Tunable spin-phonon polarons in a chiral molecular qubit framework

Authors: Aimei Zhou[1,2†], Ruihao Bi[1,2†], Zhenghan Zhang[3], Luming Yang[4], Xudong Tian[3], Denan Li[5], Mingshu Tan[6], Weibin Ni[2,5], Haozhou Sun[1,2], Jinkun Guo[7], Xinxing Zhao[8], Zhifu Shi[8], Wei Tong[9], Zhitao Zhang[9], Jin-Hu Dou[7], Feng Jin[6], Shi Liu[1,2,5], Mircea Dincă[4], Tijana Rajh[10,11], Jian Li[3], Wenjie Dou[1,2,5*], Lei Sun[1,2,5*]

[1] Department of Chemistry, School of Science and Research Center for Industries of the Future, Westlake University, Hangzhou, Zhejiang Province 310030, China

[2] Institute of Natural Sciences, Westlake Institute for Advanced Study, Hangzhou, Zhejiang Province 310024, China

[3] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu Province 210023, China

[4] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

[5] Department of Physics, School of Science and Research Center for Industries of the Future, Westlake University, Hangzhou, Zhejiang Province 310030, China.

[6] Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

[7] National Key Laboratory of Advanced Micro and Nano Manufacture Technology, School of Materials Science and Engineering, Peking University, Beijing 100871, China

[8] CIQTEK Co., Ltd., Hefei, Anhui Province 230021, China

[9] Anhui Key Laboratory of Low-Energy Quantum Materials and Devices, High Magnetic Field Laboratory, HFIPS, Chinese Academy of Sciences, Hefei, Anhui 230031, China

[10] Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, United States

[11] The School of Molecular Sciences, Arizona State University, Tempe, Arizona 85281, United States

[†]These authors contributed equally to this work.

[*]Email: sunlei@westlake.edu.cn; douwenjie@westlake.edu.cn

Abstract

Chiral structures that produce asymmetric spin-phonon coupling can theoretically generate spin-phonon polarons—quasiparticles exhibiting non-degenerate spin states with phonon displacements. However, direct experimental evidence has been lacking. Using a chiral molecular qubit framework embedding stable semiquinone-like radicals, we report spin dynamic signatures that clearly indicate the formation of spin-phonon polarons for the first time. Our non-adiabatic model reveals that these quasiparticles introduce an active spin relaxation channel when polaron reorganization energy approaches Zeeman splitting. This new channel manifests as anomalous, temperature-independent spin relaxation, which can be suppressed by high magnetic fields or pore-filling solvents (e.g. CH_2Cl_2, CS_2). Such field- and guest-tunable relaxation is unattainable in conventional spin systems. Harnessing this mechanism could boost repetition rates in spin-based quantum information technologies without compromising coherence.

Introduction

Chiral structures lack inversion and reflection symmetries. They exhibit reciprocity with electron spins: passing electrons through chiral biomolecules (*1*), polymers (*2*), and inorganic solids (*3*) could generate salient spin polarization, an effect called chirality-induced spin selectivity (*4*), and spin-polarized current could induce enantioselective electrochemical reactions (*2*). These intriguing phenomena have attracted great attention because they hold promise for new designs and methodologies towards high-performance spintronic devices (*5*), quantum information science (*6*), and asymmetric synthesis (*7*). Nonetheless, the underlying mechanism of the interplay between structural chirality and electron spin degree of freedom is still an open question (*8*). Recent theoretical studies indicate that chiral structures could cause asymmetric spin-phonon coupling, which infers the formation of spin-phonon polaron with energy splitting and phononic displacement between opposite spin states (*9*, *10*). As spin-phonon coupling also drives spin relaxation and implicitly decoherence (*11–13*), this quasiparticle should exhibit peculiar spin dynamics, which remains unexplored both theoretically and experimentally.

To this end, molecular qubit frameworks (MQFs) provide a tunable platform to investigate the dynamics of spin-phonon polarons. MQFs integrate molecular electron spin qubits within open framework materials, such as metal−organic frameworks (*14*, *15*) and covalent organic frameworks (*16*). Their highly ordered crystal structures engender well-defined phonon dispersion relations, their bottom-up synthesis allows rational design of spin, phonon, and chirality characteristics, and their microporosity and high surface area further allow fine tuning of phonons by harnessing host-guest interactions (*17–19*). In addition, when stable organic radicals are used as qubits, MQFs could maintain quantum coherence at room temperature, enabling spin dynamic characterization across a wide range of temperature (3 K – 300 K) (*20–22*). This empowers investigation of spin-phonon coupling involving acoustic and optical phonons that stem from long-range structural features and local chemical bonds (*11*, *12*). Hence, MQFs with chiral structures and radical qubits could enable systematic examination of spin relaxation through rational structural design and phononic modulation.

Herein, we report spin dynamic signatures that clearly indicate the formation of spin-phonon polarons in a chiral and microporous MQF, Zn_3(HOTP) (HOTP = 2,3,6,7,10,11-hexaoxytriphenylene). Spontaneous oxidation of HOTP ligands generates semiquinone-like radical qubits with room-temperature electron spin coherence. They display a fast and nearly temperature-independent spin relaxation process at 0.34 T, which is suppressed by improving the

magnetic field or filling the pores with some organic solvents including dichloromethane (DCM), tetrahydrofuran (THF), and carbon disulfide (CS_2). Considering that the chiral structure could induce asymmetric longitudinal spin-phonon coupling, we build up a non-adiabatic microscopic model that allows for the formation of spin-phonon polaron and solve it with polaron transformation as well as Fermi's golden rule similar to the manner of Marcus rate theory (*23–26*). This model shows that the anomalous and tunable spin relaxation of Zn_3(HOTP) arise from an additional relaxation channel introduced by spin-phonon polarons, which is effective when the polaron reorganization energy approaches Zeeman splitting of different spin states.

