Quantum coherent spin-electric control in a molecular nanomagnet at clock transitions

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Electrical control of spins at the nanoscale offers significant architectural advantages in spintronics, because electric fields can be confined over shorter length scales than magnetic fields. Thus, recent demonstrations of electric-field sensitivities in molecular spin materials are tantalizing, raising the viability of the quantum analogues of macroscopic magneto-electric devices. However, the electric-field sensitivities reported so far are rather weak, prompting the question of how to design molecules with stronger spin-electric couplings. Here we show that one path is to identify an energy scale in the spin spectrum that is associated with a structural degree of freedom with a substantial electrical polarizability. We study an example of a molecular nanomagnet in which a small structural distortion establishes clock transitions (that is, transitions whose energy is to first order independent of the magnetic field) in the spin spectrum; the fact that this distortion is associated with an electric dipole allows us to control the clock-transition energy to an unprecedented degree.

We demonstrate coherent electrical control of the quantum spin state and exploit it to independently manipulate the two magnetically identical but inversion-related molecules in the unit cell of the crystal. Our findings pave the way for the use of molecular spins in quantum technologies and spintronics.

The polyoxometalate molecular anion \([\text{Ho}(W_{18}O_{49})]^{9–}\) (abbreviated to HoW\(_{10}\)), within the crystal structure Na\(_9\)Na\(_8\)Ho\(_9\)(W\(_{18}O_{49})_{3}\)-35H\(_2\)O (x = 0.1%), provides an example of clock-transition (CT) molecular spin qubit. In the solid state, the sodium salt of this anion crystallizes in a primitive space group of \(P1\), where each unit cell contains two HoW\(_{10}\) anions that are related via inversion symmetry. Each HoW\(_{10}\) possesses an approximate \(D_{4h}\) symmetry. The magnetic properties of HoW\(_{10}\), which are characterized by a total electronic angular momentum of \(J = 8\) and a nuclear spin of \(I = 7/2\), can be described by the Hamiltonian

\[
H = \sum_{k=2,4,6} \sum_{q=-k}^{k} B_k^q O_k^q + J \cdot A \cdot I + \mu_B g_e B_0 \cdot I - \mu_N g_N B_0 \cdot I
\]

where \(A\) is the magnitude of the (approximately) isotropic hyperfine interaction; \(g_e\) and \(g_N\) are the electronic and nuclear gyromagnetic ratios respectively; the anisotropy is parameterized by the amplitudes \(B_k^q\) of the extended Stevens operators \(O_k^q\); and \(B_0\) is the applied magnetic field.

The crystal field terms \(\sum B_k^q O_k^q\) lead to a ground state of \(m_J = \pm 4\), where \(m_J\) is the projection of the electronic angular momentum.

Crucially, owing to interactions of HoW\(_{10}\) with counterions and crystallization water, there is a minor deviation from the ideal \(D_{4h}\) symmetry, with a continuous-shape measurement \(S < 0.1\) around the Ho\(^{3+}\) ion as defined by the SHAPE program. The crystal structures measured at three different temperatures (100, 150 and 200 K) are provided in Supplementary Information. At these three temperatures, deviations in the skew angles are 2.21°, 2.34° and 2.27°, and the off-centre distances are 0.021, 0.025 and 0.024 Å, respectively. This gives rise to an electric dipole moment and a tetragonal spin anisotropy (parameterized by terms \(B_0^q\)), which mixes the \(m_J = \pm 4\) ground states and generates a series of anticrossings in the spin spectrum, leading to four electron spin resonance (ESR) CTs, whose resonance frequencies are determined by the amplitude of tetragonal anisotropy. The four CTs correspond to resonances with different electron–nuclear spin states \((m_I, m_J)\) with \(m_I = \pm 4\) and \(m_J = -3/2, -5/2, -7/2\) (from low to high fields). Previous ESR and magnetization studies are satisfactorily simulated by the parameters \(B_0^q = 18.00 \times 10^3\,\text{MHz}, B_0^q = 209.00\,\text{MHz}, B_0^q = 1.53\,\text{MHz}, B_0^q = 94.20\,\text{MHz}, A/h = 830.00\,\text{MHz}\) and \(g_e = 1.25\).

