# Peer Review File

# Phononic Modulation of Spin-Lattice Relaxation in Molecular Qubit Frameworks

Corresponding Author: Professor Lei Sun

**This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.**

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This paper presents a study of the spin dynamics of radicals in MHOTP-style MOFs as a function of different metals (Mg v. Ti) and whether or not the structures contain hydrogen or deuterium in their structural network. They make a rather interesting observation, which is that deuteration produces low-energy phonons that hasten spin-lattice relaxation rather than suppress it. The team uses Brillouin light scattering and Raman spectroscopy to identify the low-energy phonon spectrum and back up their assignments. I think it is an exciting result. It provides some insight into some long-standing issues in the control of spin relaxation and it is quantitative, via the Raman and BLS measurements, in an admirable way compared to many other papers out there. I'd be happy to recommend this paper for publication, but I think there are a couple of issues that, if addressed, would strengthen the paper.

Science-related points:
(1) The assignment of sources of decoherence is not explained in detail. Why do the data suggest that the low-temperature Tm is limited by nuclear spins? Same for the methyl group assignment and that of using T1 to limit Tm? These assignments are not trivial, a point that the authors know, but it is presented as such. The authors do have more details in the SI about the T1 assignments, but not much about Tm. Given the "communication" nature of the paper, I understand wanting to be a little brief on details in the main manuscript, but there should be a happy medium between giving all the details in the main paper and squirreling the entirety of the assignment in the SI. Additional discussion in the main paper would make the paper clearer.
(2) The paper makes the point that TiHOTP's long T1 and high-frequency phonon dispersions stem from its rigid structure. From my view, "rigidity" in chemistry is a very poor word choice. For example, in molecules, "rigidity" is assigned from, as best I can tell, looking at chemdraw pictures, and for solids, I would think "rigidity" directly scales with hardness, but there are no indentation studies in this paper to show that. The authors also talk about the "rigidity" of primarily H-bonded lattices, but don't cite any indentation studies of those types of systems (e.g. ice or something). I think for the present discussion, would not "rigidity" be best defined as a property that stems from having only high frequency phonon dispersions? Would a less rigid species be one that has a high density of low-energy phonon modes? Can the authors sharpen this discussion in the paper?
(3) Related to point 2: I see an opportunity to broaden the appeal of their discovery by editing the discussion. A lot of pulsed EPR measurements are performed in H2O/glycerol glasses (full of H-bonds) and deuteration of these environments is done to enhance Tm. I can't recall how those deuteration studies affect T1, or if they do at all. So, how do these results compare with those older pulsed EPR studies? Providing some broader context here would be really satisfying and make the importance of the results more evident for the reader.
(4) Can nothing be done about the Raman spectra? They are fairly noisy – does a different wavelength give a better signal? There was a recent paper from Hadt and company that used resonance raman to find exact phonons relevant for relaxation, so maybe that technique would be useful here.

Stylistic points:
(1) I don't fully agree with the first statement of the abstract. We could easily find new applications for the solution phase that do not require said integration. Of course the highlighted integration is important for many applications, but I think "demands" is a bit too strong here for the incredibly broad umbrella that is quantum information science.
(2) It is not clear what figure 1 is supposed to say.
(3) What do the vertical dashed lines in fig 4 mean? Given the change in mass associated with the deuteration step,

shouldn't the spectra shift instead of just align vertically?


Reviewer #2

(Remarks to the Author)
The authors synthesize three different Metal-Organic Frameworks with organic radical linkers. Depending on whether Ti or Mg ions are used to build the MOF, two different motifs are obtained. In the case of Ti, no water molecule is present in the framework, while Mg leads to an extended network of hydrogen-bonded waters. The work provides a valuable demonstration of how molecular spins can be used in the context of sensing. In particular, the author exploits the sensitivity of spin relaxation to the molecular environment to show that depending on the presence of water or deuterated water different values of T1 are measured.

I support the publication of the work after the following points have been carefully addressed:

1) I strongly advise improving the graphics of compound structures to aid the understanding of non-chemist readers. For instance, Fig. 1 was a mystery to me at first sight and only after spending quite some time on Fig. 2 it became clearer.

2) Fig. 2 reports the spin density of the radical in 2 different oxidation states. Which one corresponds to the molecules involved in the framework? Nat Comm appeals to a broad readership and chemical concepts should be carefully introduced, albeit trivial to specialists.

3) Relaxation time is often seen to correlate with the g-shift of compounds. Can the author comment on this for their MOFs?

4) The relaxation time of TiHOTP seems particularly long. How does it compare with other spin qubits, e.g. those based on Vanadyl coordination compounds?

5) How can the authors be confident that no other phonons at lower energy are present outside Gamma? Are their techniques able to probe such optical phonons like INS and IXS?

6) I am not convinced that the interpretation of spin relaxation in terms of a direct mechanism and a power law is correct. I suspect that multiple (pseudo) localized phonon modes might be a better fit here. The fitting of the low-T data is poor, and a high-T limit of $T^2$ of some low-energy mode contributing to Raman seems a better fit. A second high-energy mode might be required to fit at high energy, although the physical nature of this is under debate: arXiv:2407.01380 (2024). Frequency-dependent measurements of T1 (X vs Q-band) could help distinguish Raman and Direct relaxation, with the former independent from frequency. This might not change the overall interpretation of experiments but would give a better understanding of what phonons are relevant in the process.

7) Fig. 4a, what are the dashed lines? Make the caption more descriptive.

8) BLS does not reveal any phonon below 10 cm-1, whilst there must be acoustic phonons in that energy window. Why is the technique not sensitive to those? Is it possible that the technique is insensitive to optical phonons for similar reasons?

9) The authors claim that DFT does not show any vibration below 200 cm-1 for TiHOTP but Supp. Fig. 18 clearly shows at least 6 modes with weak Raman intensity. Can the authors provide the list of computed normal modes? Why have these been discarded?


Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
I want to thank the authors for making such a great and thorough effort to address my concerns. I think this paper is much stronger now and happy to recommend it for publication.

Reviewer #2

(Remarks to the Author)
I support publication in its present form

# Response Letter

We thank the reviewers for their efforts on reviewing our manuscript and providing invaluable suggestions and comments for us to improve it. We have revised the manuscript accordingly and have addressed all the points raised by the reviewers. All changes have been marked as blue text in the manuscript and Supplementary Information. Detailed point-to-point replies to the reviewers' comments are listed below.

**Reviewer 1**

This paper presents a study of the spin dynamics of radicals in MHOTP-style MOFs as a function of different metals (Mg v. Ti) and whether or not the structures contain hydrogen or deuterium in their structural network. They make a rather interesting observation, which is that deuteration produces low-energy phonons that hasten spin-lattice relaxation rather than suppress it. The team uses Brillouin light scattering and Raman spectroscopy to identify the low-energy phonon spectrum and back up their assignments. I think it is an exciting result. It provides some insight into some long-standing issues in the control of spin relaxation and it is quantitative, via the Raman and BLS measurements, in an admirable way compared to many other papers out there. I'd be happy to recommend this paper for publication, but I think there are a couple of issues that, if addressed, would strengthen the paper.

**Response:** Thank you for your positive evaluation of our manuscript.

Science-related points:

(1) The assignment of sources of decoherence is not explained in detail. Why do the data suggest that the low-temperature Tm is limited by nuclear spins? Same for the methyl group assignment and that of using T1 to limit Tm? These assignments are not trivial, a point that the authors know, but it is presented as such. The authors do have more details in the SI about the $T_1$ assignments, but not much about $T_m$. Given the "communication" nature of the paper, I understand wanting to be a little brief on details in the main manuscript, but there should be a happy medium between giving all the details in the main paper and squirreling the entirety of the assignment in the SI. Additional discussion in the main paper would make the paper clearer.

**Response:** Thanks for this very helpful suggestion. Based on your advice, we re-examined the decoherence mechanisms of MgHOTP and TiHOTP. Specifically, we divided the temperature dependencies of $T_m$ for these two materials into three regions (Figure R1). In the low- and high-temperature regions, the $T_m$ decreases gradually and sharply with rising temperatures, respectively. In the medium-temperature region, the $T_m$ of MgHOTP almost remains a constant between 43 K and 113 K, whereas that of TiHOTP increases with rising temperatures between 63 K and 173 K.

