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Room-Temperature Quantitative Quantum Sensing of Lithium Ions with a Radical-Embedded Metal–Organic Framework

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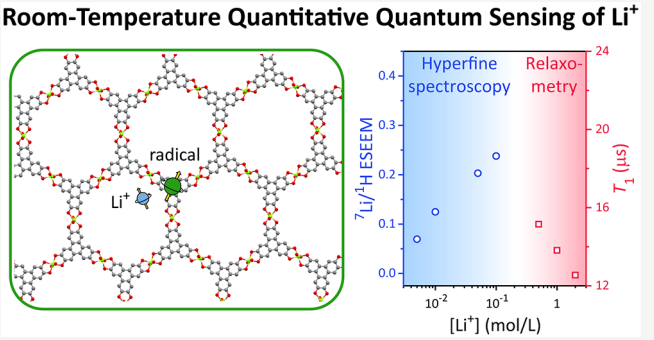
ABSTRACT: Recent advancements in quantum sensing have sparked transformative detection technologies with high sensitivity, precision, and spatial resolution. Owing to their atomic-level tunability, molecular qubits and ensembles thereof are promising candidates for sensing chemical analytes. Here, we show quantum sensing of lithium ions in solution at room temperature with an ensemble of organic radicals integrated in a microporous metal–organic framework (MOF). The organic radicals exhibit electron spin coherence and microwave addressability at room temperature, thus behaving as qubits. The high surface area of the MOF promotes accessibility of the guest analytes to the organic qubits, enabling unambiguous identification of lithium ions and quantitative measurement of their concentration through relaxometric and hyperfine spectroscopic methods based on electron paramagnetic resonance (EPR) spectroscopy. The sensing principle presented in this work is applicable to other metal ions with nonzero nuclear spin.



INTRODUCTION

Quantum sensing exploits quantum phenomena to measure physical quantities including magnetic field, electric field, temperature, pressure, pH, time, and frequency, among others.[1] The ability to coherently address single qubits and qubit ensembles has sparked revolutionary sensing technologies with nanoscale spatial resolution as well as ultrahigh sensitivity and precision,[1] enabling atomic-level magnetic resonance imaging,[2] single-molecule magnetometry,[3,4] and magnetic imaging of living cells.[5]

Despite these advances and applications, an outstanding open challenge is to apply quantum sensing for quantifying chemical analytes in ambient conditions, which could be instrumental for a range of technologies spanning biological systems and energy storage devices.[6−8] The vast majority of qubits, including superconducting circuits,[9] semiconductor quantum dots,[10] trapped ions,[11] and neutral atoms,[12] have limited application in ambient conditions because they typically require cryogenic temperature and/or strictly controlled environments. Although qubits based on solid-state defects such as nitrogen–vacancy (NV) centers in diamond can operate at room temperature and have been used to detect chemical analytes through T_1 relaxometry[13] and magnetic resonance spectroscopy,[3,4,14] they are typically buried inside the insulating solid, preventing close contact and strong interaction with chemicals.[4,6] Furthermore, solid-state defect qubits most often lack designability and tunability that are critical for selective and simultaneous sensing of multiple species.[6] To this end, molecular qubits, a class of paramagnetic molecules that exhibit electron spin coherence,[15] are promising alternative candidates that can be modified with selective and strong binding sites for chemical analytes[16] and, in certain cases, can operate at room temperature.[17−22] Integrating solid-state materials with molecular qubits can therefore create a powerful new platform for quantum sensing.

Recent research on molecular qubits based on transition-metal or lanthanide electron spin centers[15,23−25] has revealed design rules for achieving millisecond phase memory time[26,27] or optical addressability[28] at cryogenic temperature and has established strategies to construct spatially ordered molecular qubit arrays.[29,30] Nonetheless, except for a small number of examples with Cu(II), V(IV), or Y(II) as spin centers,[17−22] most metal-based molecular qubits do not operate at room temperature due to fast spin–lattice relaxation induced by spin–orbit couplings at the metal sites.[20,31,32] In this regard, organic radicals with unpaired electron spins residing on light atoms with negligible spin–orbit coupling, such as carbon,

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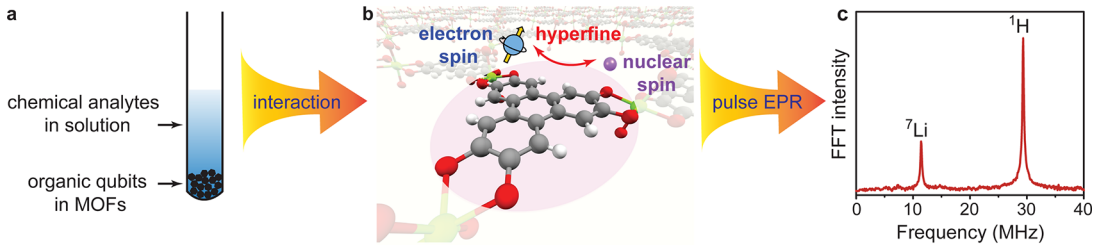