Thus, the broken inversion symmetry causes the spin-electric-coupled phenomena of an electric dipole and a CT. This, in turn, allows us to linearly manipulate the CT frequency by applying an external electric field (E field).

We investigated the spin–electric coupling (SEC) in HoW\(_{10}\) by embedding E-field pulses in an ESR Hahn-echo sequence, as described in ref. 4. Methods and Supplementary Information. Figure 1c shows typical data recorded with the E field applied parallel to \(B_0\), at \(\varphi = 0\). The in-phase part of the spin echo shows a pronounced oscillation on varying the length of the E-field pulse. The oscillation arises because the molecular spin Hamiltonian is modulated by the E field via the SEC, leading to a shift \(\delta f\) in the ESR frequency while the E field is applied. This shift in the ESR frequency manifests as an additional phase of \(\delta f \times t_e\) in the spin echo signal, causing the oscillation with a period of \(1\,\mu\text{s}\) in the echo amplitude (Supplementary Fig. 1). The decay in the echo amplitude over \(0 < t_e < 6\,\mu\text{s}\) is due to a small inhomogeneity in the E field across the crystal; during the second period of free evolution, namely, \(6 < t_e < 12\,\mu\text{s}\), the inhomogeneity is refocused and the echo amplitude recovers.

The lack of a dependence of the quadrature channel of the echo on \(t_e\) is evidence of a linear—as opposed to quadratic—SEC in...
The orientation dependence of the SEC is shown in Fig. 2a. The shift in ESR frequency ($\delta f$) is calculated by taking the fast Fourier transform of the oscillation in the in-phase echo intensity. It depends on orientation as $|\delta f| \propto |\cos(q - \varphi)|$ (the presence of both inversion-related populations means that we cannot distinguish the sign of $\delta f$ from this measurement). This yields a lower bound on the scale of the SEC; a full mapping of the SEC orientation dependence would be required to establish the orientation with the maximum $E$-field sensitivity. This would depend on the two-axis rotation of the electric field, which is beyond the scope of this study.

The linearity of the SEC is further confirmed by varying the amplitude of an $E$-field pulse with fixed duration. Figure 2b demonstrates that the frequency shift is proportional to the voltage (and hence, since the electrode geometry is fixed, the amplitude of the $E$ field). The data were recorded at orientation $\varphi$ that shows the strongest SEC. The linear fit to the data yields a SEC constant of $11.4 \pm 0.3$ Hz $(\text{V m}^{-1})^{-1}$.

The relative strength of the SEC in HoW$_{10}$ showcases the potential for chemical design in enhancing the desired molecular properties via a prudent choice of the coordination environment of the metal ion. Such engineering is not possible in, for example, atomic defects in solid state materials, in which structures and therefore properties are much less tunable. Furthermore, the possibility of tuning the ESR transition at the CT fields allows the exploitation of the strong spin–orbit coupling characteristic of $4f$ electrons to enhance the electrical control of molecular qubits while retaining substantial coherence times. Such tuning of the HoW$_{10}$ CT can only be efficiently achieved by directly adjusting the tetragonal anisotropy interaction since at the CT fields, the ESR transitions are insensitive to $g$, or $A$ to first order (Supplementary Information).

The ESR frequency at the CT fields is determined by the tetragonal anisotropy. Therefore, all ESR transitions at 9.15 GHz exhibit the same response to the applied electric fields (filled squares in Fig. 2d) and can be fitted with $\delta B = h = (8.8 \pm 0.2) \times 10^{-4}$ MHz $(5.9 \times 10^{-4}$ Hz $(\text{V m}^{-1})^{-1}$). However, other spin Hamiltonian terms, such as Zeeman and hyperfine interactions, may potentially also exhibit $E$-field sensitivities. These interactions modify the ESR transition frequencies away from the CT fields; we can probe their sensitivities by studying the $E$-field effect on ESR transitions away from the CT fields, as shown in Fig. 2c,d.