In the high-temperature region, although the $T_m$ is much shorter than the $T_1$, it seems to be closely related to the $T_1$. Based on a decoherence model proposed by Wilson et al. (*J. Phys. Chem. Lett.* **2023**, *14*, 10578), we used the following equation to fit the temperature dependencies of $T_m$:

$$\frac{1}{T_m} = \frac{1}{2T_1} + A_{SD,e}\frac{1}{\sqrt{T_1}} + C \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{Equation R1}$$

where the first term describes the decoherence caused directly by spin relaxation, the second term describes the relaxation-induced electron spin diffusion (also called electronic spectral diffusion (SD)), and the constant term, C, encompasses three temperature-independent decoherence processes: nuclear spin diffusion (also called nuclear spectral diffusion), electron spin flip-flop, and instantaneous diffusion (ID). Note that the second term is different from Wilson's model in which the corresponding decoherence rate is inversely proportional to the $T_1$. Wilson et al. only considered the relaxation of nearby electron spins, but did not include the situation where a distant electron spin relaxes and then the spin flipping propagates to the interested electron spin, namely electronic spectral diffusion. To correct this problem, we adopt a model widely used in condensed matter physics (e.g. *Phys. Rev. B* **2018**, *97*, 064409), which dictates that the decoherence rate is inversely proportional to the square root of $T_1$.

The temperature dependencies of $T_m$ in the high-temperature region can be well fitted by the Equation R1 for both MgHOTP and TiHOTP (Figure R1). It turns out that for each material, the electronic SD causes the sharp decrease of $T_m$, and the constant term also significantly contributes to the decoherence. Therefore, although $1/2T_1$ is negligible,

the $T_m$ is indirectly limited by $T_1$ in the high-temperature region due to the electronic SD. We then extrapolated the above fitting results to the low- and medium-temperature regions and subtracted them from the $1/T_m$ of MgHOTP and TiHOTP. The constant term is dominant in these temperature regions, indicating that nuclear spin diffusion, electron spin flip-flop, and/or instantaneous diffusion play major roles in spin decoherence. The residual decoherence rate in each material shows a peak-shape curve with the maximum value at the same temperature, 28 K. Such coincidence might indicate similar origins of the motions.
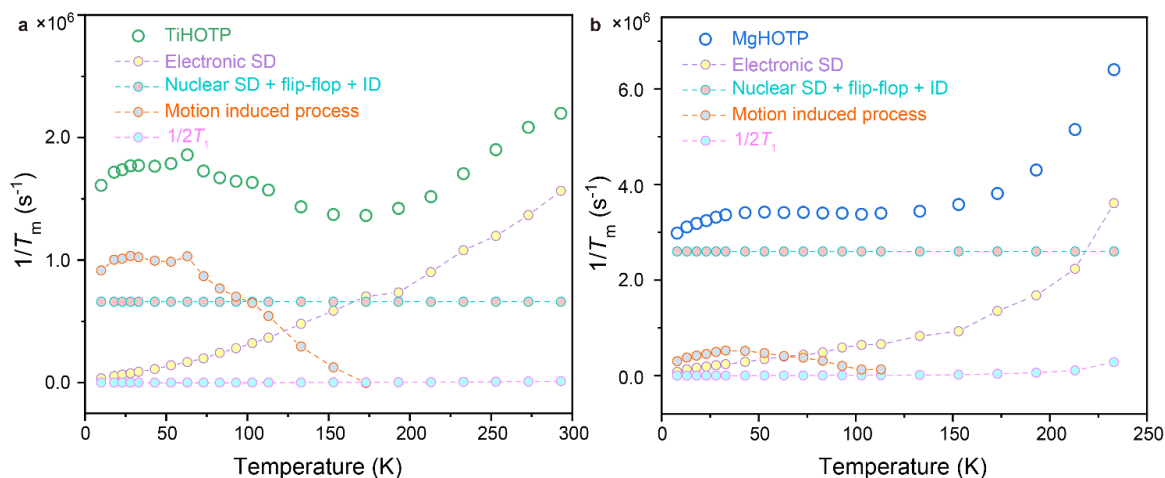


**Figure R1.** Simulation of temperature dependencies of $1/T_m$ for **a**, TiHOTP and **b**, MgHOTP. Circles represent experimental data. Dotted dash lines represent contributions from various spin decoherence processes.

The thermally activated behavior of the residual decoherence rate is similar to what was observed for the motion-induced decoherence process, where a slow motion at low temperature expedites the decoherence but a fast motion at high temperature improves coherence, the latter of which is called motional narrowing (*Nat. Phys.* **2019**, *15*, 814). The motion may involve the methyl tunneling within $(CH_3)_2NH_2^+$ in TiHOTP and proton tunneling within hydrogen bonds in both MQFs (the O−H···O bond between coordinating water and HOTP in MgHOTP and the N−H···O bond between $(CH_3)_2NH_2^+$ and HOTP in TiHOTP). Because methyl and proton tunneling rates typically show complex temperature dependencies and are highly dependent on the molecular structure (*Phys. Chem. Chem. Phys.* **2023**, *25*, 11145; *J. Phys. Chem. C* **2022**, *126*, 7169; *Prog. Nucl. Magn. Reason. Spectrosc.* **2008**, *52*, 170), we cannot derive equations for these motions to fit their contributions to the decoherence.

The temperature dependence of $T_m$ of MgHOTP-$D_2O$ is comparable to that of MgHOTP below 173 K (Supplementary Figure 30). Above 173 K, the $T_m$ of MgHOTP-$D_2O$ increases with rising temperatures. Such thermal behavior indicates the presence of two motion-induced decoherence processes in MgHOTP-$D_2O$ at different temperatures. The upturn of $T_m$ in the high temperature region prevents us from performing the abovementioned quantitative analysis with Equation R1, so we could not identify exact peak temperatures of these processes. Nonetheless, these results indicate that the motion in MgHOTP stems from proton tunneling in hydrogen bonds. As deuterium is twice as heavy as hydrogen, deuterium tunneling is much slower than proton tunneling and needs a higher temperature to activate (*J. Chem. Phys.* **2004**, *120*, 11107). Therefore, we assign the high-temperature motion to the deuterium tunneling in O−D···O hydrogen bond between coordinating $D_2O$ and HOTP, and rationalized the low-temperature motion to the proton tunneling in O−H···O hydrogen bond between residual coordinating $H_2O$ and HOTP.

The exact origins of motions and the associated decoherence mechanisms in MgHOTP and TiHOTP are beyond the scope of this work and will be examined in the future. We have revised the manuscript by adding this discussion into Page 5−6 of the main text and Page 16−17 and 45 of Supplementary Information (Supplementary Figure 9).

(2) The paper makes the point that TiHOTP's long T1 and high-frequency phonon dispersions stem from its rigid structure. From my view, "rigidity" in chemistry is a very poor word choice. For example, in molecules, "rigidity" is assigned from, as best I can tell, looking at chemdraw pictures, and for solids, I would think "rigidity" directly scales with hardness, but there are no indentation studies in this paper to show that. The authors also talk about the "rigidity" of primarily H-bonded lattices, but don't cite any indentation studies of those types of systems (e.g. ice or something). I think for the present discussion, would not "rigidity" be best defined as a property that stems from

**Response:** Thank you for this insightful comment. We agree that "rigidity" is a relatively vague word. We would like to clarify that we use the Debye temperature ($T_D$) as a proxy for structural rigidity, which is a common practice in the field of solid state materials (*ACS Appl. Mater. Interfaces* **2015**, *7*, 7264; *J. Phys. Chem. C* **2013,***117*, 17955). $T_D$ is calculated by the isotropic atomic displacement parameters, so a higher rigidity corresponds to smaller displacements and a higher $T_D$. (*Phys. Bull.* **1975***, 26,* 498*)* In the Debye model, a higher $T_D$ corresponds to a higher cutoff frequency ($\omega_D$) for acoustic phonons, leading to a lower acoustic phonon density of states (DOS):

$$T_D = \frac{\hbar \omega_D}{k_B}$$ ................................................................. Equation R2

$$\rho_D(\omega) = \frac{9N\omega^2}{\omega_D^3}, 0 \ll \omega \ll \omega_D$$ ................................................ Equation R3

where $\rho_D(\omega)$ represents the acoustic phonon density of states, $\omega$ the phonon frequency, and *N* the number of phonon modes. As the $T_D$ of TiHOTP ($T_D$ = 302 K; see detailed discussion in Page 10 of the revised manuscript) is higher than that of MgHOTP ($T_D$ < 35 K), the former should exhibit lower acoustic phonon DOS (Supplementary Figure 18, 19), leading to lower direct and Raman relaxation rates and in turn longer $T_1$. Therefore, for frameworks containing the same type of radicals, their structural rigidity is positively related to the $T_1$.