Results

Chiral structure with incommensurate modulation

Zn_3(HOTP) was synthesized via a solvothermal reaction between Zn(acetate)$_2 \cdot 2H_2O$ and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP), which yielded hexagonal rod-like crystals with longitudinal lengths of 30 – 70 μm and cross-sectional lengths of 1 – 2 μm (fig. S1). The product is crystalline, air-stable, and microporous with a Brunauer−Emmett−Teller surface area of 362 $m^2 \cdot g^{-1}$ (fig. S2, S3) that is comparable with the previously reported value (*27*). Its structure remains intact in various organic solvents, e.g. DCM and *N*,*N*-dimethylformamide (DMF) (fig. S3). Individual single crystal of Zn_3(HOTP) displays second harmonic generation (SHG) activity at 100 K and 295 K (fig. 1D), indicating spontaneous inversion symmetry breaking in this material (*28*).

Single-crystal structure of Zn_3(HOTP) was characterized by continuous rotation electron diffraction (cRED) at 96 K and further refined by extended X-ray absorption fine structure (EXAFS) spectroscopy (fig. 1A, fig. S4 and S5, table S1 and S2). Based on the SHG activity of this framework, we solved its structure with non-centrosymmetric space groups and found that it crystalizes in *P*6$_3$, a Sohncke space group, with a chiral structure (fig. 1F) (*29*). Zn_3(HOTP) exhibits a honeycomb-like non-van-der-Waals three-dimensional (3D) framework with cylindrical pores whose diameters are approximately 1.6 nm (fig. 1E). HOTP ligands form eclipsed-stacked columns along the crystallographic *c* axis, which aligns with the long axis of single crystal as revealed by high-resolution transmission electron microscopy (HR-TEM), with an intermolecular distance of 3.305 Å (fig. 1C and E). These columns are connected via zigzag Zn−O ladders constructed by [Zn_2O_2] pseudo-squares where Zn^{2+} ions are not co-planar with HOTP ligands (fig. 1E). Each Zn^{2+} displays a trigonal bipyramidal coordination geometry with an axial water pointing into the pores (fig. 1E). Notably, Zn_3(HOTP) is structurally and compositionally distinct from Zn_3(HOTP)$_2$, an alternative phase recently reported by Dincă et al (*30*). The latter, which is produced by a different synthetic procedure, consists of 4- and 5-coordinated Zn^{2+} ions without coordinating water (*30*).

Electron diffraction of Zn_3(HOTP) along the crystallographic *c* axis displays satellite reflections at 96 K (fig. 1A). Their periodicity is approximately 3.57 times of the corresponding unit cell parameter, yet it is irrational relative to the latter, characteristic of incommensurate modulation. Such structural aperiodicity is also observed in several other HOTP-based MOFs including Zn_3(HOTP)$_2$ (*30*), La_3(HOTP)$_2$, and Nd_3(HOTP)$_2$ (*31*). It reduces 6$_3$ screw axes to 3-fold rotation axes while retains structural chirality (fig. S6). Notably, Zn_3(HOTP) transforms into a periodic structure at 295 K (fig. 1B), yet it still exhibits SHG activity (fig. 1D), showing that the chirality is intrinsic to this structure and is not a result of the incommensurate modulation.

We employed Raman and Fourier-transform infrared (FT-IR) spectroscopy for Zn$_3$(HOTP) to investigate phonons near the Gamma point of 1st Brillouin zone. Vibrational peaks at 3420 cm^{-1} and 699 cm^{-1} are assigned to stretch modes of O−H and Zn−O bonds, respectively, and those at 1200 cm^{-1} − 1600 cm^{-1} are attributed to C−C and C−O stretches within HOTP (fig. 1G to I). Raman spectrum collected at 2 K and 0.34 T shows multiple peaks below 200 cm^{-1} with the lowest-frequency peak is at 15 cm^{-1} (fig. 1G). These low-frequency Raman features are well reproduced by calculations, indicating that they are inherent for the framework (fig. S7B). They pose the upper limit to Debye temperature (T$_D$ < 22 K), which indicates relatively low structural rigidity. A strong peak at 163 cm^{-1} red-shifts to 151 cm^{-1} for Zn$_3$(HOTP) synthesized in D$_2$O (fig. S7A), showing its stemming from hydrogen bonds formed between adsorbed H$_2$O and HOTP or between adsorbed and coordinating H$_2$O. As the electron spin of HOTP radical mainly resides on its oxygen atoms (22), vibrations of hydrogen bonds between HOTP and H$_2$O, Zn−O bonds, and C−O bonds may contribute to local-mode spin relaxation of Zn$_3$(HOTP).

Fig. 1. Structure and optical phonons of Zn$_3$(HOTP). (A, B) cRED images in reciprocal space acquired at (A) 96 K and (B) 295 K. Red, green, and blue lines represent *a**, *b**, and *c**, respectively. Main and satellite reflections are labeled. (**C**) HR-TEM image viewed perpendicular to crystallographic *c* axis. Bottom-left inset: Fourier transform of the HR-TEM image. Top-right

inset: HR-TEM image viewed along the crystallographic c axis. (**D**) SHG signals under 1064 nm pumping acquired at 100 K and 295 K. (**E**) Portions of the structure viewed along and perpendicular to the crystallographic c axis. Inset: coordination sphere of Zn^{2+}. Blue, grey, and red spheres represent Zn, C, and O, respectively. H atoms are omitted for clarity. (**F**) Left: Double-layer crystal packing showing structural chirality. Each circular plate represents a HOTP ligand and nearby secondary building units. They are marked with different colors to articulate the 6_3 screw-axis symmetry. Yellow and green arrows indicate clockwise and counterclockwise rotations corresponding to left and right handedness, respectively. Right: Chiral structures with left and right handedness in $P6_3$ space group viewed perpendicular to the crystallographic c axis. (**I, J**) Raman spectra collected at 2 K under 0.34 T. (**K**) FT-IR spectrum collected at 295 K under 0 T.