Figure 1. Room-temperature quantum sensing using organic radicals in MOFs. (a) MOF particles with organic qubits are suspended in a solution containing the desired analyte, in this case a solution of $LiClO_4$ in THF. (b) Chemical analytes are adsorbed into the MOF and interact with the embedded radicals through hyperfine coupling. The pink circle indicates that the electron spin delocalizes throughout the HOTP ligand. (c) Nuclei interacting with the radical qubit can be identified based on the hyperfine spectrum, which further allows quantification of the chemical analytes.

nitrogen, and oxygen, are promising alternatives. When dilute, these can maintain spin coherence at room temperature with microsecond-scale phase memory time.[31,33] Although these properties have enabled wide use of organic radicals as spin labels in biological systems[34] and as polarizing agents in dynamic nuclear polarization,[35] organic radicals remain unexplored for quantum sensing.

One powerful approach for achieving room-temperature quantitative sensing of chemical analytes is relaxometry, which probes spin relaxation to relay information about concentration.[36] Although widely used in magnetic resonance imaging and recently demonstrated for quantum sensors based on NV centers in diamond,[13] this technique still has limited application in chemical identification and simultaneous sensing of multiple analytes. A related, but potentially more versatile approach is the detection of nuclear hyperfine fields stemming from the coupling between an electron spin qubit and nuclear spins in its environment. This can be achieved by hyperfine spectroscopy, which can identify the nuclear species and possibly characterize coupling strengths (Figure 1c).[37] Because hyperfine fields are typically limited to short distances, close contact between the electron spin qubit and the target nuclei is a key requirement for implementing this sensing scheme.[6]

Because of their high surface area, MOFs are ideal hosts for molecular qubits to promote qubit−analyte accessibility. MOFs are porous ordered solids composed of inorganic and organic molecular building blocks.[38] They typically contain nanoscale or subnanoscale pores that have enabled their use in traditional sensing applications.[39,40] Previously, it has been shown that electron spins in microporous zeolites and MOFs can be used to detect guest species by hyperfine spectroscopy, but these demonstrations were performed at cryogenic temperatures (below 10 K) due to the limitation of electron spin coherence and/or sensitivity.[41−43] Here, we seek to incorporate organic radicals into the MOF backbone to enable room-temperature operability while preserving pore accessibility, leading to close radical−analyte contacts through adsorption (Figure 1b). In addition, MOFs can be elaborated as inert and insoluble solids for either liquid or solution phase analytes (Figure 1a). This suppresses radical tumbling typical for liquids[31] and improves detection sensitivity by concentrating the solid-embedded radicals to an extent that is unreachable with soluble species.

A material that showcases these concepts is $\{[Mg(H_2O)_2]_3HOTP_2\}\{[Mg(H_2O)_4]_3HOTP\}_2$ (MgHOTP, HOTP = 2,3,6,7,10,11-hexaoxytriphenylene), a new MOF bearing closed-shell metal ions, nanoscale pores, and organic radicals as the only paramagnetic centers (Figure 1). Besides avoiding electron−electron relaxation pathways, diamagnetic Mg^{2+} ions are ideal for this application because the high natural abundance of ^{24}Mg (90%), an isotope with zero nuclear spin, also minimizes electron−nucleus relaxation. The tritopic ligand 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) is a common building block in two-dimensional (2D) porous MOFs,[44] whose spontaneous oxidation generates a radical.[45,46] Using EPR spectroscopy, we demonstrate that the radicals in MgHOTP behave as electron spin qubits, whose quantum states can be partially polarized by an external magnetic field, manipulated by microwave pulses, and read out through electron spin echo schemes. We further demonstrate quantitative detection of lithium ions (Li^+) in solution at room temperature using MgHOTP qubits with relaxometry and hyperfine spectroscopy.