We have incorporated this discussion into Page 8 of the main text.

Based on your suggestion, we tried to characterize the hardnesses of MgHOTP and TiHOTP by a nanoindenter (KLA G200). The instrument is equipped with an optical microscope with a magnification of 40x. However, since MgHOTP forms rod-shaped crystals with lengths ranging from 3 to 10 μm (Figure R2C), and TiHOTP forms tetragonal bipyramidal crystals with sizes between 200 and 400 nm (Figure R2A), it was difficult to observe individual crystallite under the optical microscope, making single-crystal indentation measurements unfeasible. Instead, we attempted to use a hydraulic press to prepare pressed pellets of these two materials, which were then fixed onto the sample stage with adhesives. The indentation measurement for the pressed pellet was also unreliable (Table R1). Cracks frequently appeared in the samples upon indentation, indicating weak cohesion between the mechanically compacted crystallites (Figure R2B, D). As a result, the results from the indentation measurements were not reproducible and do not reflect the intrinsic hardness of the sample. In conclusion, due to the limited crystallite size of our samples, single-crystal particles could not be measured, and the hardness of pressed pellet was influenced by collapse and cracking. Thus, indentation characterization could not accurately characterize the intrinsic hardness of MgHOTP and TiHOTP.
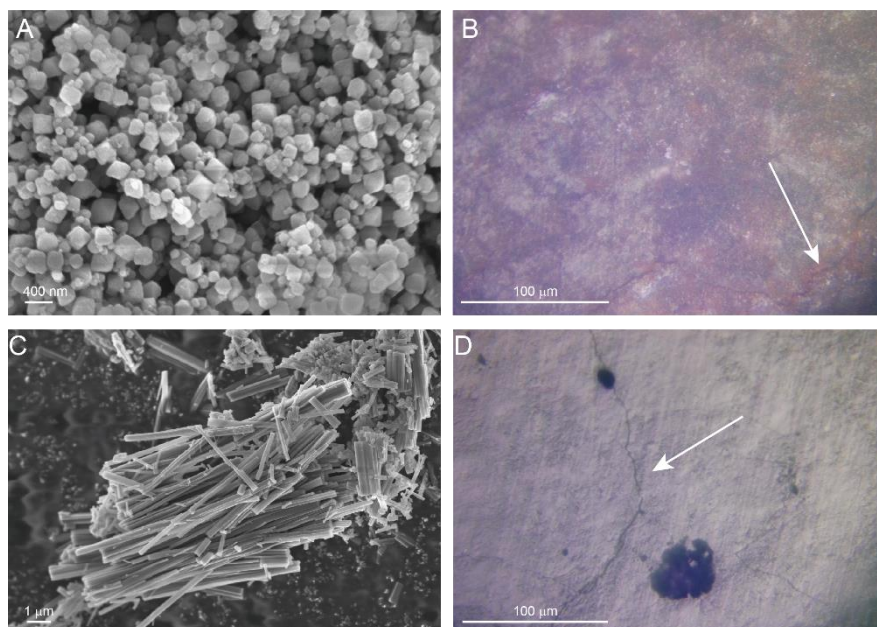


**Figure R2.** Scanning electron micrographs of (A) TiHOTP and (C) MgHOTP. Optical micrographs of (B) TiHOTP and (D) MgHOTP acquired with the nanoindenter.

**Table R1**. Indentation results of TiHOTP and MgHOTP.

| Sample | Temperature (℃) | $h_{max}$ (nm) | $P_{max}$ (mN) | E-IT (GPa) | H-IT (GPa) |
|--------|-----------------|----------------|----------------|------------|------------|
| TiHOTP | 32.5 | 2858 | 5.049 | 0.78 | 0.033 |
| MgHOTP-1 | 32.8 | 565.5 | 4.999 | 21.58 | 0.803 |
| MgHOTP-2 | 33 | 729.9 | 4.997 | 17.93 | 0.452 |
| MgHOTP-3 | 33 | 708.3 | 4.998 | 15.89 | 0.496 |

Note: $P_{max}$ = maximum load; $h_{max}$ = maximum displacement; E-IT = modulus; H-IT = hardness. MgHOTP-X means the *X*th region tested on the same sample.

(3) Related to point 2: I see an opportunity to broaden the appeal of their discovery by editing the discussion. A lot of pulsed EPR measurements are performed in $H_2O$/glycerol glasses (full of H-bonds) and deuteration of these environments is done to enhance $T_m$. I can't recall how those deuteration studies affect $T_1$, or if they do at all. So, how do these results compare with those older pulsed EPR studies? Providing some broader context here would be really satisfying and make the importance of the results more evident for the reader.

**Response:** We appreciate your suggestion. Deuterated solvent has been widely used in EPR characterization of organic radicals, coordination complexes, endohedral fullerenes, etc. Previous studies have demonstrated the positive effect of deuteration on improving the spin coherence due to the low gyromagnetic ratio of $^2$H (e.g. *J. Magn. Reson.* **2005**, *172*, 168; *J. Am. Chem. Soc.* **2016**, *138*, 14678; *Phys. Rev. B* **2010**, *82*, 033410;). However, the influence of deuteration on the spin-lattice relaxation is complex. Different influences have been reported in the literature, which show that deuteration could improve or maintain the $T_1$ depending on the molecular structure, solvent type, temperature, magnetic field, etc. For instance, for trityl-$CD_3$ radicals dissolved in $H_2O$ or 35% glycerol, deuteration of the solvent improves $T_1$ at room temperature under 250 MHz EPR (*J. Magn. Reson.* **2005**, *172*, 168); for vanadium-based coordination complexes dissolved in a mixture of *N,N*-dimethylformamide and toluene, deuteration of the solvent barely changes the $T_1$ below 140 K at X-band (*J. Am. Chem. Soc.* **2016**, *138*, 14678). In previous studies, solvent deuteration mainly affects the spin-lattice relaxation of molecules by altering the nuclear spin environment, which affects tumbling relaxation processes through superhyperfine coupling (*J. Magn. Reson.* **2005**, *172*, 168). Although protic solvent (e.g. water, glycerol, ethanol) could form hydrogen bonds with nitroxide and semiquinone radicals, the influence of such hydrogen bonds on the $T_1$ remains unclear. In our studies, MgHOTP-$D_2O$ shows shorter $T_1$ than MgHOTP at below 213 K, which is distinct from the abovementioned phenomena. This highlights the distinct phononic environment in MgHOTP and its rational tunability provided by the ordered structure.

We have incorporated this discussion into Page 14 of the main text.

(4) Can nothing be done about the Raman spectra? They are fairly noisy- does a different wavelength give a better signal? There was a recent paper from Hadt and company that used resonance raman to find exact phonons relevant for relaxation, so maybe that technique would be useful here.

**Response:** Per your suggestion, in order to identify the appropriate laser wavelengths for resonant Raman spectroscopy, we acquired diffuse-reflectance UV-Vis absorption spectra of MgHOTP and TiHOTP (Figure R3). MgHOTP shows three broad absorption peaks centered at 230, 370, and 600 nm and its absorption extends to near-infrared bands; TiHOTP shows two broad peaks centered at 231 and 480 nm. Accordingly, we compared Raman spectra of these two materials under 473 nm, 532 nm, 633 nm, and 785 nm laser excitation at room temperature (Figure R4). The peak intensity under 785 nm excitation was very weak. The 473 nm and 532 nm tended to broaden and weaken some peaks. For MgHOTP, the peak at 169 $cm^{-1}$ disappeared under these laser excitations, and the peaks between 1150 $cm^{-1}$ and 1700 $cm^{-1}$ become too broad to discern fine features. Similar phenomena were observed for TiHOTP. Therefore, we chose 633 nm laser for Raman spectroscopic characterization. We have incorporated this discussion into Page 19 of Supplementary Information (Supplementary Figure 10).