Conventional polarons and spin coherence

We probed the spin characteristics of Zn_3(HOTP) with continuous-wave electron paramagnetic resonance (CW-EPR) spectroscopy. The X-band (9.6 GHz, 0.34 T) CW-EPR spectrum acquired at 295 K reveals two types of $S = 1/2$ electron spins exhibiting Lorentzian line shape: one at $g = 2.00341$ with a linewidth of 0.40 mT and the other at $g = 2.00237$ with a linewidth of 2.37 mT (fig. 2A). Both g-factors are close to the free-electron value ($g_e = 2.0023$) and consistent with radical characteristics. As the temperature rises from 130 K to 295 K, the double integration, which is proportional to magnetic susceptibility (χ), of the first type drops significantly (fig. 2B and C). This is consistent with Curie-like paramagnetism (*32*, *33*). In contrast, the second type displays nearly temperature-independent paramagnetism (TIP). Q-band (34 GHz, 1.22 T) and millimeter-wave (214 GHz, 7.64 T) CW-EPR spectra acquired at 295 K can be fitted using one type of electron spin with a slight g-anisotropy ($g_\parallel = 2.00046$ and $g_\perp = 2.00218$) and narrow linewidth (fig. S8). The TIP-type electron spin is absent at high magnetic field, consistent with field-induced suppression of TIP observed in magnetometry (fig. S9).

The drastically different linewidths and paramagnetic properties of the two types of electron spins suggest their distinct physical origins. These behaviors are comparable with previous observations of doped polyaniline (*32*) and fully reduced $Cu_3(C_6O_6)_2$ ($H_4C_6O_6$ = tetrahydroxy-1,4-benzoquinone) (*33*). Accordingly, we assign the TIP-type spins to large (Fröhlich) polarons that originate from coupling between delocalized electrons and phonons (*32–34*). Their formation is facilitated by the $\pi-\pi$ stacking between HOTP ligands, consistent with the relatively high pressed-pellet electrical conductivity of Zn_3(HOTP) at 295 K ($\sigma = 3.35 \times 10^{-5}$ S·cm^{-1}; fig. S10). On the other hand, the Curie-like spins are attributed to small (Holstein) polarons residing at localized defects (*33*, *34*), i.e. semiquinone-like radicals formed from spontaneous oxidation of HOTP in the air. Quantitative CW EPR analysis revealed that approximately 1% of HOTP ligands form small polarons (Table. S3).

Our previous studies have shown that localized HOTP radicals in MQFs behave as electron spin qubits with room-temperature quantum coherence (*15*, *22*). This prompted us to investigate the spin dynamics of Zn_3(HOTP) and to explore its potential as an MQF with X-band pulse EPR spectroscopy. At both 100 K and room temperature, the echo-detected field sweep spectra display single peaks with Gaussian line widths of approximately 0.51 mT (fig. S11). Hence, only the small polarons can be probed by pulse EPR spectroscopy, whereas the large polarons lose coherence so fast that they are not measurable. Nutation experiments conducted at 295 K revealed Rabi oscillations, demonstrating coherent addressability (fig. S12). The phase memory time (T_m), which represents the spin decoherence time (T_2) for ensemble systems, is approximately 700 ns at 13 K.

It increases to 1.01 µs at 63 K and gradually decreases to 376 ns at 295 K (fig. 2D). Overall, the small polarons of $Zn_3(HOTP)$ behave as room-temperature electron spin qubits, qualifying this material as an MQF.

Fig. 2. CW-EPR spectra of $Zn_3(HOTP)$. (**A**) CW-EPR spectrum collected at X-band and 295 K and associated fitting results. (**B**) CW-EPR spectra collected at X-band from 130 K to 290 K. (**C**) EPR area × T (proportional to χT) vs temperature (T) data for large and small polarons. (**D**) T_1 and T_m of small polarons collected at X-band from 13 K to 295 K.

Anomalous and tunable spin relaxation of small polarons

$Zn_3(HOTP)$ exhibits exceptionally short spin relaxation time (T_1) at X-band with weak temperature dependence from 13 K to 295 K. T_1 is 31.9 µs at 13 K, which is shorter than the value of another HOTP-based MQF, TiHOTP, at the same temperature by 3 orders of magnitude (*22*). It gradually decreases as the temperature rises, reaching nearly 10 µs at 295 K (fig. 2D). This spin relaxation behavior differs from all other stable organic radical qubits (*11, 21*). To articulate spin relaxation mechanisms of $Zn_3(HOTP)$, we further acquired its T_1 at various temperatures with Q-band (1.22 T, 34 GHz) and W-band (3.34 T, 94 GHz) pulse EPR spectroscopy (fig. 3A and B). Raising the magnetic field significantly suppresses spin relaxation below 100 K and induces a significant temperature dependence of T_1 (fig. 3C). Specifically, T_1 became 3.39 ms and 1.59 ms at 13 K under 1.22 T and 3.34 T, respectively, both of which are nearly two orders of magnitude longer than the value observed under 0.34 T. The spin relaxation rates ($1/T_1$) collected at Q-band and W-band exhibit comparable temperature dependencies above 18 K, yet they diverge below this temperature with T_1 being slightly shorter under higher magnetic field. This comparison indicates contributions of a field-dependent direct process and field-independent two-phonon (Raman and

local-mode) relaxation processes to the spin relaxation in Zn_3(HOTP) at Q-band and W-band (*12*, *22*).