RESULTS AND DISCUSSION

Synthesis and Structure of MgHOTP. A solvothermal aerobic reaction between magnesium acetate and HHTP in a mixture of water and dimethyl sulfoxide yields MgHOTP as a navy-black microcrystalline powder composed of hexagonal rodlike single crystals, with the longest dimension ranging from 0.5 to 13 μm (Figures S1−S3). The single-crystal structure of MgHOTP was solved through a combined refinement of continuous rotation electron diffraction (cRED) and synchrotron powder X-ray diffraction (PXRD) data (Figures S4−S7, Table S1).[47,48] It consists of two components: extended 2D honeycomb sheets with the formula $[Mg(H_2O)_2]_3HOTP_2$ (Figure 2a,c) and isolated molecular clusters with the formula $[Mg(H_2O)_4]_3HOTP$ (Figure 2b,d; see discussion about charge assignment in the Supporting Information). The molecular clusters sit in-between neighboring sheets and manifest alternating interlayer spacing of 3.2 and 3.5 Å (Figure 2e); HOTP ligands in the clusters and those within the sheets are eclipsed with a rotation (Figure 2b). Cryogenic electron microscopy (cryo-EM) and fast Fourier transform (FFT) analysis of MgHOTP corroborate the structure obtained by cRED and PXRD (Figure 2f−h). The eclipsed stacking in MgHOTP leads to one-dimensional (1D) pores with a diameter of ∼1.4 nm (Figure 2a,b). This structure remains stable in ambient conditions, in solvents including tetrahydrofuran (THF) and water, and upon activation under vacuum at 60 °C (Figures S1 and S4). Activation produces a desolvated framework that exhibits a Brunauer−Emmet−Teller surface area of 481 m^2/g, as determined by N_2 adsorption at 77 K (Figures S8 and S9). Critically, these pores provide sufficiently large apertures for solvated metal ions to enter and interact with the HOTP radicals.

Organic Electron Spin Qubits in MgHOTP. There are two crystallographically distinguishable HOTP ligands in the

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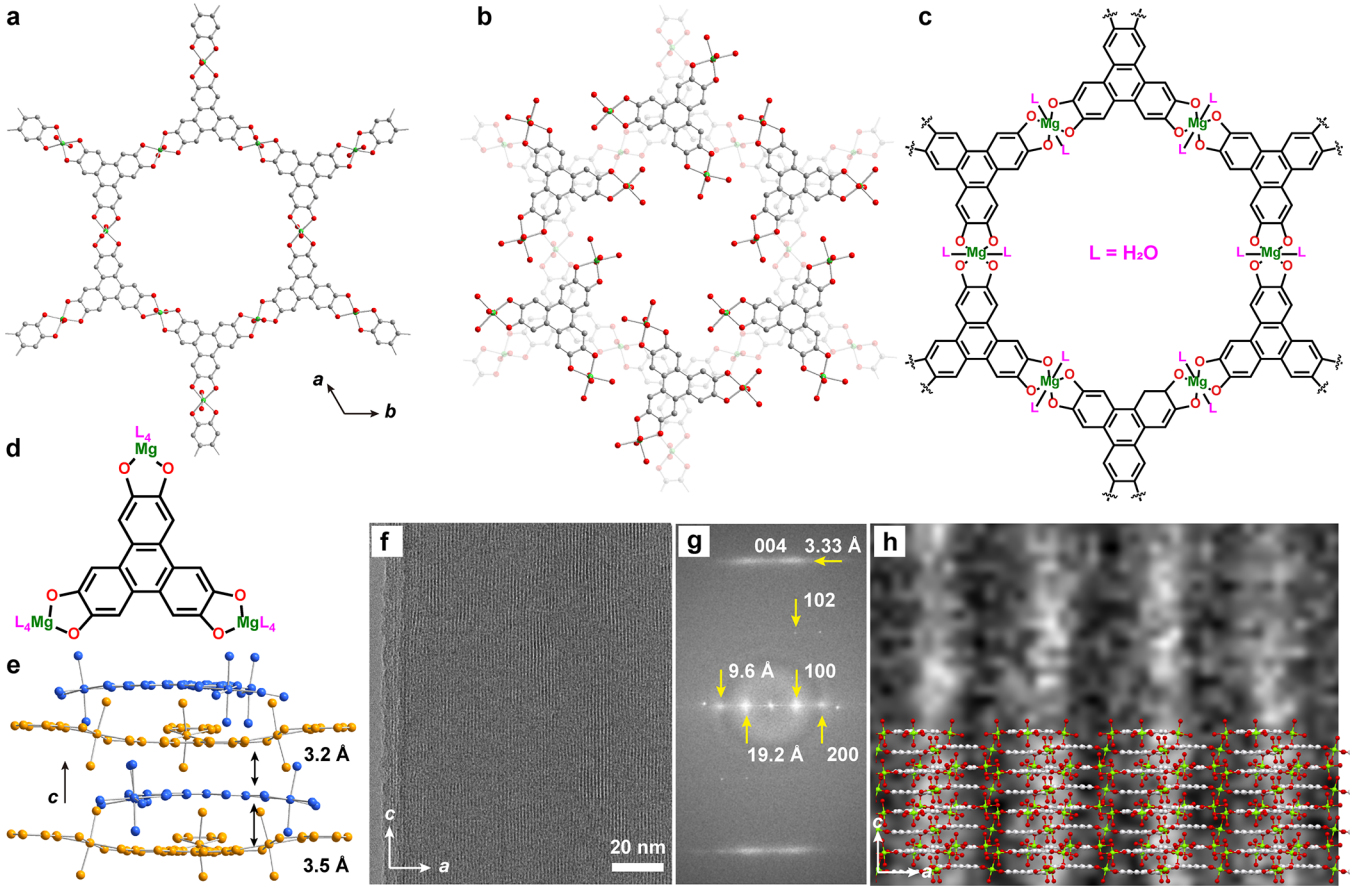