We have re-acquired the low-frequency Raman spectrum of MgHOTP using the same experimental conditions as before except for the integration time. Increasing the integration time from 10 min to 40 min significantly improved the signal-to-noise ratio of the spectrum. The new spectrum is shown in Figure 3c.
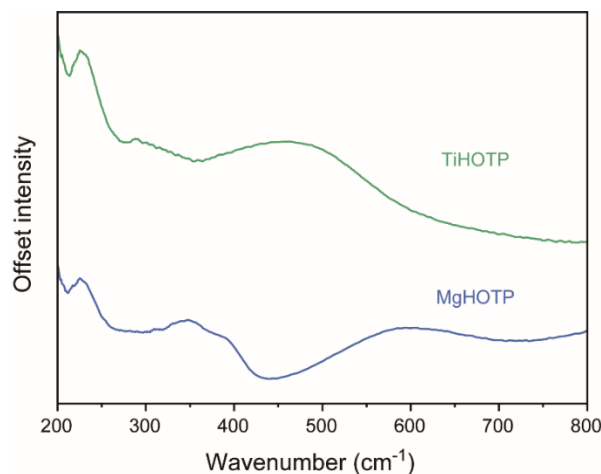


**Figure R3.** UV-Vis spectra of TiHOTP and MgHOTP collected at room temperature.
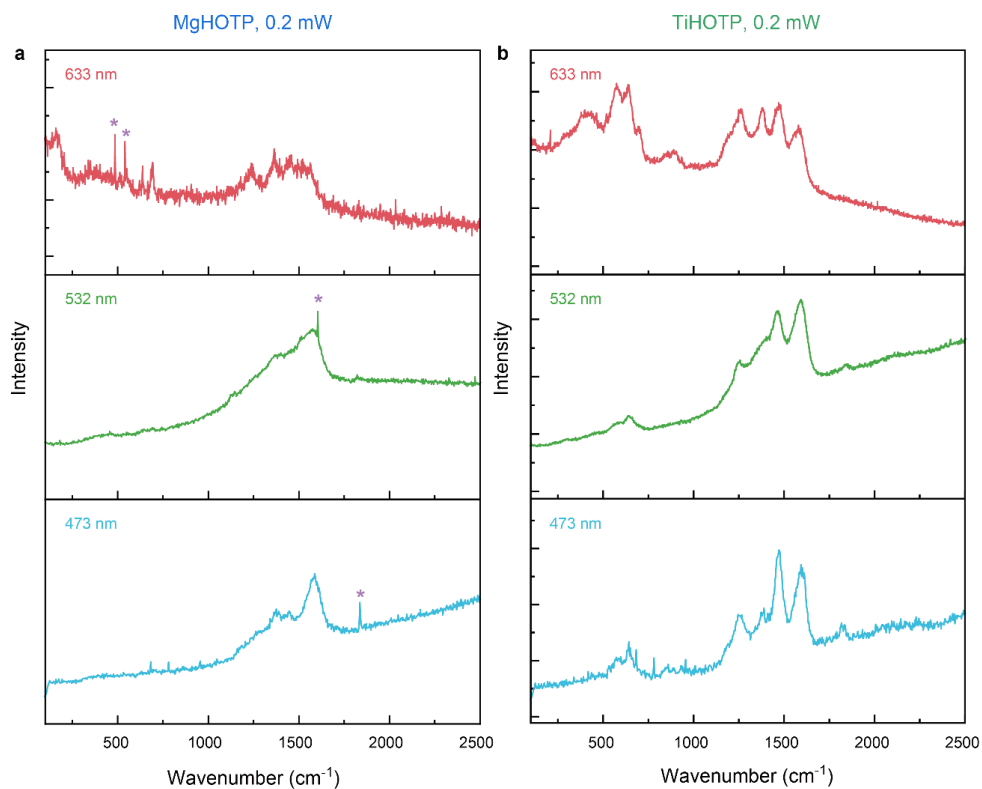


**Figure R4.** Raman spectra of **a**, MgHOTP and **b**, TiHOTP acquired with different laser wavelengths and 0.2 mW laser power at 295K without magnetic field. The laser wavelength is indicated in each sub-plot. Peaks marked by asteroids are caused by cosmic rays.

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5

**Response:** We agree with you that "demands" is not an appropriate word in the abstract. We have revised the first sentence of the abstract as "The solid-state integration of molecular electron spin qubits could promote the advancement of molecular quantum information science".

(2) It is not clear what figure 1 is supposed to say.

**Response:** We have replaced schemes shown in the original Figure 1 by portions of crystal structures of MgHOTP, MgHOTP-D$_2$O, and TiHOTP. The new figure is shown in Figure R5 and in Figure 1a.
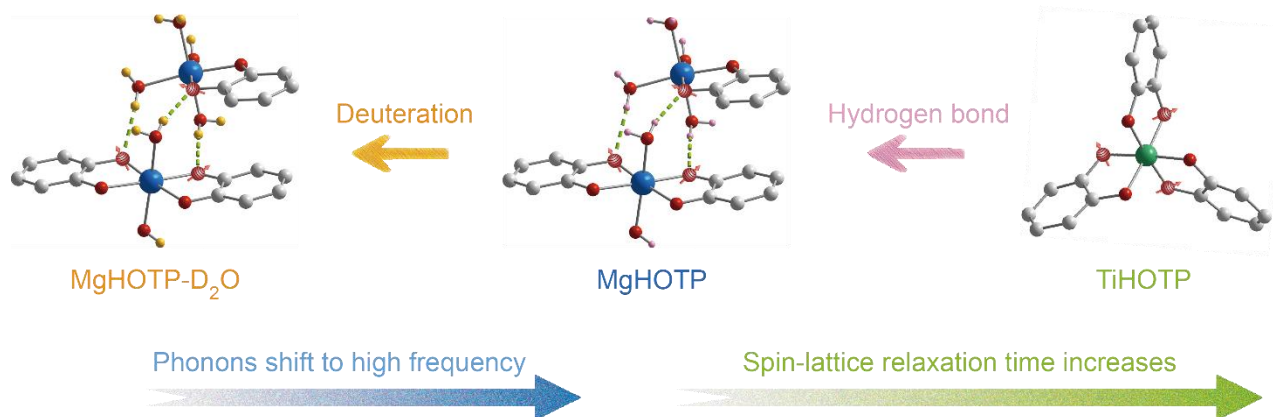


**Figure R5.** Phononic modulation of spin-lattice relaxation in MQFs via hydrogen-bonded networks and their deuteration. Green dotted lines represent hydrogen bonds. Grey, pink, yellow, red, blue, and green spheres represent C, H, D, O, Mg, and Ti, respectively. Red spheres with arrows represent possible oxygen sites where electron spins mainly reside. H atoms of HOTP ligands, solvent molecules, and $(CH_3)_2NH_2^+$ cations are omitted for clarity.

(3) What do the vertical dashed lines in fig 4 mean? Given the change in mass associated with the deuteration step, shouldn't the spectra shift instead of just align vertically?

**Response:** We apologize for this confusion. The dashed lines were meant to clarify the wavenumbers of Raman peaks of MgHOTP-D$_2$O. We agree with you that deuteration should shift some phonons towards lower frequencies, as exemplified by the red shift of the peak at 175 cm$^{-1}$ to 169 cm$^{-1}$ and another peak at 24 cm$^{-1}$ to 15 cm$^{-1}$. We have re-drawn the figure of Raman spectra and have explained the meaning of these dash lines in the figure caption (Figure R6; Figure 5a in the revised manuscript).
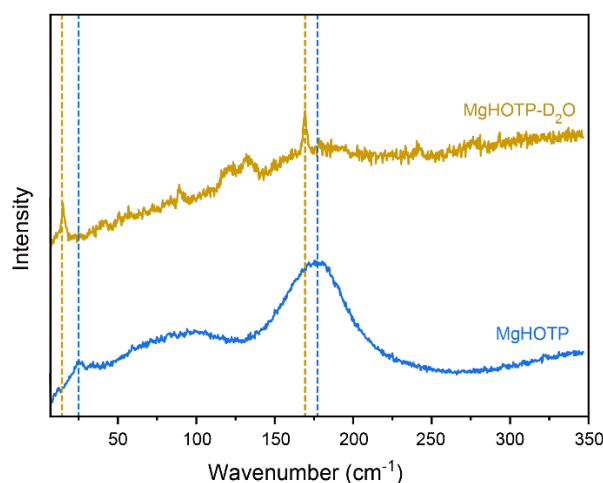


**Figure R6.** Raman spectra of MgHOTP and MgHOTP-D$_2$O collected at 2 K and under 0.34 T with 633 nm excitation. Blue dash lines mark the maxima of peaks at 24 cm$^{-1}$ and 177 cm$^{-1}$ for MgHOTP. Yellow dash lines mark the maxima of peaks at 15 cm$^{-1}$ and 169 cm$^{-1}$ for MgHOTP-D$_2$O.

**Reviewer 2**

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(2) Fig. 2 reports the spin density of the radical in 2 different oxidation states. Which one corresponds to the molecules involved in the framework? Nat Comm appeals to a broad readership and chemical concepts should be carefully introduced, albeit trivial to specialists.