Based on these results, we tentatively analyzed spin relaxation mechanisms of Zn_3(HOTP) with the following equation:

$$\frac{1}{T_1} = C + A_{Dir}T + \sum_i A_{Loc,i} \frac{e^{h\nu_i/k_BT}}{\left(e^{h\nu_i/k_BT}-1\right)^2} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

where the three terms describe a temperature-independent spin relaxation process, the direct process, and local-mode processes. C is a constant; ν, k_B, and T represent linear vibrational frequency, Boltzmann constant, and temperature. A_{Dir} and A_{Loc} are pre-factors of direct and local-mode processes, respectively. Fitting the temperature dependence of $1/T_1$ reveals that the spin relaxation at X-band involves a temperature-independent process and a local-mode process driven by the vibration of hydrogen bonds (ν/c = 163 cm^{-1}; c represents the speed of light; fig. S13). The former is dominant below 170 K with an exceptionally high rate (C = 4.5×10^4 s^{-1}) that indicates a fast spin relaxation, and the latter causes a slight decrease of T_1 towards room temperature. At Q-band and W-band, the direct process plays a major role below 50 K, and local-mode processes driven by vibrations of hydrogen bonds and Zn−O bonds (ν/c = 699 cm^{-1}) dominate at higher temperatures (fig. 3E and F). Notably, the temperature-independent process is quenched at these magnetic fields, indicating that this process is field-tunable and sensitive to the electronic Zeeman splitting of small polarons (fig. 3B).

Fig. 3. Magnetic field modulation of spin relaxation. (**A**) Schematic diagram of a sample of Zn_3(HOTP) crystallites in an EPR spectrometer. B_0 represents a static magnetic field and B_1 a microwave magnetic field. (**B**) Zeeman splitting of small polarons in Zn_3(HOTP). Magnetic fields and corresponding microwave frequencies used in experiments are indicated. The red sphere with an arrow represents an electron spin. E represents energy. α and β represent different spin states. (**C**) Temperature dependence of $1/T_1$ for Zn_3(HOTP) powders acquired at X-band (0.34 T), Q-

band (1.22 T), and W-band (3.34 T). (**D−F**) Spin relaxation mechanisms of Zn_3(HOTP) powders at (D) X-band, (E) Q-band, (F) W-band. Dash lines labeled as "Thermal" and "υ/c" represent thermally activated and local-mode processes, respectively.

We further probed the influence of phonons on the spin relaxation in Zn_3(HOTP) by immersing this material in various organic solvents while measuring its T_1 at X-band (the sample is named as Zn_3(HOTP)@solvent). The immersion enforces adsorption of solvent molecules into the nanoscale pores of Zn_3(HOTP) (fig. 4A), which could tweak phonon dispersions through host-guest interactions (*18*). When Zn_3(HOTP) is immersed in DCM, THF, and CS_2, its T_1 becomes significantly longer below 100 K and exhibits a strong temperature dependence (fig. 4B). The spin relaxation involves a direct process and local-mode processes driven by vibrations of hydrogen bonds and Zn−O bonds, whereas the temperature-independent process is quenched (fig. 4D and fig. S14).

Distinct from the above observation, when Zn_3(HOTP) is immersed in DMF, *N,N*-diethylformamide (DEF), *N,N*-dimethylacedamide (DMAc), and dimethoxyethane (DME), its T_1 becomes slightly longer while remaining nearly temperature-independent below 110 K, and it decreases acutely above this temperature (fig. 4C). Whereas the temperature-independent process persists with a slightly lower rate, the local-mode process becomes mainly driven by the stretch mode of Zn−O bond (fig. S15). The vibration of hydrogen bonds contributes negligibly to spin relaxation, indicating that these hydrogen-accepting and water-miscible solvents tend to disrupt hydrogen bonds between the adsorbed H_2O and HOTP radicals by replacing the former in the pores. These observations demonstrate subtle tunability of phonons in Zn_3(HOTP) with guest molecules. Such phononic modularity is typically unfeasible for dense inorganic solids as their phonon dispersion relations are determined by crystal structures (*35*), yet it is easily achievable for microporous materials by harnessing host-guest interactions.

Notably, although T_1 of Zn_3(HOTP) powders at X-band is much shorter than those under higher magnetic fields or soaked in DCM, THF, and CS_2, T_m of these samples are comparable, indicating that spin decoherence is not governed by relaxation for this material (fig. S16). Hence, the temperature-independent process can be harnessed to improve repetition rates of quantum operations for quantum information technologies while maintaining the qubit coherence (*36, 37*). Typically, quantum operations need to be repeated many times, where qubits should be reset to thermal equilibrium at the beginning of each repetition (*35*). Accordingly, the time required for each repetition should well exceed five times of T_1 to reach more than 99% relaxation (*38*), which often leads to compromise between experimental time and signal-to-noise ratio (SNR). To demonstrate this point, we conducted dynamical decoupling for Zn_3(HOTP) powders (T_m = 750 ns) and Zn_3(HOTP)@DCM (T_m = 690 ns) at X-band and 30 K with a Carr−Purcell−Meiboom−Gill (CPMG) pulse sequence consisting of 6 spin-locking π pulses. The CPMG sequence improved T_m of these samples to 2.16 μs and 1.65 μs, respectively. Nonetheless, the corresponding measurements took 20 min and 180 min, respectively, under the same experimental parameters except for the repetition time (fig. 4F). Thus, the temperature-independent process facilitates spin relaxation without deteriorating coherence in Zn_3(HOTP), which helps enhance the repetition rate for dynamical decoupling by 9 times.