Figure 2. Single-crystal structure of MgHOTP derived from cRED and synchrotron PXRD. (a, b) Structural representation of single and double layers of MgHOTP viewed down the crystallographic *c*-axis, with (b) depicting the rotated eclipsed stacking between the clusters and the sheets. Green, red, and gray spheres represent Mg, O, and C atoms, respectively. H atoms are omitted for clarity. (c, d) Chemical structures of a portion of the $[Mg(H_2O)_2]_3HOTP_2$ sheet and one $[Mg(H_2O)_4]_3HOTP$ cluster, respectively. (e) View parallel to the crystallographic *ab*-plane, showing the deviation from planarity in the sheets (yellow) and the clusters (blue), as well as the two distinct interplanar distances. (f) Cryo-EM image of MgHOTP. (g) FFT of (f). (h) High-magnification micrograph from (f), with visible lattice fringes. High-contrast fringes perpendicular to the pore walls are spaced at 19.2 Å. They are overlaid with a structural model of MgHOTP showing the fringes that match well with the *d*-spacing along the crystallographic *a*-axis.

two structural components of MgHOTP. Each HOTP-centered radical may display one of three EPR-active oxidation states ($HOTP^{-}$, $HOTP^{3-}$, $HOTP^{5-}$).[49] To probe these organic radicals, we performed continuous-wave (CW) and pulse EPR measurements on MgHOTP crystallites at room temperature (296 K). The X-band (9−10 GHz) CW EPR spectrum displays a single resonance peak at $g = 2.00373$ with a Dysonian line shape and a line width of 0.33 mT (Figure 3a). The D-band (140 GHz) echo-detected field sweep (EDFS) spectrum further revealed *g* anisotropy values $g_{\parallel} = 2.00221$ and $g_{\perp} = 2.00497$ with anisotropic line broadening (Figure S10). These *g* values are typical for phenoxyl radicals.[45] Quantitative CW EPR analysis revealed that 1−2% of HOTP ligands contain a radical (Figure S11, Tables S2 and S3), corresponding to an electron spin concentration between 2×10^{-2} and 4×10^{-2} mol/L. Note that saturated solutions of the free-ligand HHTP in typical organic solvents such as THF do not show observable CW or pulse EPR signals. The relatively high radical concentration on HOTP is thus available only by integrating this ligand within the MOF.

Notably, only one type of spin center can be resolved even at the D band. The absence of other species infers the delocalized nature of the radical electron spins in MgHOTP. On the one hand, the HOTP-based radical is expected to be delocalized within each HOTP unit over the triphenylene core and the oxygen atoms, as suggested by previous computational studies on HHTP and related trimetallic clusters.[49] On the other hand, electrical characterization of other HOTP-based MOFs and analogues further revealed that electrons can hop between different HOTP moieties along the out-of-plane direction.[44,47,50] Such intra-HOTP and inter-HOTP electron delocalization is likely facilitated by in-plane π-conjugation and out-of-plane $\pi-\pi$ stacking interactions, respectively.[47] Because of such delocalization, the radicals residing on different structural components and with different oxidation states may not be discernible; accordingly, their contribution to the quantum sensing performance should be taken as an ensemble.

Pulse EPR characterization provided key evidence in testing qubit-type behavior of HOTP radicals. Appropriate microwave pulses can orient electron spin qubits on arbitrary positions, contrasting with electron spin bits used in regular spintronic devices, which exclusively use binary positions for information processing.[23,24] When electron spins behave like qubits, under magnetic field, they satisfy the Rabi relationship $\hbar\omega_{Rabi} = g\mu_B SB_1$, where $\hbar$ is the reduced Planck constant, ω_{Rabi} is the Rabi frequency, μ_B is the Bohr magneton, and B_1 is the microwave magnetic field strength. Importantly, under micro-