**Response:** Thanks for your kind advice. HOTP could undergo six steps of oxidation, resulting in multiple oxidation states from HOTP-1 to HOTP-6 (Supplementary Figure 4). It might exist as a mixture of these oxidation states in MgHOTP and TiHOTP due to spontaneous oxidation in the air. In the previous study about MgHOTP (*J. Am. Chem. Soc.* **2022**, *144*, 19008), we assigned the oxidation states of HOTP ligands as −6 and −3 in the extended sheets and molecular clusters, respectively, based on their average C−O bond lengths. The antiferromagnetic coupling between adjacent HOTP$^{3−}$ mediated by the HOTP$^{6−}$ gives rise to singlet π-dimers, which may be broken by stacking faults to generate radicals. Meanwhile, the spontaneous oxidation of HOTP ligands could also lead to radicals. In TiHOTP, the charge balance and the average C−O bond length (1.399 Å) indicates an oxidation state of −6 for the HOTP ligand (*J. Am. Chem. Soc.* **2015**, *137*, 15394), which may form a radical upon spontaneous oxidation as well. As the HOTP radicals act as defects in these materials, we could not resolve their exact oxidation states. Nonetheless, as the DFT calculation indicates, the 1, 3, and 5-electron-oxidated HOTP all behave as $S = 1/2$ radicals, and their spin distributions are similar (Figure 1c, d; Supplementary Figure 5). Therefore, we do not have to articulate the exact oxidation state of HOTP when investigating its spin dynamics.

We have incorporated this discussion into the Page 4−5 of the main text.

(3) Relaxation time is often seen to correlate with the g-shift of compounds. Can the author comment on this for their MOFs?

**Response:** Thank you for this insightful suggestion. The magnitude of the *g*-shift reflects the strength of spin-orbit coupling (SOC), which is generally related to the element, molecular motion, and vibrational coupling. (*Relaxation mechanisms. In EPR Spectroscopy: Fundamentals and Methods* **2018**, pp. 175–192) In MgHOTP and TiHOTP, since the electron spin is concentrated on the organic ligands, which mainly consist of light C, H, and O atoms, the SOC is very weak. Molecular motion typically has a greater impact on radicals in solution because they tumble rapidly at room temperature and the associated modulation of *g*-anisotropy increases SOC (*Mol. Phys.* **2007**, *105*, 2137). This is not relevant to solid-state materials as MQFs. Vibrational modes can alter the energy of electronic levels and influence the spin states through SOC. Therefore, the magnitude of the *g*-shift also reflects the influence of vibrations on SOC.

7

The room-temperature $g_{//}$ and $g_{\perp}$ values of MgHOTP, MgHOTP-$D_2O$, and TiHOTP are close to the free electron $g$-factor ($g_e$ = 2.00232), which confirms their negligible SOC. Due to the relatively broad CW-EPR linewidths, the effects of $g_{//}$ and $g_{\perp}$ is intermingled at X-band, so we calculated the $g$-shifts of these three materials with their isotropic $g$-factors ($g_{iso}$) using $g_e$ as the reference (Table R2). The $g$-shift of TiHOTP is smaller than that of MgHOTP, which is consistent with longer $T_1$ of the former. The $g$-shift of MgHOTP is nearly the same with that of MgHOTP-$D_2O$, which is inconsistent with the much shorter $T_1$ of the former at room temperature. Thus, the $g$-shift is not a straightforward evaluator for the $T_1$ of these three MQFs. This is because the spin-lattice relaxation is determined by not only the SOC, but also the phonon dispersion relation, as discussed in this work. Therefore, it is essential to articulate the phonon dispersion and to understand how acoustic phonons and different optical phonons affect the spin-lattice relaxation.

We have added a discussion about the g-shift into Page 4 in the main text and have added Table R2 into Supplementary Information (Supplementary Table 1).

**Table R2**. Comparison between isotropic $g$-factors ($g_{iso}$) of MQFs and the free electron value ($g_e$).

| MOF | $g_{//}$ | $g_{\perp}$ | $g_{iso} = \sqrt{\dfrac{1}{3}\left(g_{\parallel}{}^2 + 2g_{\perp}{}^2\right)}$ | $\lvert g_{iso} - g_e \rvert$ |
|---|---|---|---|---|
| TiHOTP | 2.00193 | 2.00227 | 2.00216 | 0.00016 |
| MgHOTP | 2.00292 | 2.00335 | 2.00321 | 0.00089 |
| MgHOTP-$D_2O$ | 2.00245 | 2.00371 | 2.00329 | 0.00097 |

(4) The relaxation time of TiHOTP seems particularly long. How does it compare with other spin qubits, e.g. those based on Vanadyl coordination compounds?

**Response:** TiHOTP exhibits longer $T_1$ than most metal-based molecular electron spin qubits at both liquid-helium temperature and room temperature (Table R3). We further conducted in-depth comparison of spin-lattice relaxation processes between TiHOTP and other molecular electron spin qubits (Table R4). Compared with Cu(II)- and V(IV)-based coordination complexes, TiHOTP exhibits significantly smaller $A_{Dir}$, $A_{Ram}$, $A_{Loc}$ as well as higher $T_D$ and v (please refer to the response of Question 6). The relatively small values of these parameters are attributed to the weak spin-orbit coupling, low acoustic phonon DOS, and high optical phonon frequencies. They give rise to much slower direct process, Raman process, and local-mode process, together leading to longer $T_1$ of TiHOTP. In addition, TiHOTP displays comparable $A_{Dir}$, $A_{Ram}$, and $A_{Loc}$ with semiquinone radicals, indicating that incorporating semiquinone radicals into this MQF does not significantly alter their spin-lattice relaxation behaviors.

We have incorporated this discussion into Page 6 and Page 10−11 of the main text and have added Table R3 and R4 into Supplementary Information (Supplementary Table 5 and 12).

**Table R3.** $T_1$ of selected molecular electron spin qubits.

| Spin qubit[b] | $T_1$ / µs | Temperature/K | Frequency | Reference |
|---|---|---|---|---|
| VOPc:TiOPc = 1:1000 | 10000[a] | 5[a] | X band | *J. Am. Chem. Soc.* **2016**, *138*, 2154–2157. |
| | 1[a] | 300[a] | | |
| (PPh$_4$)$_2$[Cu(mnt)2]$_{0.001\%}$ | 100000[a] | 7[a] | Q band | *Nat. Commun.* **2014**, *5*, 5304. |
| | 1[a] | 300[a] | | |
| (Ph$_4$P)$_2$[V(C$_8$S$_8$)$_3$] | 36141[a] | 10[a] | X-band | *ACS Central Sci.* **2015**, *1*, 488–492. |
| (Ph$_4$P)$_2$[V(β-C$_3$S$_5$)$_3$] | 23237[a] | | | |
| (Ph$_4$P)$_2$[V(α-C$_3$S$_5$)$_3$] | 16825[a] | | | |
| (Ph$_4$P)$_2$[V(C$_3$S$_4$O)$_3$] | 17539[a] | | | |
| [VO(H$_2$O)$_5$]$^{2+}$ | 1000[a] | 20[a] | Q band | *Inorg. Chem. Front.* |

| | | | | |
|---|---|---|---|---|
| [VO(nta)(H$_2$O)]$^-$ | 200[a] | | | **2023**, *10*, 1999–2013. |
| [VO(Hdtpa)]$^{2-}$ | 1000[a] | | | |
| [VO(ox)$_2$(H$_2$O)]$^{2-}$ | 2000[a] | | | |
| [VO(acac)$_2$(H$_2$O)] | 30[a] | | | |
| Cu(acacen)$_{1\%}$ | 14000 | 5 | X-band | *Chem. Sci.* **2022**, *13*, 7034–7045. |
| | 0.27 | 260 | | |
| [Ni(phen)$_3$](BF$_4$)$_2$ | 10[a] | 5[a] | W-band | *J. Am. Chem. Soc.* **2020**, *142*, 14826–14830. |
| [Ni(pyr$_3$)$_2$](BF$_4$)$_2$ | 10[a] | 5[a] | | |
| [Cr(2,4-dimethylphenyl)$_4$]$_{1\%}$ | 400[a] | 5[a] | X-band | *J. Am. Chem. Soc.* **2021**, *143*, 21350–21363. |
| [Cr(o-tolyl)$_4$]$_{1\%}$ | 5000[a] | 5[a] | | |
| [Cr(2,3-dimethylphenyl)$_4$]$_{1\%}$ | 2000[a] | 5[a] | | |
| [Cr(2,2,2-triphenylethyl)$_4$]$_{1\%}$ | 1000[a] | 5[a] | | |
| [Cr((trimethylsilyl)methyl)$_4$]$_{1\%}$ | 2000[a] | 8[a] | | |
| [Cr(cyclohexyl)$_4$]$_{1\%}$ | 3000[a] | 5[a] | | |

[a]value estimated from a figure in the reference.
[b]VOPc = vanadyl phthalocyanine; TiOPc = titanyl phthalocyanine; mnt = 1,2-dicyanoethylene-1,2-dithiolate; Ph = phenyl; nta = nitrilotriacetate; ox = oxalate; dtpa = diethylenetriaminepentaacetate; acac = acetylacetonato; acacen = bis(acetylacetone)ethylenediamine; phen = 1,10-phenanthroline; pyr$_3$ = tris-2-pyridyl-methane.

