smearing of the divergence in T_2. In general, the strongest/narrowest divergences
410   were obtained for the smallest crystals, which have the smallest mosaic spread. It is for this reason that
411   the data for the most dilute samples in Figs. 2 and 3 were obtained for two different crystals: the large
412   crystal employed in Fig. 2a did not produce particularly strong T_2 divergences, with maximum values
413   reaching only ~2 μs. Meanwhile, a smaller crystal was employed in Fig. 3: this sample gave very good
414   echoes right at the CTs, in spite of its reduced spin count; however, its ESE spectra vanish into the noise
415   upon moving appreciably away from the CTs. These trends can be attributed both to a T_2 weighting
416   effect, which amplifies the otherwise weak ESE signals at the CTs for the more ordered (longer T_2)
417   sample, and to the narrower mosaic distribution that further enhances echoes at the CTs. Multiple small
418   samples were studied, and optimum T_2 values at the CTs in the 6 to 8 μs range were found in nearly all
419   cases for the $x = 0.001$ and 0.01 samples (See Fig. 3 and Extended Data Figs. 1 and 2).
420

421 (ii) Other sources of inhomogeneous broadening include: strains in the spin Hamiltonian parameters (B_k^q,

422 $\overleftrightarrow{A}$, and $\overleftrightarrow{g}$), caused by microscopic disorder, and inhomogeneities in B_0 due to electron and nuclear dipolar

423 fields. The latter may be ruled out as a major source of broadening at X-band (and 5 K) due to weak

424 sample magnetization and the lack of any systematic dependence of the EPR linewidth on Ho

425 concentration. Meanwhile, the only effect of the diagonal ($q = 0$) CF terms in eq. 3 is to ensure an isolated

426 $m_J = \pm 4$ doublet ground state with $\gamma_z = g_J J \mu_B / h = 139.9$ GHz/T ($J = 8$ and $g_J = 1.25$). Other than that, the

427 low energy spectrum exhibits little or no dependence on B_2^0, B_4^0 and B_6^0,[24] and should thus be insensitive to

428 strains in these parameters. For related reasons, and because of the contracted nature of the 4f shell and

429 strong spin-orbit coupling, the $\overleftrightarrow{g}$ and $\overleftrightarrow{A}$ tensors are relatively immune to local strains in the crystal

430 structure (although the effective interactions will of course be sensitive to sample alignment due to the

431 strong axial character of the CF). This leaves B_4^4 which, indeed, has a profound influence on the X-band

432 EPR spectrum, as clearly seen in Fig. 1a and discussed in detail in Ref. [24]: B_4^4 directly sets the scale of

433 the tunneling gap, Δ, which is responsible for the CTs.

434

435 The finite B_4^4 parameter arises because of a small deviation of the coordination environment around the

436 Ho ion from exact D_{4d} symmetry.[22] The superposition of disorder onto this weakly distorted structure can

437 then give rise to a relatively strong modulation of the local B_4^4 parameter and, hence, to a broad

438 distribution for the ensemble. Working under this assumption, we re-simulated CW X-band spectra

439 obtained for an $x = 0.1$ sample at a frequency of 9.64 GHz (Fig. 8 of Ref. [24]), assuming that the main

440 source of broadening is a Gaussian distribution in B_4^4. The best simulation is obtained with a FWHM of

441 5.0×10^{-5} cm^{-1}, i.e., ~1.6% of B_4^4 (or a standard deviation, $\sigma_{B44} = 2.1 \times 10^{-5}$ cm^{-1}). This, in turn, produces a

442 vertical distribution in the corresponding tunneling gap, Δ. Because $\hat{O}_4^4$ connects the $m_J = \pm 4$ states at the

443 2nd order of perturbation, the resultant standard deviation of the gap distribution is given approximately by

444 $\sigma_\Delta \approx 2\Delta\sigma_{B44}/B_4^4 = 4.1 \times 10^{-3}$ cm^{-1} = 123 MHz (FWHM of 290 MHz), where $\Delta = 0.306$ cm^{-1} = 9.18 GHz is the

445 mean gap value (the factor of '2' emerges because of the quadratic dependence of Δ on B_4^4).