Fig. 4. Guest modulation of spin relaxation. (**A**) Schematic diagram of Zn_3(HOTP) crystallites soaked in solvents. Solvent molecules are adsorbed into pores. (**B**) Temperature dependence of $1/T_1$ for Zn_3(HOTP) soaked in DCM, THF, and CS_2 acquired at X-band. (**C**) Temperature dependence of $1/T_1$ of Zn_3(HOTP) soaked in DMF, DEF, DMAc, and DME acquired at X-band. (**D, E**) Spin relaxation mechanisms of Zn_3(HOTP) soaked in (D) DCM and (E) DMF at X-band. Dash lines labeled as "Thermal" and "υ/c" represent thermally activated and local-mode processes, respectively. (**F**) CPMG echo decay traces for Zn_3(HOTP) powders and Zn_3(HOTP)@DCM collected at X-band and 30 K. Sharp spikes are electron spin echo envelope modulation signals.

Analysis of spin relaxation mechanism

The efficient and temperature-independent spin relaxation in the powder of Zn_3(HOTP) at X-band is rarely observed for electron spin systems. This anomalous behavior cannot be rationalized by common molecular spin relaxation mechanisms including direct, Raman, Orbach, and local-mode processes, whose scaling factors are equal to or above 1 in our experimental temperature range (*11, 12*). Tumbling-induced spin relaxation is irrelevant as HOTP radicals are fixed by the lattice and cannot freely tumble. To our knowledge, similar phenomenon has only been analyzed for nanomagnets as well as heavily doped insulators and semiconductors, where it is attributed to quantum tunneling of magnetization (QTM) (*39*), cross relaxation between localized spins (*40, 41*), or mutual scattering between mobile and localized electrons (*42–44*). Nonetheless, our experimental results rule out these mechanisms for Zn_3(HOTP). First, QTM takes place between degenerate spin states (*39*), yet HOTP radicals possess non-degenerate spin states under external magnetic field due to Zeeman splitting. Second, the adsorption of DCM in Zn_3(HOTP) significantly suppresses its temperature-independent spin relaxation. However, DCM should not change the spin density, charge density, or charge mobility of Zn_3(HOTP) as it is redox-innocent and it does not alter the crystal structure of the framework (fig. S3). Accordingly, its adsorption should not modulate spin-spin interaction (cross relaxation) or mutual scattering between mobile

9

and localized electrons, excluding these two mechanisms. In addition, common semiconductor spin relaxation mechanisms, e.g. Elliot−Yafet mechanism, D'yakonov−Perl' mechanism, Bir−Aronov−Pikus mechanism, etc., are not applicable because they are derived for delocalized electrons rather than small polarons (45, 46).

As the adsorption of DCM could subtly tweak phonons of Zn₃(HOTP) through host-guest interactions, the seemingly temperature-independent spin relaxation likely stems from spin-phonon coupling. Indeed, it is consistent with the thermally activated process where T_1 could be temperature-independent when the activation energy barrier (E_a, in the unit of temperature) is much lower than the lowest experimental temperature. Hence, we revised Equation 1 as follows:

$$\frac{1}{T_1} = A_{Therm} \frac{2\tau_c}{1+\omega^2\tau_c^2} + A_{Dir}T + \sum_i A_{Loc,i} \frac{e^{h\nu_i/k_BT}}{\left(e^{h\nu_i/k_BT}-1\right)^2} \quad \dots\dots\dots\dots\dots\dots(2)$$

Here, A_{Therm}, τ_c, and ω represent the pre-factor, correlation time, and electron spin Larmor frequency of the thermally activated process, respectively, with $\tau_c = \tau_c^0 \exp(E_a/k_BT)$ where τ_c^0 is a preexponential factor (11). Fitting the temperature dependence of T_1 with Equation 2 revealed E_a of 5 K for Zn₃(HOTP) powder at 0.34 T, which drops to 2 K upon soaking in DMF, DEF, and DME (fig. 3D and fig. 4E; fig. S17, table S16). Although a low-barrier thermally activated process could account for the experimental data, its underlying microscopic mechanism remains unclear. Key questions persist: what is the nature of the barrier-crossing event? Why is the spin relaxation rate sensitive to both magnetic fields and pore-filling solvents? A new mechanism is demanded to explain the anomalous spin relaxation behavior of Zn₃(HOTP).

Spin-phonon polarons

Motivated by the intrinsic structural chirality as well as the unique field- and guest-tunable spin relaxation behaviors of Zn₃(HOTP), we introduce an additional relaxation channel assisted by spin-phonon polarons, which is described by the following nonadiabatic microscopic model:

$$\hat{H} = \frac{\Delta}{2}\hat{\sigma}_z + \hat{H}_B + \left(\alpha_1\hat{Q}_{sl} + \alpha_2\hat{Q}_{sl}^2\right)\hat{\sigma}_x + \gamma_1\hat{Q}_{sp}\hat{\sigma}_z \quad \dots\dots\dots\dots\dots(3)$$

Here, $\hat{\sigma}_z$ and $\hat{\sigma}_x$ are Pauli matrices; α_1, α_2, and γ_1 are spin-phonon coupling constants. The coupling constant γ_1 is proportional to the external magnetic field strength (B) originated from the vibrational dependence of the Landé g-factor (47, 48). The four terms describe the electronic Zeeman splitting, lattice phonon bath, linear and quadratic transverse spin-phonon coupling, as well as longitudinal spin-phonon (polaron-like) interaction, respectively. The spin system with Zeeman splitting Δ couples with two bands of phonons: the collective mode $\hat{Q}_{sl}$ drives conventional spin-lattice relaxation, e.g. direct, Raman, and local-mode processes, while an additional mode $\hat{Q}_{sp}$ asymmetrically couples with different spin states, enabling the formation of a spin-phonon polaron (fig. 5A). Notice that the polaron displacement is proportional to γ_1, which is again proportional to B, and that the sign of γ_1 reflects the handedness of the chirality (9, 49).