**Table R4.** Spin-lattice relaxation parameters of selected molecular electron spin qubits.

| Spin qubit[c] | $A_{Dir}$ (K$^{-1}$ · s$^{-1}$) | $A_{Raman}$ (s$^{-1}$) | $T_D$ (K) | $A_{Loc}$ (s$^{-1}$) | v (cm$^{-1}$) | $T_1$ (µs)[b] | Reference |
|---|---|---|---|---|---|---|---|
| Cu (Me$_2$Nac)$_2$ (1%) | 39 | 1.5e6 | 75 | 1.85e8 | 290 | 0.47 | *Chem. Sci.* **2022**, *13*, 7034–7045. |
| Cu(acacen)$_2$ (1%) | 13.8 | 7e5 | 63 | 6e6 | 213 | 2.43 | |
| Cu(tmtaa) (1%) | 18 | 2.7e5 | 81 | 1.1e7 | 328 | 8.71 | |
| [V(C$_6$H$_4$S$_2$)$_3$]$^{2-}$ (0.5%) | 4.7e3 | 5e8 | 98 | 5.4e9 | 275 | 2.67 | *Chem. Sci.* **2019**, *10*, 6707–6714. |
| [Cu(C$_6$H$_4$S$_2$)$_2$]$^{2-}$ (0.5%) | 4.8e3 | 1.4e8 | 94.9 | 2.6e9 | 488 | 34.80 | |
| [V(C$_6$H$_4$Se$_2$)$_3$]$^{2-}$ (0.5%) | 5.1e2 | 5.1e8 | 71 | 3.14e9 | 161 | 1.39 | |
| [Cu(C$_6$H$_4$Se$_2$)$_2$]$^{2-}$ (0.5%) | 2.25e3 | 2.1e9 | 89 | 3.1e9 | 343.9 | 5.72 | |
| Cu$_{0.1}$-MOF-525 | 32 | 2.37e5 | 77 | 7e6 | 198.08 | 9[b] | *Chem. Sci.* **2023**, *14*, 9389–9399. |
| Cu$_{0.1}$-PCN -223 | 51 | 1.64e5 | 74 | 5e6 | 189.74 | 9[b] | |
| 0.2C$_{60}$@Cu$_{0.1}$-PCN-223 | 29 | 2.22e5 | 82 | 4e6 | 195.30 | 9[b] | |
| 1.0C$_{60}$@Cu$_{0.1}$-PCN-223 | 32 | 1.77e5 | 94 | 6e6 | 200.87 | 9[b] | |
| $^{13}$C$_1$-PTMTC | 0.22 | 1.4e4 | 160 | 4.9e5 | 590.78 | 2000[b] | *Appl. Magn. Reson.* **2022**, *53*, 797–808. |
| $^{13}$C$_1$-dFT | 0.6 | 1.3e4 | 160 | 1.1e6 | 695.03 | 2000[b] | |
| pegylated nitroxide diradicals | 5.4 | 1.5e4 | 100 | 1.3e7 | 660.28 | 800[b] | *J. Phys. Chem. B* **2008**, *112*, 2818–2828. |
| 2,5PSQ | 0.4 | 1.08e4 | 150 | 8.9e4 | 417.02 | 1000[b] | *J. Magn. Reson.* **2009**, *198*, |
| 2,5tASQ | 0.41 | 1.24e4 | 150 | 1.07e5 | 417.02 | 1000[b] | |

| 2,5tBSQ | 0.41 | 1.28e4 | 150 | 1.10e5 | 417.02 | 1000[b] | 111–120. |
|---|---|---|---|---|---|---|---|
| 2,6tBSQ | 0.56 | 1.47e4 | 150 | 1.28e5 | 417.02 | 1000[b] | |
| THSQ | 0.1 | 1.5e4 | 150 | 1.29e5 | 417.02 | 1300[b] | |

[a]Temperature is between 80-90 K.
[b]Value estimated from a figure in the reference.
[c]Me$_2$Nac = N,N'-dimethyl-4-amino-3-penten-2-imine; acacen = bis(acetylacetone)ethylenediamine; tmtaa = tetramethyltetraazaannulene; C$_6$H$_4$S$_2$ = dithiocatecholate; C$_6$H$_4$Se$_2$ = diselenocatecholate; PTMTC = perchlorotriarylmethyl tricarboxylic acid radical; dFT = perdeuterated Finland trityl; 2,5PSQ = 2,5-di-phenyl-1,4-benzosemiquinone; 2,5tASQ = 2,5-di-t-amyl-1,4-benzosemiquinone; 2,5tBSQ = 2,5-di-t-butyl-1,4-benzosemiquinone; 2,6tBSQ = 2,6-di-t-butyl-1,4-benzosemiquinone; THSQ = tetrahydroxy-1,4-benzosemiquione.

**(5) How can the authors be confident that no other phonons at lower energy are present outside Gamma? Are their techniques able to probe such optical phonons like INS and IXS?**

**Response:** Thank you for your thoughtful comments. With FT-IR, Raman, and BLS spectroscopy, we can only probe phonons that are very close to the Γ-point of Brillouin zone. We acknowledge that there could be other phonons at lower energies outside the Γ-point. First, there must be acoustic phonons at lower energy than optical phonons. Second, for the optical phonon on the same phonon dispersion, the phonon energy at the edge of Brillouin zone is typically lower than that at the Γ-point (G. Grosso & G. P. Parravicini, *Solid State Physics* (2$^{nd}$ Ed.) **2014**, 391−436). Therefore, in the manuscript, we can only provide the upper limit of the Debye temperature of each MQF, and we suspect that the Debye frequency is much lower than the lowest optical phonon frequency observed by spectroscopy.

In the revised manuscript, we used optical phonon frequencies observed by spectroscopy to analyze spin-lattice relaxation mechanisms. Specifically, we used these frequencies to simulate the local-mode relaxation processes (see detailed discussions in the answer to the next question). This is valid for two reasons. First, the optical phonon dispersion is typically relatively flat, meaning that the energy is weakly dependent on the momentum (G. Grosso & G. P. Parravicini, *Solid State Physics* (2$^{nd}$ Ed.) **2014**, 391−436). Thus, the energy at the zone edge should not significantly deviate from that at the Γ-point. Second, the local-mode relaxation is not strongly dependent on the phonon frequency. Therefore, it is reasonable to use the optical phonon frequency at the Γ-point for simulation.

Inelastic neutron scattering (INS) and Inelastic X-ray scattering (IXS) could reveal the full phonon dispersion relations of solid-state materials. Unfortunately, our sample is not suitable for these techniques. INS requires high-quality samples, specifically millimeter-sized crystals that can withstand high-energy neutron scattering without decomposition. Additionally, samples must be fully deuterated to minimize the interference of hydrogen atoms with coherent phonon signals. The crystal sizes of our samples do not meet these requirements. The size of MgHOTP crystallite is below 10 μm and the size of TiHOTP crystallite is less than 400 nm (Figure R2A, C). Moreover, achieving complete deuteration of the phenyl rings in HOTP is particularly challenging (*Nat. Commun.* **2020**, *11*, 1751). While IXS has lower requirements for crystal size and does not demand deuteration, it requires the sample to be stable under the strong synchrotron X-ray. For this reason, very few molecular crystals have been characterized with this technique, and those that have been characterized typically have near millimeter-size crystals (*Nat. Commun.* **2023**, *14*, 1653). Besides, calculation of the phonon dispersion relations is also very challenging for MgHOTP and TiHOTP as their unit cells contain hundreds of atoms. In summary, our samples do not meet the basic requirements for INS and IXS, making related characterization difficult. We hope that advancements in crystal growth, calculation methods, and instrumentation will facilitate further research for such systems.

