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 T1 relaxometry13 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 analytes16 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 centers15,23–25 has revealed design rules for achieving millisecond phase memory time26,27 or optical addressability28 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, 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 systems34 and as polarizing agents...
in dynamic nuclear polarization, 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. Although widely used in magnetic resonance imaging and recently demonstrated for quantum sensors based on NV centers in diamond, 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). 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.

Thanks to 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. They typically contain nanoscale or sub-nanoscale pores that can enable their use in traditional sensing applications. 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. 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, 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 MgHOTP, 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\textsuperscript{2+} ions are ideal for this application because the high natural abundance of \textsuperscript{24}Mg (90%), an isotope with zero nuclear spin, also minimizes electron–nuclear relaxation. The tritopic ligand 2,3,6,7,10,11-hexaoxytriphenylene (HOTP) is a common building block in two-dimensional (2D) porous MOFs, whose spontaneous oxidation generates a radical. 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\textsuperscript{+}) 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 rod-like single crystals, with the longest dimension ranging from 0.5 μm 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). It consists of two components: extended 2D honeycomb sheets with the formula of [Mg(H\textsubscript{2}O)\textsubscript{2}\textsubscript{2}]\textsubscript{2}HOTP\textsubscript{2} (Figure 2a, c) and isolated molecular clusters with the formula of [Mg(H\textsubscript{2}O)\textsubscript{4}]\textsubscript{2}HOTP (Figure 2b, d; see discussion about charge assignment in the Supporting Information). The molecular clusters sit between neighboring sheets and manifest alternating interlayer spacing of 3.2 Å 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 approximately 1.4 nm (Figure 2a, b). The desolvated framework exhibits a Brunauer–Emmet–Teller surface area of 481 m\textsuperscript{2}/g, as determined by N\textsubscript{2} adsorption at 77 K (Figure S8–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. To probe the HOTP-centered organic radicals, we performed continuous-wave (CW) and pulsed 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 linewidth of 0.33 mT (Figure 3a). The D-band (140 GHz) echo-detected field sweep (EDFS) gave $g$-anisotropy values $g_\parallel = 2.00221$ and $g_\perp = 2.00497$ (Figure S10). These $g$ values are typical for phenoxyl radicals. Quantitative CW EPR analysis revealed that 1–2% of HOTP ligands contain a radical (Figures S11, Table S2–S3), corresponding to an electron spin concentration between $2 \times 10^{-2}$ mol/L and $4 \times 10^{-2}$ mol/L. Note that saturated solutions of the free-ligand HHTP in typical organic solvents such as tetrahydrofuran (THF) do not show observable CW or pulsed EPR signals. The relatively high radical concentration on HOTP is thus available only by integrating this ligand within the MOF.

Pulsed 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. When electron spins behave like qubits, under magnetic field, they satisfy the Rabi relationship $\hbar \omega_{\text{Rabi}} = g \mu_B S B_1$, where $\hbar$ is the reduced Planck constant, $\omega_{\text{Rabi}}$ is the Rabi frequency, $\mu_B$ is the Bohr magneton, and $B_1$ is the microwave magnetic field. Importantly, under microwave pulses of various power and length, MgHOTP exhibits oscillations of spin orientations with frequencies $\omega_{\text{Rabi}}$ that are linearly dependent on $B_1$ (Figure 3b, Figure S12), providing key evidence that radicals in MgHOTP are suitable for single-qubit quantum gate operations. 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. 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 µs to 21.34 µs and $T_m$ ranging from 153 ns to 239 ns at 296 K (Figure 3c, d, Figure 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 towards the oxygen atoms lining the pores of MgHOTP,\(^50\) 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 the \(g\)-factor of the organic radical or its qubit behavior (Figures S12, S14, Table S4). However, \(T_1\) and \(T_m\) changed when the concentration of Li\(^+\) ([Li\(^+\)]) ranged between 0.1 mol/L 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 (\(T_1 = 20 \sim 21\) μs, \(T_m = 190 \sim 200\) 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 (Figure 4a, Figure S15, Table S5), likely a result of radical–Li\(^+\) hyperfine interaction. Indeed, \(^6\)Li solid-state nuclear magnetic resonance (NMR) spectroscopic studies confirmed a significant reduction of the nuclear \(T_1\) of \(^6\)Li\(^+\) upon incorporation into MgHOTP (Figures S16–S17).

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,\(^37,51\) which balances sensitivity, resolution, and acquisition time (Figure S18) by employing a 4–pulse sequence (\(\pi/2 - \tau - \pi/2 - T - \pi - T - \pi/2 - \tau - \text{echo}\)), 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 (\(\omega_N\)), as is the case for MgHOTP radical–\(^7\)Li and radical–\(^1\)H hyperfine interactions revealed by hyperfine sublevel correlation (HYSCORE) spectroscopic studies (Figure S19–S20), the frequency-domain CP-ESEEM spectrum displays peaks at \(2\omega_N\) of the hyperfine nuclei.\(^37\) Therefore, CP-ESEEM can serve as a decisive technique for the detection of various elements, \(^7\)Li and \(^1\)H in this case, that bear distinguishing Larmor frequencies.