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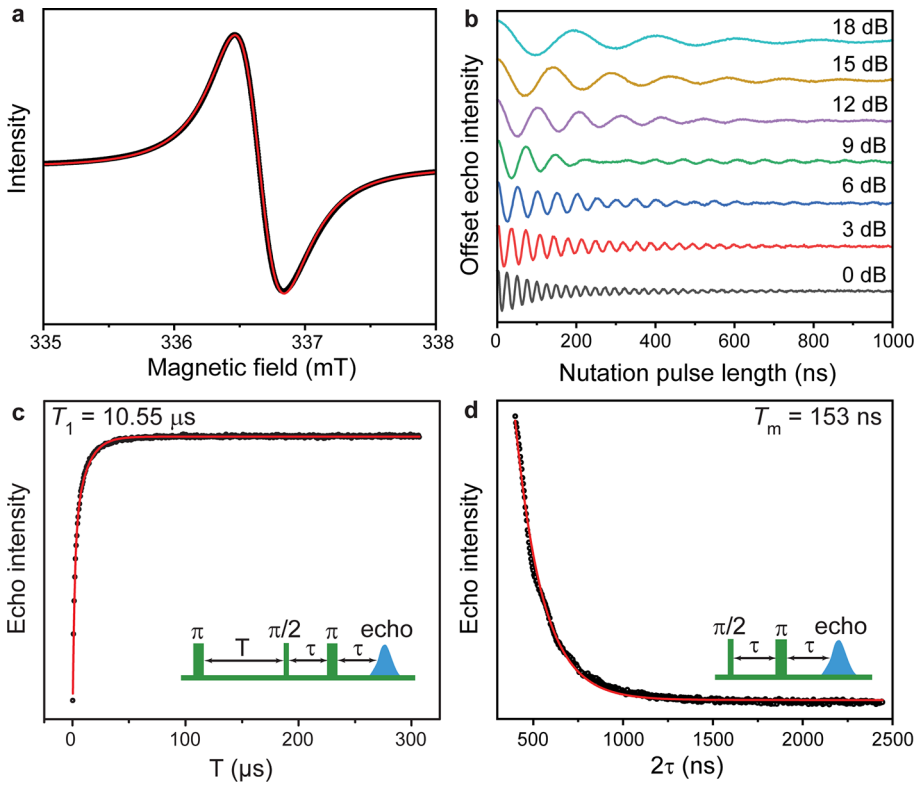

Figure 3. Organic electron spin qubits in dry powders of MgHOTP at room temperature. (a) CW EPR spectrum. The red line is the fitting curve obtained from Dysonian line shape using $S = 1/2$ and $g = 2.00373$. (b) Nutation experiments at various microwave attenuations. (c) Inversion recovery measurement of T_1. The red line is a biexponential decay fitting curve. Inset: pulse sequence for the inversion recovery experiment. (d) Hahn echo decay measurement of T_m. The red line is a monoexponential decay fitting curve. Inset: pulse sequence for the Hahn echo decay experiment. These data were collected with X-band EPR at 296 K.

wave pulses of various power and length, MgHOTP exhibits oscillations of spin orientations with frequencies ω_{Rabi} that are linearly dependent on B_1 (Figures 3b and S12), providing key evidence that radicals in MgHOTP are suitable for single-qubit quantum gate operations.[24] More practically, an electron spin qubit must also possess long spin−lattice relaxation time (T_1) and phase memory time (T_m) to ensure sufficient duration of its polarization and coherence.[31,51] To measure T_1 and T_m, we employed inversion recovery and Hahn echo decay pulse sequences, respectively, on dry powders of MgHOTP. Depending on the synthetic conditions of each batch of MgHOTP, these measurements gave room-temperature values of T_1 ranging from 9.48 to 21.34 μs and T_m ranging from 153 to 239 ns at 296 K (Figures 3c,d and S13), qualifying MgHOTP as a potential candidate for quantum sensing of chemical analytes under ambient conditions.

Quantitative Quantum Sensing of Lithium Ions by MgHOTP. To demonstrate the utility of MgHOTP in quantum sensing, we targeted the detection of Li^+ ions because of their important role in energy-related and biological applications.[8] Additionally, Li^+ should show affinity toward the oxygen atoms lining the pores of MgHOTP,[52] and the major Li isotope, ^{7}Li (92.4% natural abundance), has a unique nuclear Larmor frequency, which minimizes potential interference from other nuclei. Treatment of MgHOTP powders with solutions of $LiClO_4$ in THF leads to incorporation of Li^+ within the MOF without significantly affecting its structural integrity (Figure S4), the g factor of the organic radical, or its qubit behavior (Figures S12 and S14, Table S4). However, T_1 and T_m changed when the concentration of Li^+ ($[Li^+]$) ranged between 0.1 and 2.0 mol/L, giving rise to relaxometric detection in this range. For instance, in a given MgHOTP batch whose dry powder exhibits T_1 = 10.55 μs and T_m = 153 ns (Figure 3c,d), when $[Li^+] < 0.1$ mol/L, both T_1 and T_m remain relatively constant (T_1 = 20−21 μs, T_m = 190−200 ns), but increasing $[Li^+]$ reduces both T_1 and T_m significantly, reaching T_1 = 12.55 μs and T_m = 169 ns for $[Li^+]$ = 2 mol/L (Figures 4a and S15, Table S5). Moreover, ^{6}Li solid-state nuclear magnetic resonance (NMR) spectroscopic studies showed a significant reduction of the nuclear T_1 of $^6Li^+$ upon incorporation into MgHOTP (Figures S16 and S17). These observations point toward radical−Li^+ hyperfine interaction, indicating close contact between Li^+ in the MgHOTP pores and the negatively charged atomic sites of the delocalized radicals as a result of Coulombic attraction. This hypothesis is corroborated by previous computational and crystallographic studies on alkali metal complexes with HHTP and catecholate derivatives.[52−56]