**(6) I am not convinced that the interpretation of spin relaxation in terms of a direct mechanism and a power law is correct. I suspect that multiple (pseudo) localized phonon modes might be a better fit here. The fitting of the low-T data is poor, and a high-T limit of T$^2$ of some low-energy mode contributing to Raman seems a better fit. A second high energy mode might be required to fit at high energy, although the physical nature of this is under debate: arXiv:2407.01380 (2024). Frequency-dependent measurements of T1 (X vs Q-band) could help distinguish Raman and Direct relaxation, with the former independent from frequency. This might not change the overall interpretation of experiments but would give a better understanding of what phonons are relevant in the process.**

**Response:** We would like to express our sincere appreciation to your very insightful suggestions, which are dramatically helpful for us to improve our manuscript.

To articulate spin-lattice relaxation mechanisms, we conducted W-band (94 GHz) pulse EPR spectroscopic characterization on newly synthesized MgHOTP and TiHOTP samples across 10–93 K (Figure R7). Compared with $T_1$ values acquired at X-band, $T_1$ values of MgHOTP decreased at 10–53 K, while those of TiHOTP decreased at 10–73 K. This behavior appears characteristic of the direct process, but the observed trends do not scale with $B^2$ or $B^4$ (B represents the magnetic field strength). Consequently, it seems that multiple relaxation processes are involved in the low-temperature region. Above the inflection point, the $T_1$ closely align with those obtained from X-band pulse EPR measurements, suggesting that the Raman process or local-mode processes become dominant in this region.

We have incorporated this section into Page 9−10 of the main text and Page 30−31 of Supplementary Information (Supplementary Figure 20 and Table 9, 10).
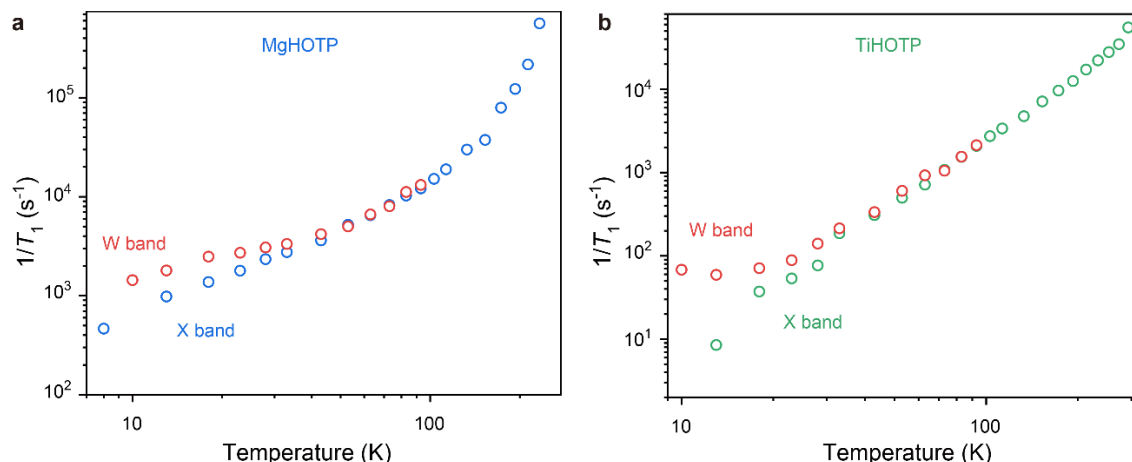


**Figure R7.** Variable-temperature $T_1$ of **a,** MgHOTP and **b,** TiHOTP acquired at X-band and W-band.

Accordingly, we analyzed the temperature dependencies of $T_1$ for MgHOTP, MgHOTP-D$_2$O, and TiHOTP with the following equation:

$$\frac{1}{T_1} = A_{Dir}T + A_{Ram}(\frac{T}{T_D})^9 \int_0^{\frac{T_D}{T}} x^8 \frac{e^x}{(e^x-1)^2} dx + \sum_i A_{i,Loc} \frac{e^{h\nu_i/k_BT}}{(e^{h\nu_i/k_BT}-1)^2} \dots\dots\dots\dots \text{Equation R4}$$

where the three terms describe the direct process, Raman process, and the sum of multiple local-mode processes. After many trials (see detailed discussions in Supplementary Section 11), we found that the spin-lattice relaxation behavior of MgHOTP can be simulated by the direct process and two local-mode processes with phonon wavenumbers of 24 cm$^{-1}$ and 1489 cm$^{-1}$, respectively. The latter two indicate that the extended hydrogen-bonded networks and the C−O stretches cause spin-lattice relaxation in different temperature regions. Simulation for MgHOTP-D$_2$O revealed contributions from the direct process and a local-mode process with the phonon wavenumber of 15 cm$^{-1}$. The latter reinforces the essential role of the extended hydrogen-bonded networks in spin-lattice relaxation. The temperature dependence of $T_1$ of TiHOTP can be simulated by the direct process, the Raman process with the Debye temperature of 302 K, and a local-mode process with the phonon wavenumber of 1459 cm$^{-1}$. Thus, the high Debye temperature helps improve the $T_1$ of TiHOTP.

With these simulation results, we fitted $1/T_1$ vs. T data for MgHOTP and TiHOTP with Equation R4 and obtained decent fitting results (Figure R8, R9). This analysis helps us identify the optical phonons that are responsible for the spin-lattice relaxation, and it greatly improves the depth of mechanistic discussion in our manuscript. We sincerely thank you for your great advice.

We have incorporated this discussion into Pages 9−13 of the main text (Figure 4 and Figure 5b) and Pages 32–41 of Supplementary Information (Supplementary Figure 21–26, and Table 11).
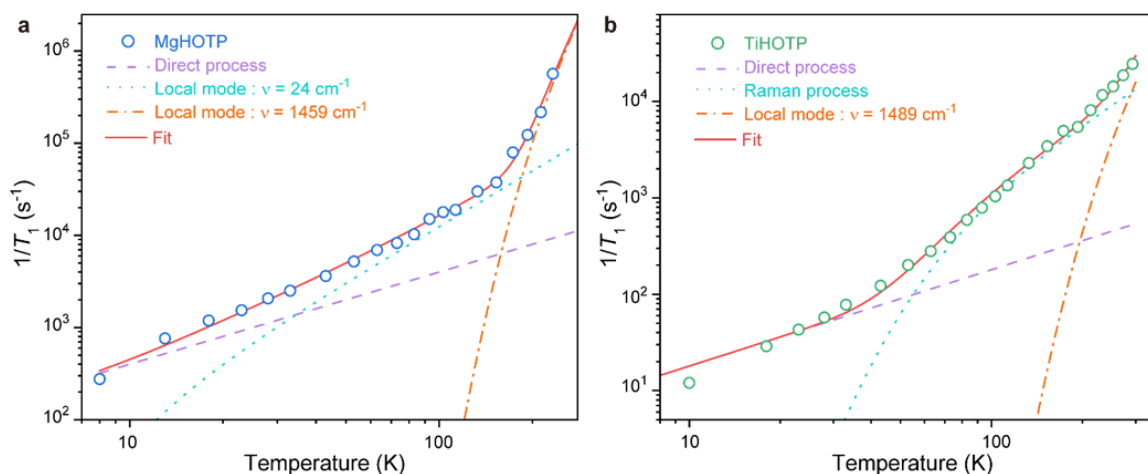
**Figure R8.** Spin-lattice relaxation rates ($1/T_1$) of **a,** MgHOTP and **b,** TiHOTP acquired at various temperatures and their fitting results based on Equation R4. Circles represent experimental data. Red solid lines represent overall fits. Purple dash lines represent contributions from direct processes. Light blue dot lines represent contributions from the local-mode process driven by the 24 cm$^{-1}$ optical phonon for MgHOTP or the Raman process for TiHOTP. Orange dash-dot lines represent contributions from local-mode processes driven by C−O stretches in semiquinone moieties.
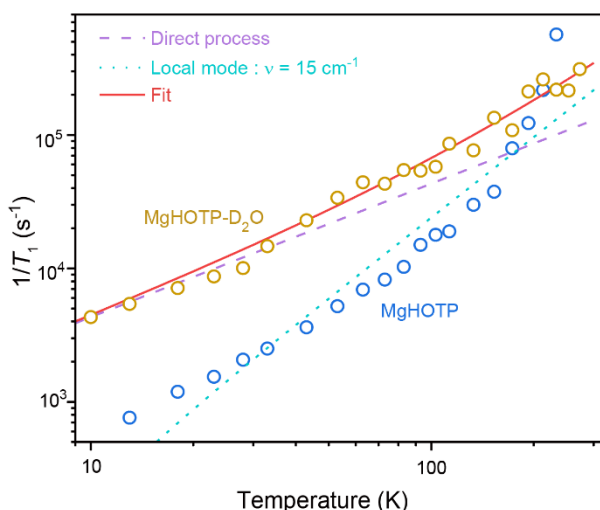


**Figure R9.** Spin-lattice relaxation rates of MgHOTP and MgHOTP-D$_2$O. Circles represent experimental $1/T_1$ data acquired at various temperatures. Simulation results are only shown for MgHOTP-D$_2$O. The red solid line presents the overall fit. The purple dash line and light blue dot line represent contributions from the direct process and the local-mode process driven by the 15 cm$^{-1}$ optical phonon for MgHOTP-D$_2$O, respectively.