The $E$-field-induced ESR frequency shift decreases as the ESR frequency increases, which is expected as the ‘anticrossing’ effect of $B_1^7$ reduces when moving away from the CTs. On the other hand, the SEC effects also fluctuate considerably from peak to peak at 9.45 and 9.88 GHz. Such fluctuation is likely due to the $E$-field modulation of Hamiltonian parameters other than $B_1^7$: the appreciable dependence of $\delta f$ on the magnetic field and nuclear spin projection away from the CT fields (that is, between the states with varying contributions from different nuclear spin projections $m_I$ and electron spin projections $m_i$) suggest that Zeeman and hyperfine interactions may also be sensitive to the $E$ field, though less than $B_1^7$ (Supplementary Information).

We seek insight into the relationship between the $E$-field-induced distortion and CT frequency by noting that any molecular distortion may be decomposed into displacements of the normal modes of HoW$_{10}$, which we obtain using density functional theory (DFT, implemented by Gaussian$^{17}$). Each normal mode is associated with force constant $k_i$ and reduced mass $\mu_i$ (yielding eigenfrequency $\omega_i = \sqrt{k_i/\mu_i}$). The electric dipole $\mathbf{p}$ depends on the displacement of mode $\chi_i$ and this determines the coupling of the mode to an applied $E$ field or to incident light, that is, its infrared intensity.

When an external electric field $E$ is incremented by $dE$, it elastically distorts the molecule by $d\chi_i$ and modifies the molecular electric dipole by $d\mathbf{p}$, for mode $i$. In this process, it does work $W = \sum_i d\mathbf{p} \cdot \delta \mathbf{E} = \sum_i k_i d\chi_i$. Thus, by calculating the electric dipole moment as a function of the mode displacements, we can quantitatively...
extract the displacements as a function of the applied $E$ field and hence the $E$-field-induced evolution of the molecular electronic structure (Methods).

This reasoning yields the criteria by which we may determine whether a particular molecular mode leads to a strong contribution to the SEC at the CT frequency: it should be relatively soft (that is, small $\kappa$), allowing a substantial molecular displacement without excessive elastic energy cost; it should strongly couple to the molecular electric dipole (that is, $d_{ij}$), and therefore its infrared intensity, should be large); and it should modify the Ho environment such that the energy of the anticrossing levels is modulated. Our analysis of the basis of the HoW10 vibrational modes of the crystallographic structure reveals that the molecular displacement responsible for the SEC can be approximated by the distortion displacing the Ho and coordinating oxygen atoms, as shown in Fig. 2b, inset. The analysis based on the relaxed structure yields a very similar result. Animations showing each of these collective distortions are available in the Supplementary Information. The differences between the SECs predicted using the optimized and crystal structures (blue dashed/solid lines in Fig. 2b) can be understood by considering how the structure deviates from the ideal $D_4$ symmetry. A departure from the $D_4$ structure, which is inversion symmetric, is necessary to afford a linear SEC in HoW$_{10}$. Compared with the optimized molecular geometry, the actual crystal structure shows a larger distortion due to the presence of Na$^+$ counterions and crystallization of H$_2$O molecules. Therefore, it is conceivable that the optimized structure leads to an underestimation of the SEC. Nevertheless, the theoretical results are in reasonable agreement with the experimental data.

We note in passing that from a practical perspective, any external electric field that can be experimentally applied is very small compared with the intramolecular fields associated with chemical bonds, justifying our perturbative approach. Others have investigated the effects of electric fields on the scale of $\sim$10 V nm$^{-1}$ on lanthanide single-ion molecular magnets, a regime that can be directly explored in DFT\textsuperscript{11}.

Finally, we demonstrate a protocol to selectively manipulate the spins of inversion-related HoW$_{10}$ anions assisted by an $E$ field\textsuperscript{14}. Since the two spins within the unit cell are related by inversion symmetry, they are magnetically identical and cannot be distinguished in conventional ESR or magnetometry experiments. However, they exhibit opposite frequency shifts in the presence of an $E$ field, which can be exploited, using a modified Hahn-echo sequence, as shown in Fig. 3a, to excite them selectively. The first pulse—a $\pi/2$ pulse at the CT frequency of $f_\text{CT} = 9.15$ GHz—places all molecular spins in the superposition state. An $E$ field is applied simultaneously with the refocusing $\pi$ pulse, lifting the degeneracy of the ESR transitions in the two inversion-related populations. Thus, it is possible to refocus

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**Fig. 2 | SEC dependence on orientation, $E$ field and magnetic field.**