Interrogating the radical−Li^+ hyperfine interaction can provide much higher sensitivity for Li^+ sensing. This interaction can be probed by combination-peak electron spin echo envelope modulation (CP-ESEEM) spectroscopy,[37,57] which balances sensitivity, resolution, and acquisition time (Figure S18) by employing a four-pulse sequence ($\pi/2-\tau-\pi/2-T-\pi-T-\pi/2-\tau-$echo), with the nuclear spin precession modulating electron spin echo decay during evolution times T (Figure 4b). In the weak-coupling regime, where the hyperfine constant is much smaller than the nuclear Larmor frequency (ω_I), as is the case for MgHOTP radical−^{7}Li and radical−^{1}H hyperfine interactions revealed by hyperfine sublevel correla-

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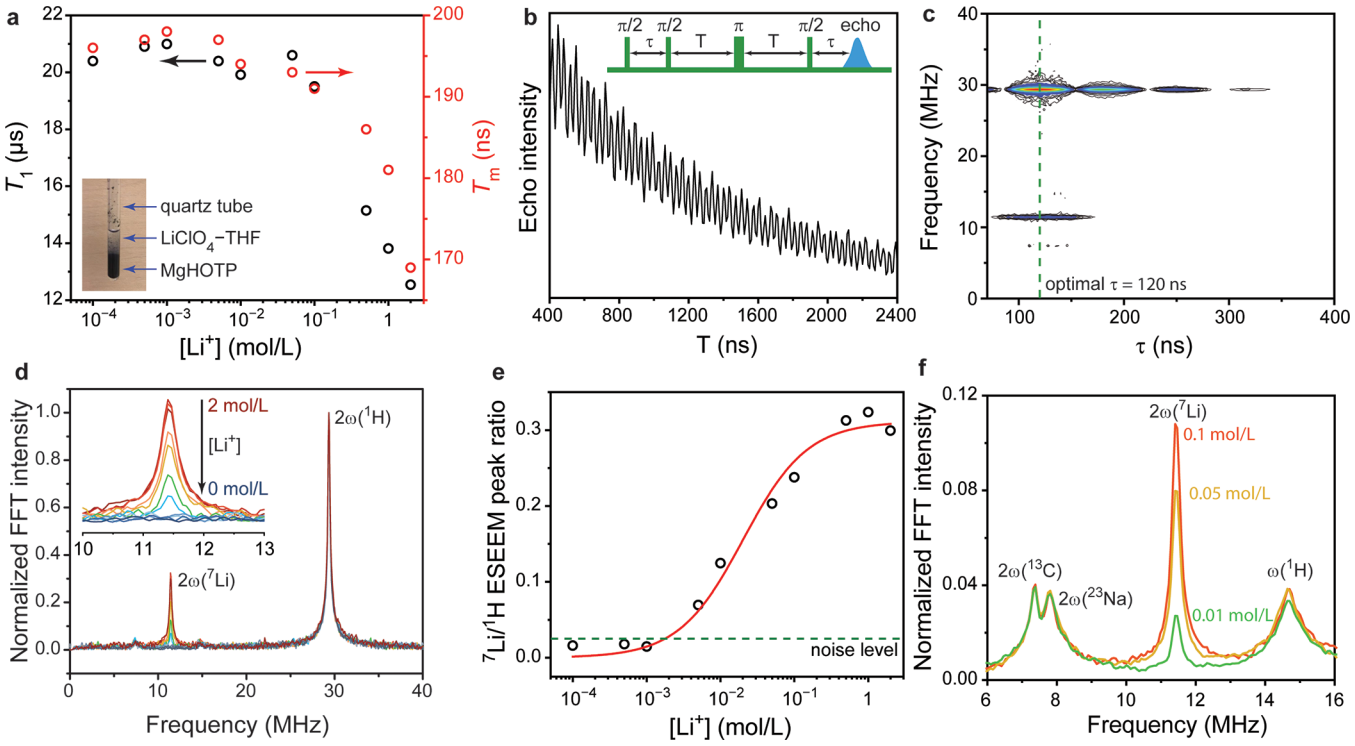