(7) Fig. 4a, what are the dashed lines? Make the caption more descriptive.

**Response:** We apologize for this confusion. The dashed lines were meant to clarify the wavenumbers of Raman peaks of MgHOTP-D$_2$O. We agree with you that deuteration should shift some phonons towards lower frequencies, as exemplified by the red shift of the peak at 175 cm$^{-1}$ to 169 cm$^{-1}$ and another peak at 24 cm$^{-1}$ to 15 cm$^{-1}$. We have re-drawn the figure of Raman spectra and have explained the meaning of these dash lines in the figure caption (Figure R6; Figure 5a in the revised manuscript).

(8) BLS does not reveal any phonon below 10 cm$^{-1}$, whilst there must be acoustic phonons in that energy window. Why is the technique not sensitive to those? Is it possible that the technique is insensitive to optical phonons for similar reasons?

**Response:** Thank you for raising these concerns. Diffuse-reflence UV-Vis absorption characterization of MgHOTP and TiHOTP revealed that they could absorb a wide range of visible light (Figure R2). Meanwhile, the thermal conductivity of MQFs is generally poor, making them susceptible to damage under high-power laser (Figure R10C−F). Therefore, we typically use low laser powers (0.1 or 0.2 mW) for Raman and BLS spectroscopic characterization (Fig. R10A, B). However, the collection efficiency of BLS spectroscopy is significantly lower than that of Raman spectroscopy, making it more difficult to acquire BLS signals. Additionally, the Fabry-Pérot interferometer of our BLS spectrometer is only suitable for the 532 nm laser, which is not the most appropriate excitation wavelength. The BLS signals could be weak under 532 nm excitation (the optimal excitation wavelength is 633 nm; please see detailed discussions in the answer to question 4 raised by Reviewer 1 and in Supplementary Section 7).

We attempted to extend the integration time of BLS experiments but did not observe low-frequency phonons. In addition to the abovementioned reasons, we suspect that the acoustic phonon DOS could be low in MgHOTP and TiHOTP such that they do not show up in BLS spectra. There could be optical phonons below 8 cm$^{-1}$ (lower wavenumber limit of Raman spectroscopy) that was not discerned by BLS spectroscopy, and optical phonon dispersion typically shows lower energy at the zone edge than at the Γ-point. With these concerns, we only provide the upper limit of Debye temperature based on vibrational spectroscopic characterization. We look forward to further advancements in BLS techniques to improve signal collection efficiency, enabling the study of low-frequency phonons in the MQFs. We have also designed and synthesized other MQFs that exhibit decent BLS signals at room temperature, which will be reported in the future.
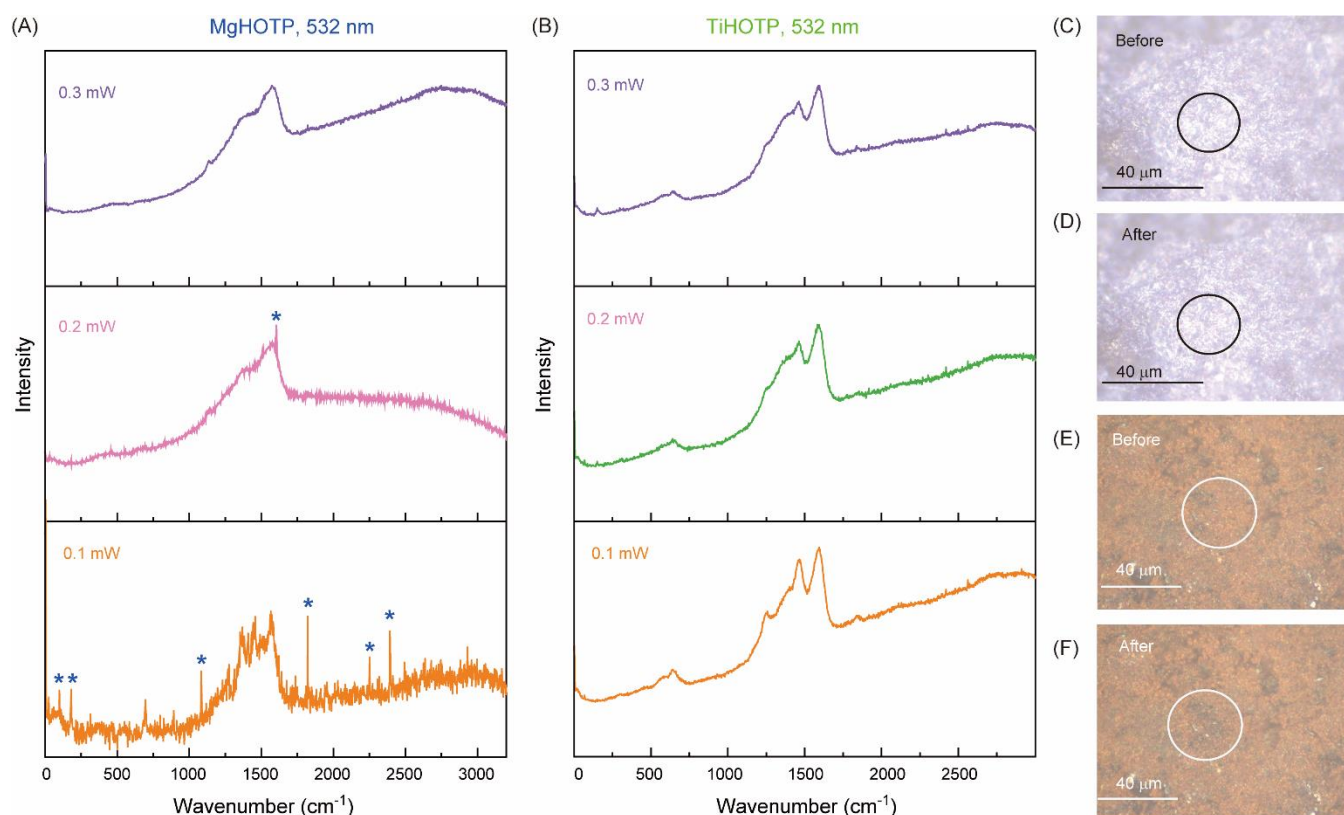


**Figure R10.** Raman spectra of (A) MgHOTP and (B) TiHOTP acquired at different laser powers. Peaks marked with asteroids are caused by cosmic rays. Optical micrographs of (C, D) MgHOTP and (E, F) TiHOTP before and after laser illumination.

(9) The authors claim that DFT does not show any vibration below 200 cm$^{-1}$ for TiHOTP but Supp. Fig. 18 clearly shows at least 6 modes with weak Raman intensity. Can the authors provide the list of computed normal modes? Why have these been discarded

**Response:** We apologize for the misunderstanding in this statement. The calculated molar absorption coefficients of normal modes below 200 cm$^{-1}$ are very small for TiHOTP, so the corresponding vibrational intensities are

negligible (Supplementary Figure 19). We have made corrections to the discussion of DFT results in Page 8 of the main text. We have also added molar absorption coefficients of normal modes of MgHOTP and TiHOTP into the Supplementary Information (Supplementary Table 7 and Table 8).

# Response Letter

We thank the reviewers for their efforts on reviewing our manuscript and providing invaluable suggestions and comments for us to improve it.

## Reviewer 1

I want to thank the authors for making such a great and thorough effort to address my concerns. I think this paper is much stronger now and happy to recommend it for publication.

**Response:** Thank you for your positive evaluation of our manuscript.

## Reviewer 2

I support publication in its present form.

**Response:** Thank you for your positive evaluation of our manuscript.