**a.** Orientation dependence of the $E$-field-induced frequency shift. The measurements were performed at $f = 9.15$ GHz, $V = 300$ V and $B_\text{app} = 0.0304$ T. The $E$ field was rotated between being parallel to $B_\text{app}$ (that is, $38^\circ$ away from the molecular easy axis) at $\varphi = 0^\circ$ ($180^\circ$) and perpendicular to $B_\text{app}$ (that is, in the molecular hard plane) at $\varphi = 90^\circ$. **b.** Measured frequency shift (squares) versus applied voltage $V$, showing a linear $E$-field coupling in HoW$_{10}$. The data were recorded at the orientation with the strongest SEC ($\varphi = 145^\circ$). The red line is a linear fit to the data. The blue lines represent the ab initio prediction based on molecular geometry extracted from (solid) single-crystal X-ray crystallography or (dashed) structure fully optimized at the DFT level (Supplementary Information). Inset: the local environment of Ho showing the electric dipole direction (magenta arrow) and the $E$-field-induced atomic displacement directions (orange arrows). **c.** ESR spectra recorded at various frequencies close to the CT frequency. The $E$-field effect measured on the corresponding ESR transitions. Error bars indicate the full-width at half-maximum of the Fourier transform of the in-phase echo signal. The dashed lines illustrate the expected $f_E$ if only $B_0^2$ were modified by the $E$ field; the scatter in $f_E$ at frequencies away from the CT indicates that the $E$-field sensitivity of other Hamiltonian terms becomes important. The error bars for $f_E$ in a and b are approximately equal to the size of the symbols (not shown).

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**Table 1**

| Frequency (GHz) | Magnetic Field (T) |
|-----------------|-------------------|
| 9.15            | 0.0304            |
| 9.45            | 0.0304            |
| 9.88            | 0.0304            |

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**Data**

$f_E$ is the $E$-field-induced frequency shift, $f_\text{CT}$ is the critical frequency, $B_0$ is the external magnetic field, and $B_\text{app}$ is the applied magnetic field. The error bars indicate the full-width at half-maximum of the Fourier transform of the in-phase echo signal.
As is generally the case in quantum information experiments, strong coupling to a control field means strong coupling to a source of noise that shares the same physics as the control. In the case described here, we reduce the sensitivity to magnetic fields by working at a CT, but this, in turn, increases the sensitivity to molecular distortions and E-field fluctuations. We note, however, that reducing the temperature (which, will—in any case—be required for initialization) suppresses environmental phonons (the principal source of molecular distortions), but cannot remove all magnetic field fluctuations, which may have their origin in, for example, environmental spin flip-flop processes.

Our results guide us to distil the general recipe for a high-SEC molecule: a soft and electrically polarizable environment for the spin carriers, and a spin spectrum that is highly sensitive to distortions. These principles are satisfied in HoW₁₀ where a CT frequency is modulated by soft modes that shift the magnetic charge distribution. The SEC is about an order of magnitude larger than the previously reported values for transition-metal-based molecular nanomagnets (δf/E < 1 Hz m⁻¹) and it also surpasses the SEC measured for rare-earth atoms doped in YAG (ref. 24) (δf/E ≈ 1 Hz m⁻¹). It is similar to the SEC for Mn²⁺ in ZnO (ref. 25) (δf/E_up to 12.7 Hz (V m⁻¹)⁻¹), in which the SEC is associated with the piezoelectric nature of the host lattice. The HoW₁₀ coupling is sufficiently strong that a modest E field of ~10⁵ V m⁻¹ or 100 µV nm⁻¹ is adequate to tune the spin at a practically useful level, that is, to shift the frequency by much more than the natural line width; this demonstrates the principle that local E-field tuning allows for the selective addressing of spins in otherwise identical molecules. The strong SEC in HoW₁₀ raises the tantalizing possibility of engineering a coherent spin–photon interface in molecular spintronic devices, allowing coherent spin control by an oscillating electric field. These results pave the way for the use of molecular components in quantum or classical spintronic technologies in which local electrical control can surpass the performance of conventional magnetic spin control.

**Online content**

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/s41567-021-01355-4.