446

447 Fig. 1b depicts the Gaussian broadening of the EPR transition frequencies as a 3D color map, with

448 contours shown at the $\pm\sigma_\Delta$ and $\pm 2\sigma_\Delta$ levels of the distribution. Because B_4^4 affects only Δ, this mode of

449 disorder does not shift the magnetic fields (B_{min}) at which the CTs occur for the different molecules in the

450 distribution. However, it does distribute them vertically over a relatively wide frequency range (approx.

451 ± 0.25 GHz at the $2\sigma_\Delta$ level). This can explain the observation of ESE intensity exactly at the CTs over a

452 wide frequency range for the concentrated ($x = 0.1$) sample seen in Fig. 4. Because the cavity employed

453 for these investigations has a center frequency at 9.75 GHz, its sensitivity improves upon increasing the

454 frequency from 9.1 to 9.4 GHz. Meanwhile, the number of Ho^{+3} spins in the distribution decreases with

455 increasing frequency. These two factors approximately offset, explaining the relatively constant ESE

456 intensity and signal-to-noise ratio across the studied frequency range. The ESE intensity does peak at

457 9.2 GHz, above which it decays, although not as rapidly as one may expect purely on the basis of the gap

458 distribution. This is due to the increasing B_1 field of the spectrometer, which enables excitation of more

459 spins and hence the generation of stronger echoes at higher frequencies.

460

461 Finally, the question arises as to whether this same behavior is observable at the other concentrations.

462 Indeed, it is. For example, CTs are very clearly observable in between the 'normal' EPR transitions over a

463 wide frequency range at B_{0z} = 165 mT for the x = 0.01 sample, as seen in Extended Data Fig. 3. Further

464 evidence can also be found at some of the higher frequencies, where inspection of Fig. 1a reveals

465 crossings between nuclear sub-levels (Δm_I = ±1) at fields exactly half way between the B_{min} values. If the

466 applied field is not well aligned to the crystal z-axis, these become avoided crossings (with <10 MHz

467 gaps), giving rise to new CTs at these higher frequencies. This is a subtlety of the perpendicular field

468 component, $B_{0\perp}$, which will be the subject of a future publication. The avoided nuclear sub-level crossings

469 *do not* influence any of the conclusions concerning the CTs at the B_4^4 gap minima (Δ). Nevertheless, the

470 higher frequency CTs are observable, particularly at low fields where the effects of disorder due to

471 sample mosaicity are less pronounced, and the 'normal' ESE transitions are quenched due to very short

472 T_2's.[2,9] This is the explanation for the sharp double peaks seen for the x = 0.001 sample at ~50 mT

473 between 9.4 and 9.7 GHz in Fig. 2a, as well as the sharp zero-field peaks and some of the fine structures

474 seen between B_{min} values at higher fields and frequencies. On the basis of the 50 mT CTs, one can see

475 that the vertical broadening spans less than 400 MHz in this sample, i.e., less than ±200 MHz from the

476 peak of the distribution. In other words, σ_{B44} clearly varies from sample-to-sample, being smaller for the

477 x = 0.001 concentration. This is the reason why intensity due to the low-frequency CTs (@ B_{min}) is not

478 discernible in between the broad 'normal' transitions in the most dilute sample in Fig. 2a.

479

480 **References**

[31] Rudowicz, C., Chung, C. Y. The generalization of the extended Stevens operators to higher ranks and spins, and a systematic review of the tables of the tensor operators and their matrix elements. *J. Phys.: Condens. Mat.* **16**, 5825-5847 (2004)

[32] Stoll, S., Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. *J. Magn. Reson.* **178**, 42-55 (2006)