Figure 4. Quantitative sensing of Li^+ in THF solution by MgHOTP at room temperature. (a) T_1 and T_m of MgHOTP in THF solutions of $LiClO_4$ with various $[Li^+]$. Inset: picture of a sample for the EPR measurement. (b) Portion of a time-domain CP-ESEEM spectrum of MgHOTP in a THF solution of $LiClO_4$ where $[Li^+]$ = 2.0 mol/L. This measurement takes ~40 min to gain high signal-to-noise ratio. Inset: pulse sequence of CP-ESEEM. (c) 2D spectrum of CP-ESEEM collected with various τ values. (d) Frequency-domain CP-ESEEM spectra of MgHOTP in THF solutions of $LiClO_4$ with various $[Li^+]$. The spectra were normalized to the $2\omega(^1H)$ peaks. Inset: zoom-in view on the $2\omega(^7Li)$ peaks. (e) Relationship between $2\omega(^7Li)$/ $2\omega(^1H)$ ESEEM peak ratio and $[Li^+]$. The former was calculated by dividing the maximum of the $2\omega(^7Li)$ peak with the maximum of the $2\omega(^1H)$ peak in each spectrum. Red curve represents fit of the data to the Langmuir adsorption model. Green dashed line represents the noise level estimated based on the spectrum of MgHOTP in pure THF. (f) Frequency-domain CP-ESEEM spectra of MgHOTP in THF solutions with 0.1 mol/L $NaClO_4$ and various concentrations of $LiClO_4$. The spectra were normalized to the $2\omega(^1H)$ peak, which is not shown for clarity.

tion (HYSCORE) spectroscopic studies (Figures S19 and S20), the frequency-domain CP-ESEEM spectrum displays peaks at $2\omega_I$ of the hyperfine nuclei.[37] Therefore, CP-ESEEM can serve as a decisive technique for the detection of various elements, ^7Li and ^1H in this case, that bear distinguishing Larmor frequencies.

The X-band CP-ESEEM spectrum of MgHOTP soaked in a THF solution with $[Li^+]$ = 2 mol/L displays two peaks at 11.41 and 29.34 MHz under a field of 344.53 mT, corresponding to $2\omega_I$ of ^7Li and ^1H, respectively (Figure 4d). These peaks reflect the modulation of the HOTP electron spin by the nuclear spins of ^7Li and ^1H in the subnanometer proximity. They decisively identify ^7Li and ^1H in the environment surrounding HOTP. The ^1H peak relates to MOF components or guest solvent molecules, as also confirmed by control CP-ESEEM studies of MgHOTP in deuterated solvents (Figures S21–S23). In contrast, the ^7Li peak unambiguously confirms that MgHOTP behaves as a quantum sensor for Li^+ at room temperature. The absence of ^{35}Cl and ^{37}Cl signals in CP-ESEEM spectra suggests negligible interaction between the MgHOTP qubits and ClO_4^-, likely due to Coulombic repulsion between the anions and the oxygen-rich pore surface of the framework. Indeed, CP-ESEEM signals from anions are also absent when employing other Li^+ salts such as LiCl and LiBr (Figure S24), demonstrating the selectivity of MgHOTP toward cations.

Notably, CP-ESEEM with MgHOTP enables quantitative detection of even lower concentrations of Li^+ because the ESEEM signal from ^7Li can be referenced to that of an internal standard, here ^1H (see theoretical analysis in the Supporting Information).[58,59] We took advantage of the narrow line width of MgHOTP (Figures 3a and S25)[51] and adopted an optimal CP-ESEEM delay time τ = 120 ns, which gives maximum modulation depth from ^7Li (Figures 4c and S26–S28). With these parameters, all CP-ESEEM measurements display ^1H peaks with the same line shape for any $[Li^+]$ in the range 1×10^{-4}–2 mol/L (Figure 4d), showing minimal influence of ^7Li nuclear spins on the radical–^1H interactions. For $[Li^+] \geq 5 \times 10^{-3}$ mol/L, the relative peak intensity of ^7Li increases sigmoidally with $\log[Li^+]$, approaching a plateau above 0.5 mol/L (Figures 4e, S29, and S30, Tables S6–S8).

This relationship fits well to the Langmuir adsorption model,[60] which leads to the following correlation with the ESEEM intensity (see detailed discussion in the Supporting Information):

$$\frac{I_{^7Li}}{I_{^1H}} = c_k \frac{K_{eq}[Li^+]}{1 + K_{eq}[Li^+]}$$

Here, $I_{^7Li}$ and $I_{^1H}$ represent the ESEEM intensity of ^7Li and ^1H, respectively, c_k is a prefactor, and K_{eq} represents the equilibrium adsorption constant. The Langmuir adsorption model describes monolayer physical adsorption on a surface. It

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suggests that sensing with MgHOTP is reserved to Li^+ ions proximal to the pore surface, as would be expected given the fast decay of the radical−^{7}Li hyperfine interaction with distance. Interestingly, the Langmuir behavior provides thermodynamic data that calibrate the strength of Li^+ adsorption onto MgHOTP: fitting the data to the above equation gives $K_{eq} = 49.5 \pm 10.2$ L/mol, consistent with a weak Li^+−MOF interaction.[61] Altogether, these results demonstrate that using CP-ESEEM with MgHOTP enables quantitative sensing of Li^+ ions in the range 5×10^{-3}−0.5 mol/L under ambient conditions, a 2 orders of magnitude improvement over relaxometry. CP-ESEEM and relaxometry are nevertheless complementary: their combination enables an effective quantum sensing range of 5×10^{-3}−2 mol/L.