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**References**

1. Kane, B. E. A silicon-based nuclear spin quantum computer. *Nature* **393**, 133–137 (1998).
2. Trif, M., Tristani, F., Stepanenko, D. & Loss, D. Spin-electric coupling in molecular magnets. *Phys. Rev. Lett.* **101**, 217201 (2008).
3. Laucht, A. et al. Electrically controlling single-spin qubits in a continuous microwave field. *Sci. Adv.* **1**, e1500022 (2015).
4. Tosi, G. et al. Silicon quantum processor with robust long-distance qubit couplings. *Nat. Commun.* **8**, 450 (2017).
5. Assaad, S. et al. Coherent electrical control of a single high-spin nucleus in silicon. *Nature* **579**, 205–209 (2020).
6. Liu, J. et al. Electric field control of spins in molecular magnets. *Phys. Rev. Lett.* **122**, 037202 (2019).
7. Fittipaldi, M. et al. Electric field modulation of magnetic exchange in molecular helices. *Nat. Mater.* **18**, 329–334 (2019).
8. Robert, J., Parriel, N., Turek, P. & Boudalis, A. K. Polyoxoanisotropic magnetoelectric coupling in an electrically controlled molecular spin qubit. *J. Am. Chem. Soc.* **141**, 19765–19775 (2019).
9. Patil, A., Clemente-Juan, J. M., Tsukerblat, B. & Coronado, E. Electric field control of the optical properties in magnetic mixed-valence molecules. *Chem. Sci.* **5**, 3598–3602 (2014).
10. Cardona-Serra, S. et al. Electrically switchable magnetic molecules: inducing a magnetic coupling by means of an external electric field in a mixed-valence polyoxovanadate cluster. *Chem. Eur. J.* **21**, 763–769 (2015).
11. Gaita-Arifo, A., Luis, F., Hill, S. & Coronado, E. Molecular spins for quantum computation. *Nat. Chem.* **11**, 301–309 (2019).
12. Atzori, M. & Sessoli, R. The second quantum revolution: role and challenges of molecular chemistry. *J. Am. Chem. Soc.* **141**, 11339–11352 (2019).
13. Godfrin, C. et al. Operating quantum states in single magnetic molecules: implementation of Grover’s quantum algorithm. *Phys. Rev. Lett.* **119**, 187702 (2017).
14. Eerenstein, W., Mathur, N. D. & Scott, J. F. Multiferroic and magnetoelectric materials. *Nature* **442**, 759–765 (2006).
15. Matsukura, F., Tokura, Y. & Ohno, H. Control of magnetism by electric fields. *Nat. Nanotechnol.* **10**, 209–220 (2015).
16. AlDamen, M. A. et al. Mononuclear lanthanide single molecule magnets based on the polyoxometalates [Ln(W5O18)2]9− and [Ln(β2-SiW11O39)2]13− (LnIII = Tb, Dy, Ho, Er, Tm, and Yb). *Inorg. Chem.* **48**, 3467–3479 (2009).
17. Shiddiq, M. et al. Enhancing coherence in molecular spin qubits via atomic clock transitions. *Nature* **531**, 348–351 (2016).
18. Ghosh, S. et al. Multi-frequency EPR studies of a mononuclear holmium single-molecule magnet based on the polyoxometalate [HoIII (W5O18)2]9−. *Dalton Trans.* **41**, 13697–13704 (2012).
19. Alvarez, S., Alemany, P., Casanova, D., Cirera, J. & Llunell, M. Shape maps and polyhedral interconversion paths in transition metal chemistry. *Coord. Chem. Rev.* **249**, 1693–1708 (2005).
20. Frisch, M. J. et al. Gaussian 16 Revision A.03 (Gaussian, 2016).
21. Sarkar, A. & Rajaraman, G. Modulating magnetic anisotropy in Ln(III) single-ion magnets using an external electric field. *Chem. Sci.* **11**, 10324–10330 (2020).
22. Wedge, C. J. et al. Chemical engineering of molecular qubits. *Phys. Rev. Lett.* **108**, 107204 (2012).
23. Kintzel, B. et al. Spin-electric coupling in a cobalt(II)-based spin triangle revealed by electric-field-modulated electron spin resonance spectroscopy. *Angew. Chem. Int. Ed.* **60**, 8832–8838 (2021).
24. Liu, Z. et al. Electric field manipulation enhanced by strong spin-orbit coupling: promoting rare-earth ions as qubits. *Nat. Sci. Rev.* **7**, 1557–1563 (2020).
25. George, R. E., Edwards, J. P. & Ardavan, A. Coherent spin control by electrical manipulation of the magnetic anisotropy. *Phys. Rev. Lett.* **110**, 027601 (2013).
26. Mi, X. et al. A coherent spin–photon interface in silicon. *Nature* **555**, 599–603 (2018).