A straightforward Fermi's Golden Rule calculation (see Supplementary Materials) indicates that the spin-phonon polaron modulates the spin relaxation rate with a factor of $\exp\left[-\frac{(\Delta-E_r)^2}{4k_BTE_r}\right]$, analogous to the Marcus theory (50). The reorganization energy E_r depends on both the phonon spectral density and B. In particular, E_r shows a strong field dependence as $E_r \propto \gamma_1^2 \propto B^2$. In the high-temperature limit, the quantum Fermi's Golden Rule reduces to a classical thermally activated transition with $E_a = (\Delta - E_r)^2/4E_r$, indicating that the thermally activated spin

relaxation process is a natural consequence of the spin-phonon polaron-assisted relaxation. Notably, the spin-phonon polaron modulation is independent of the structural chirality as E_r is quadratic to γ_1. As a result, this mechanism is applicable to the racemate of $Zn_3(HOTP)$ used in the experiments.

This microscopic model explains the abovementioned fast and nearly temperature-independent spin relaxation. As the magnetic field increases, both Δ and spin-phonon polaron displacement scale with B linearly, whereas E_r is quadratic to B (fig. 5B). At lower magnetic fields, the spin-state transitions are more accessible because little thermal fluctuation is required to reach the potential crossing. As a result, the spin-phonon polaron-assisted relaxation channel is open and dominant, leading to efficient spin relaxation with weak temperature dependence (see Supplementary Materials). This is likely the situation for $Zn_3(HOTP)$ powders and those soaked in DMF, DEF, DMAc, and DME at X-band. The temperature dependencies of T_1 observed for these samples can be well fitted by the rate function derived from Equation 3 (fig. 5C and D; fig. S18).

This model also explains the field- and guest-induced suppression of the above spin relaxation behavior. Raising the magnetic field from 0.34 T to 1.22 T (or 3.34 T) raises E_r. Changing guest molecules in the pores might alter the vibrational environment around the radical, which varies the spin-phonon coupling strength and density of states thereby enhancing E_r. In either case, E_r could become too large to be overcome by thermal fluctuations, effectively suppressing the spin-phonon polaron-assisted relaxation channel. As a result, the conventional direct and local-mode processes dominate the relaxation dynamics. This is likely the situation for $Zn_3(HOTP)$ powders at Q- and W-band as well as those soaked in DCM, THF, and CS_2 at X-band. The temperature dependencies of T_1 observed for these samples can be successfully fitted using the standard rate expressions for conventional spin relaxation mechanisms (fig. 3E and F; fig. 4D; fig. S14).

Fig. 5. **Spin-phonon polaron-assisted spin relaxation.** (**A**) Potential energy surfaces of different spin states ($|0\rangle$ and $|1\rangle$) of a $S = 1/2$ system as a function of polaron distortion coordinate $\hat{Q}_{sp}$. (**B**)

Mechanism for the magnetic-field-controlled activation and suppression of the spin-phonon polaron-assisted relaxation channel. (**C, D**) Fitting of the temperature dependence of spin relaxation rates for (C) $Zn_3(HOTP)$ powders and (D) $Zn_3(HOTP)@DMF$ acquired at X-band based on rate functions derived from Equation 3 (see Supplementary Materials).

Conclusions

Our studies reveal experimental evidence of spin-phonon polarons for the first time in a chiral and microporous MQF, $Zn_3(HOTP)$. They likely emerge from chirality-induced asymmetric spin-phonon coupling and cause anomalous and tunable spin relaxation behaviors by introducing an additional relaxation channel. As a result, the seemingly unexpected temperature-independent feature of spin relaxation rate can be then explained by the existence of barrierless spin-phonon polaron state. The presence of these quasiparticles should not be limited to MQFs—they should be able to form in chiral polymers, soft inorganic solids (e.g. chiral halide perovskites), and artificial structures under appropriate magnetic fields. Further investigations of their dynamics and their influence on electron (or spin) transport could reveal insights into the interplay between structural chirality and electron spin degree of freedom. In addition, spin-phonon polarons could facilitate relaxation while maintaining coherence for electron spin qubits, which might occur in solid-state defects and semiconductor quantum dot qubits as well. Harnessing this unique property could shorten the time needed for qubit initialization thereby improving repetition rates in quantum operations, leading to new strategies for high-efficiency spin-based quantum computing and quantum sensing.

References and Notes

1. B. Göhler, V. Hamelbeck, T. Z. Markus, M. Kettner, G. F. Hanne, Z. Vager, R. Naaman, H. Zacharias, Spin selectivity in electron transmission through self-assembled monolayers of double-stranded DNA. *Science* **331**, 894–897 (2011).

2. D. K. Bhowmick, T. K. Das, K. Santra, A. K. Mondal, F. Tassinari, R. Schwarz, C. E. Diesendruck, R. Naaman, Spin-induced asymmetry reaction—The formation of asymmetric carbon by electropolymerization. *Sci. Adv.* **8**, eabq2727 (2022).

3. H. Lu, J. Wang, C. Xiao, X. Pan, X. Chen, R. Brunecky, J. J. Berry, K. Zhu, M. C. Beard, Z. V. Vardeny, Spin-dependent charge transport through 2D chiral hybrid lead-iodide perovskites. *Sci. Adv.* **5**, eaay0571 (2019).

4. R. Naaman, Y. Paltiel, D. H. Waldeck, Chiral molecules and the electron spin. *Nat. Rev. Chem.* **3**, 250–260 (2019).

5. S.-H. Yang, R. Naaman, Y. Paltiel, S. S. P. Parkin, Chiral spintronics. *Nat. Rev. Phys.* **3**, 328–343 (2021).

6. A. Chiesa, A. Privitera, E. Macaluso, M. Mannini, R. Bittl, R. Naaman, M. R. Wasielewski, R. Sessoli, S. Carretta, Chirality−induced spin selectivity: an enabling technology for quantum applications. *Adv. Mater.* **35**, e2300472 (2023).