Crucially, the principles and methods above can be extended to the detection of other metal ions with nonzero nuclear spin and, by extension, should allow simultaneous detection of multiple metal ions that display distinguishable Larmor frequencies. We demonstrated this concept by using a sample of MgHOTP soaked in a THF solution of 0.1 mol/L $LiClO_4$ and 0.1 mol/L $NaClO_4$. The CP-ESEEM spectrum of this sample at 296 K under a field of 344.64 mT revealed a peak at 7.81 MHz, the expected $2\omega_I$ value for ^{23}Na, in addition to peaks corresponding to ^{1}H, ^{7}Li, and ^{13}C (Figure 4f). The ^{23}Na peak is significantly weaker than the ^{7}Li peak, indicating weaker interaction between the framework and Na^+. With the $2\omega_I$ of ^{1}H peak as an internal reference, decreasing the $[Li^+]$ to 0.05 and 0.01 mol/L while maintaining a constant $[Na^+]$ caused concomitant decrease in the intensity of the ^{7}Li peak without distinguishable changes in the ^{23}Na peak (Figures 4f and S31, Table S9). These experiments demonstrate that MgHOTP is capable of simultaneous detection of Li^+ and Na^+ as well as quantification of Li^+ in the presence of Na^+. Because sensitivity is a proxy for the binding strength of metal ions to MgHOTP, it is reasonable to expect that quantum sensing of divalent and multivalent metal ions would be even more efficient. Applying this methodology to multivalent ions and particular combinations of ions relevant for different technologies are obvious future extensions for this work.

Potential Strategies to Improve Sensitivity. The detection limit of Li^+ (5×10^{-3} mol/L) in our current setup highlights a conceptually novel detection technique but evidences limitations relative to optical or electrochemical sensing strategies,[8,62] which can quantify Li^+ at the ppm level. Nonetheless, we expect the sensitivity would improve by optimizing material design and the quantum sensing protocols.

For instance, because the proportion of HOTP bearing radicals is merely 1−2% of all the ligands in MgHOTP, some of the Li^+ interacting with MgHOTP remains undetectable. Thus, MOFs possessing higher concentrations of electron spins should give rise to significant sensitivity enhancement. However, as high spin concentration leads to stronger electron−electron dipolar interaction, which tends to reduce T_1 and T_m,[31] additional strategies, such as engineering the interspin distance, would have to be considered. This has been recently demonstrated in two MOFs containing copper porphyrin moieties, whose T_m remains nearly 50 ns at 10 K even with a high spin density of 0.30−0.35 mol/L.[29,30]

Further improvements may be observed by employing hyperfine spectroscopic methods based on dynamical decoupling.[63,64] Specifically, implementing a microwave pulse train as a frequency filter could suppress environmental magnetic noise, improve coherence, and amplify the frequency corresponding to the analyte, thus enhancing sensitivity.[1,64]

CONCLUSIONS AND OUTLOOK

The foregoing results convey the first demonstration of room-temperature quantum sensing using a MOF containing organic qubits. Relaxometry and CP-ESEEM combine to provide a wide range (5×10^{-3}−2 mol/L) of sensitivity for Li^+ ions as well as direct quantification of mixed ion solutions. This range is sufficient for quantitative detection in battery applications, where $[Li^+]$ is typically at least millimolar.[7,65]

The demonstration of quantum sensing herein is limited to metal ions in weakly polar solvents with a relatively high concentration. Nonetheless, the methodology derived in this work suggests several clear directions that could offer additional breadth and utility. Functionalization of the MOF with specific metal-binding groups should further enhance selectivity for those ions,[16] while integration of positively charged radicals, e.g., tetrathiafulvalene radical cations,[66] may enable anion sensing. MOFs incorporating various binding sites may be applicable for simultaneous quantitative sensing of multiple species that possess nonzero nuclear spin. Moreover, adapting this methodology to lower frequency EPR measurements, where the microwave permittivity of strongly polar solvents is much higher,[67] should further broaden the utility of this quantum sensing protocol to biological and battery-related applications. Finally, the quantum sensing principles demonstrated herein are transferrable to other pulse EPR techniques. Ultimately, single ion/molecule sensitivity may be achieved by addressing single molecular electron spin qubits with optically or electrically detected magnetic resonance.[28,68]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c07692.

Full descriptions of experimental methods, electron diffraction micrographs, PXRD patterns, thermogravimetric analysis, N_2 adsorption isotherm, quantitative EPR analysis, solid-state nuclear magnetic resonance spectroscopic studies, pulse EPR characterization results, and theoretical analysis for quantitative sensing by CP-ESEEM (PDF)

Accession Codes

CCDC 2103823 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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J. Am. Chem. Soc. XXXX, XXX, XXX−XXX

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