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Methods

ESR apparatus and sample configuration. The HoW\textsubscript{10} crystal was mounted in an ESR quartz tube (outer diameter, 1.6 mm) and inserted between parallel metallized plates separated by 2.0 mm, which were used to apply the E-field pulses. Both conductive plates and the sample were mounted in a standard Bruker MD5 resonator and could be independently rotated around the x axis, as shown in Fig. 1b. By first studying the CT fields as a function of the sample rotation, we were able to determine the angle between the magnetic easy axis and the experimental rotation axis. In all the experiments presented in this study, the magnetic easy axis was aligned as close as possible to $\mathbf{B}_0$. We applied the E field at a variable orientation $\phi$ with respect to $\mathbf{B}_0$ (Fig. 1b).

Note that the magnetic easy axis is neither coincident with any of the crystal facets or edges\textsuperscript{17,18} nor collinear with the pseudo-fourfold molecular symmetry axis, so it is not possible to guarantee the alignment by inspecting the crystal morphology. Thus, repeating the experiment on a different crystal gives a similar orientation dependence for the SEC, albeit the extrema of the SEC appear at different laboratory directions (see section IV in Supplementary Information). This cosine-shaped orientation dependence of the SEC is indicative of the existence of an axial-type SEC in HoW\textsubscript{10}. The differences in behaviour between the two crystals arise from the variation in the orientation of crystals in the apparatus and therefore the plane through which they are rotated in the laboratory frame (section V in Supplementary Information provides more details).

Microwave pulse sequences. A standard two-pulse Hahn-echo sequence of duration $2\tau (\pi/2-\tau-x-\tau-\pi/2-\text{echo})$ was employed to measure an electron spin echo on the HoW\textsubscript{10} crystals. Short broadband pulses, namely, 32 ns for $\pi/2$ pulses and 64 ns for $\pi$ pulses, were used for measuring the SEC parameters (data shown in Figs. 1 and 2). These pulse parameters were adjusted to optimize the echo intensity. By contrast, long selective pulses, namely, 400 ns for $\pi/2$ pulses and 800 ns for $\pi$ pulses, were applied in the selective spin manipulation experiments (Fig. 3). These pulse lengths were chosen to excite a narrow frequency population of spins, which can be selectively manipulated using the E-field-induced frequency shift, while still giving a reasonable signal-to-noise ratio in spin echo measurements.

Calculation of SEC. The E-field-induced change in the CT frequency is evaluated by computing the evolution of the molecular electronic structure using the multireference complete active self-consistent field spin–orbit method (implemented by OpenMolcas\textsuperscript{27}) with the combined effect of the crystal field and spin–orbit coupling calculated using the SINGLE\_ANISO module\textsuperscript{28}. The effect of E field on the easy-axis orientation was also estimated (section VIII in Supplementary Information provides more details). The theoretical study was performed using both the obtained crystal structure and the relaxed structure optimized at the DFT level.

Data availability

Experimental data supporting the conclusions are available at https://doi.org/10.5281/zenodo.5167019.

References

27. Fdez. Galvan, I. et al. Openmolcas: from source code to insight. J. Chem. Theory Comput. 15, 5925–5964 (2019).
28. Ungur, L. & Chibotaru, L. F. Ab initio crystal field for lanthanides. Chem. Eur. J. 23, 3708–3718 (2017).

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Author contributions

J.L., E.C., A.G.-A. and A.A. conceived the study. Materials were synthesized by Y.D. under the supervision of E.C. ESR experiments were conducted by J.L. and J.M. Data analysis was performed by J.L. with input from A.A. Theoretical modelling was done by A.U.; assisted by J.J.B.; guided by A.G.-A.; and in discussion with J.L., E.C. and A.A. All the authors contributed to the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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