7. B. P. Bloom, Y. Lu, T. Metzger, S. Yochelis, Y. Paltiel, C. Fontanesi, S. Mishra, F. Tassinari, R. Naaman, D. H. Waldeck, Asymmetric reactions induced by electron spin polarization. *Phys. Chem. Chem. Phys.* **22**, 21570–21582 (2020).

8. B. P. Bloom, Y. Paltiel, R. Naaman, D. H. Waldeck, Chiral induced spin selectivity. *Chem. Rev.* **124**, 1950–1991 (2024).

9. J. Fransson, Vibrational origin of exchange splitting and chiral-induced spin selectivity. *Phys. Rev. B* **102**, 235416 (2020).

10. Z.-W. Wang, R.-B. Yang, Y. Cui, W.-P. Li, X.-Q. Dong, Z.-Q. Li, Polaron spin states in chiral systems. *Phys. Rev. B* **110**, 085430 (2024).

11. S. S. Eaton, G. R. Eaton, in *EPR Spectroscopy: Fundamentals and Methods*. D. Goldfarb, S. Stoll, Eds. (John Wiley & Sons Ltd, 2018), pp. 175–192.

12. A. Lunghi, in *Computational Modelling of Molecular Nanomagnets*. G. Rajaraman, Ed. (Springer, 2023), pp. 219–289.

13. J. Xu, K. Li, U. N. Huynh, M. Fadel, J. Huang, R. Sundararaman, V. Vardeny, Y. Ping, How spin relaxes and dephases in bulk halide perovskites. *Nat. Commun.* **15**, 188 (2024).

14. B. Jee, M. Hartmann, A. Pöppl, H_2, D_2 and HD adsorption upon the metal-organic framework $[Cu_{2.97}Zn_{0.03}(btc)_2]_n$ studied by pulsed ENDOR and HYSCORE spectroscopy. *Mol. Phys.* **111**, 2950–2966 (2013).

15. L. Sun, L. Yang, J.-H. Dou, J. Li, G. Skorupskii, M. Mardini, K. O. Tan, T. Chen, C. Sun, J. J. Oppenheim, R. G. Griffin, M. Dincă, T. Rajh, Room-temperature quantitative quantum sensing of lithium ions with a radical-embedded metal–organic framework. *J. Am. Chem. Soc.* **144**, 19008–19016 (2022).

16. A. K. Oanta, K. A. Collins, A. M. Evans, S. M. Pratik, L. A. Hall, M. J. Strauss, S. R. Marder, D. M. D'Alessandro, T. Rajh, D. E. Freedman, H. Li, J.-L. Brédas, L. Sun, W. R. Dichtel, Electronic spin qubit candidates arrayed within layered two-dimensional polymers. *J. Am. Chem. Soc.* **145**, 689–696 (2023).

17. C.-J. Yu, S. von Kugelgen, M. D. Krzyaniak, W. Ji, W. R. Dichtel, M. R. Wasielewski, D. E. Freedman, Spin and phonon design in modular arrays of molecular qubits. *Chem. Mater.* **32**, 10200–10206 (2020).

18. L. Vujević, B. Karadeniz, N. Cindro, A. Krajnc, G. Mali, M. Mazaj, S. M. Avdoshenko, A. A. Popov, D. Žilić, K. Užarević, M. Kveder, Improving the molecular spin qubit performance in zirconium MOF composites by mechanochemical dilution and fullerene encapsulation. *Chem. Sci.* **14**, 9389–9399 (2023).

19. W. Gong, Z. Chen, J. Dong, Y. Liu, Y. Cui, Chiral metal–organic frameworks. *Chem. Rev.* **122**, 9078–9144 (2022).

20. K. Orihashi, A. Yamauchi, S. Fujiwara, M. Asada, T. Nakamura, J. K.-H. Hui, N. Kimizuka, K. Tateishi, T. Uesaka, N. Yanai, Spin-polarized radicals with extremely long spin–lattice relaxation time at room temperature in a metal–organic framework. *J. Am. Chem. Soc.* **145**, 27650–27656 (2023).

21. A. Zhou, Z. Sun, L. Sun, Stable organic radical qubits and their applications in quantum information science. *The Innovation*, **5**, 100662 (2024).

22. A. Zhou, D. Li, M. Tan, Y. Lv, S. Pang, X. Zhao, Z. Shi, J. Zhang, F. Jin, S. Liu, L. Sun, Phononic modulation of spin-lattice relaxation in molecular qubit frameworks. *Nat. Commun.* **15**, 10763 (2024).

23. T. Holstein, Studies of polaron motion Part II. The "small" polaron. *Ann. Phys.* **8**, 343–389 (1959).

24. A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, W. Zwerger, Dynamics of the dissipative two-state system. *Rev. Mod. Phys.* **59**, 1–85 (1987).

25. A. Würger, Strong-coupling theory for the spin-phonon model. *Phys. Rev. B* **57**, 347–361 (1998).

26. J. Garwoła, D. Segal, Open quantum systems with noncommuting coupling operators: An analytic approach. *Phys. Rev. B* **110**, 174304 (2024).

27. J. Y. Choi, M. Stodolka, N. Kim, H. T. B. Pham, B. Check, J. Park, 2D conjugated metal-organic framework as a proton-electron dual conductor. *Chem* **9**, 143–153 (2023).

28. W. Huang, Y. Xiao, F. Xia, X. Chen, T. Zhai, Second harmonic generation control in 2d layered materials: status and outlook. *Adv. Funct. Mater.* **34**, 2310726 (2024).

29. S. Jähnigen, Vibrational circular dichroism spectroscopy of chiral molecular crystals: insights from theory. *Angew. Chem. Int. Ed.* **62**, e202303595 (2023).

30. K. J. Zhang, T. Chen, J. Oppenheim, L. Yang, L. Palatinus, P. Müller, T. V. Voorhis, M. Dincă, High-resolution structure of $Zn_3(HOTP)_2$ (HOTP = hexaoxidotri-phenylene), a three-dimensional conductive MOF. *Chem. Sci.*, doi: 10.1039/d5sc00894h (2025).

31. G. Skorupskii, K. N. Le, D. L. M. Cordova, L. Yang, T. Chen, C. H. Hendon, M. Q. Arguilla, M. Dincă, Porous lanthanide metal–organic frameworks with metallic conductivity. *Proc. Natl. Acad. Sci.* **119**, e2205127119 (2022).

32. V. Sitaram, A. Sharma, S. V. Bhat, K. Mizoguchi, R. Menon, Electron spin resonance studies in the doped polyaniline PANI-AMPSA: Evidence for local ordering from linewidth features. *Phys. Rev. B* **72**, 035209 (2005).

33. Q. Chen, O. Adeniran, Z.-F. Liu, Z. Zhang, K. Awaga, Graphite-like charge storage mechanism in a 2D π–d conjugated metal–organic framework revealed by stepwise magnetic monitoring. *J. Am. Chem. Soc.* **145**, 1062–1071 (2023).

34. C. Franchini, M. Reticcioli, M. Setvin, U. Diebold, Polarons in materials. *Nat. Rev. Mater.* **6**, 560–586 (2021).

35. A. Bienfait, J. J. Pla, Y. Kubo, X. Zhou, M. Stern, C. C. Lo, C. D. Weis, T. Schenkel, D. Vion, D. Esteve, J. J. L. Morton, P. Bertet, Controlling spin relaxation with a cavity. *Nature* **531**, 74–77 (2016).

36. C. Tornow, N. Kanazawa, W. E. Shanks, D. J. Egger, Minimum quantum run-time characterization and calibration via restless measurements with dynamic repetition rates. *Phys. Rev. Appl.* **17**, 064061 (2022).

37. J. A. Jones, Controlling NMR spin systems for quantum computation. *Prog. Nucl. Magn. Reson. Spectrosc.* **140**, 49–85 (2024).

38. C. E. Jackson, T. Ngendahimana, C.-Y. Lin, G. R. Eaton, S. S. Eaton, J. M. Zadrozny, Impact of counter ion methyl groups on spin relaxation in $[V(C_6H_4O_2)_3]^{2-}$. *J. Phys. Chem. C* **126**, 7169–7176 (2022).

39. D. Gatteschi, R. Sessoli, Quantum tunneling of magnetization and related phenomena in molecular materials. *Angew. Chem. Int. Ed.* **42**, 268–297 (2003).

40. A. Jarmola, V. M. Acosta, K. Jensen, S. Chemerisov, D. Budker, Temperature- and magnetic-field-dependent longitudinal spin relaxation in nitrogen-vacancy ensembles in diamond. *Phys. Rev. Lett.* **108**, 197601 (2012).

41. Y. Lu, Y. Fu, Z. Hu, S. Feng, M. Torabi, L. Gao, S. Fu, Z. Wang, C. Huang, X. Huang, M. Wang, N. Israel, E. Dmitrieva, H. I. Wang, M. Bonn, P. Samorì, R. Dong, E. Coronado, X. Feng, Rational construction of layered two-dimensional conjugated metal–organic frameworks with room-temperature quantum coherence. *J. Am. Chem. Soc.* **147**, 8778–8784 (2025).

42. G. Völkel, W. Brunner, Electron spin-lattice relaxation of trapped EPE active centres in O_2^- contaminated polyacetylene. *Phys. status solidi. (a)* **94**, 673–678 (1986).

43. Y. Song, O. Chalaev, H. Dery, Donor-driven spin relaxation in multivalley semiconductors. *Phys. Rev. Lett.* **113**, 167201 (2014).

44. Y. Fujita, M. Yamada, S. Yamada, T. Kanashima, K. Sawano, K. Hamaya, Temperature-independent spin relaxation in heavily doped n-type germanium. *Phys. Rev. B* **94**, 245302 (2016).

45. M. W. Wu, J. H. Jiang, M. Q. Weng, Spin dynamics in semiconductors. *Phys. Rep.* **493**, 61–236 (2010).

46. S. Schott, U. Chopra, V. Lemaur, A. Melnyk, Y. Olivier, R. D. Pietro, I. Romanov, R. L. Carey, X. Jiao, C. Jellett, M. Little, A. Marks, C. R. McNeill, I. McCulloch, E. R. McNellis, D. Andrienko, D. Beljonne, J. Sinova, H. Sirringhaus, Polaron spin dynamics in high-mobility polymeric semiconductors. *Nat. Phys.* **15**, 814–822 (2019).

47. J. H. V. Vleck, Paramagnetic relaxation times for titanium and chrome alum. *Phys. Rev.* **57**, 426–447 (1940).

48. A. Lunghi, S. Sanvito, How do phonons relax molecular spins? *Sci. Adv.* **5**, eaax7163 (2019).

49. H.-H. Teh, W. Dou, J. E. Subotnik, Spin polarization through a molecular junction based on nuclear Berry curvature effects. *Phys. Rev. B* **106**, 184302 (2022).

50. A. Nitzan, *Chemical Dynamics in Condensed Phases: Relaxation, Transfer and Reactions in Condensed Molecular Systems* (Oxford University Press, 2006).

Acknowledgements

Supplementary Materials

Materials and Methods

Supplementary text

Figs. S1 to S28

Tables S1 to S16

References (31)