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 Dyssonian line shape using \(S = \frac{1}{2}\) and \(g = 2.00373\). (b) Nutation experiments at various microwave attenuations. (c) Inversion recovery measurement of \(T_1\). The red line is a bi-exponential decay fitting curve. Inset: pulse sequence for the inversion recovery experiment. (d) Hahn echo decay measurement of \(T_m\). The red line is a mono-exponential decay fitting curve. Inset: pulse sequence for the Hahn echo decay experiment. These data were collected with X-band EPR at 296 K.
The X-band CP-ESEEM spectrum of MgHOTP soaked in a THF solution with [Li+] = 2 mol/L displays two peaks at 11.41 MHz and 29.34 MHz under a field of 344.53 mT, corresponding to $2\omega_{\text{Li}}$ and $1H$, respectively (Figure 4d). These peaks reflect the modulation of the HOTP electron spin by the nuclear spins of $\text{Li}^+$ and $1H$ in the subnanometer proximity. They decisively identify $\text{Li}^+$ 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 $\text{Li}^+$ peak unambiguously confirms that MgHOTP behaves as a quantum sensor for $\text{Li}^+$ at room temperature. The absence of $35\text{Cl}$ and $37\text{Cl}$ signals in CP-ESEEM spectra suggests negligible interaction between the MgHOTP qubits and $\text{ClO}_4^-$, 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 $\text{Li}^+$ salts such as LiCl and LiBr (Figure S24), demonstrating the selectivity of MgHOTP towards cations.

Notably, CP-ESEEM with MgHOTP enables quantitative detection of even small concentrations of $\text{Li}^+$, because the ESEEM signal from $\text{Li}^+$ can be referenced to that of an internal standard, here $1H$ (see theoretical analysis in Supporting Information).52,53 We took advantage of the narrow linewidth of MgHOTP (Figure 3a, Figure S25)49 and adopted an optimal CP-ESEEM delay time $\tau = 120$ ns, which gives maximum modulation depth from $\text{Li}^+$ (Figure 4c, Figures S26–S28). With these parameters, all CP-ESEEM measurements display $1H$ peaks with the same line shape for any [Li+] in the range $1 \times 10^{-4}$ mol/L to 2 mol/L (Figure 4d), showing minimal influence of $\text{Li}^+$ nuclear spins on the radical–$1H$ interactions. For [Li+] $\geq 5 \times 10^{-3}$ mol/L, the relative peak intensity of $\text{Li}^+$ increases sigmoidally with log[Li$^+$], approaching a plateau above 0.5 mol/L (Figure 4e, Figures S29–S30, Table S6–S8). This relationship fits well to the Langmuir adsorption model, which describes monolayer physical adsorption on a surface.54 It suggests that sensing with MgHOTP is reserved to $\text{Li}^+$ ions proximal to the pore surface, as would be expected given the fast decay of the radical–$\text{Li}^+$ hyperfine interaction with distance. Interestingly, the Langmuir behavior provides thermodynamic data that calibrate the strength of $\text{Li}^+$ adsorption onto MgHOTP: fitting the data to the Langmuir model gives an adsorption equilibrium constant of $49.5 \pm 10.2$ L/mol, consistent with a weak $\text{Li}^+$–MOF interaction.55 Altogether, these results demonstrate that using CP-ESEEM with MgHOTP enables quantitative sensing of $\text{Li}^+$ ions in the range of $5 \times 10^{-3}$ mol/L – 0.5 mol/L under ambient conditions, two-order of magnitude improvement over relaxometry. CP-ESEEM and relaxometry are nevertheless complimentary: their combination enables an effective quan-
tum sensing range of $5 \times 10^{-3}$ mol/L – 2 mol/L.

Crucially, the principles and methods above can be extended for 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 a sample of MgHOTP soaked in a THF solution of 0.1 mol/L LiClO$_4$ and 0.1 mol/L NaClO$_4$. A 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 $\omega_0$ 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 $\omega_0$ of $^1$H peak as an internal reference, decreasing the [Li$^+$] to 0.05 mol/L 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 (Figure 4f, Figure 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.

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 x $10^{-3}$ mol/L – 2 mol/L) of sensitivity for Li$^+$ ions, as well as direct quantification of mixed ion solutions. Although this Li$^+$ detection threshold is still not comparable with those of optical or electrochemical sensing strategies,$^{5,6}$ it is sufficient for quantitative detection in battery applications.$^7$ The sensitivity could be improved with high-frequency/high-field EPRs and by employing hyperfine spectroscopic methods based on dynamical decoupling,$^{27}$ which may as well assist studies of MOF-guest binding structures because these techniques reveal more detailed hyperfine spectra.

The quantum sensing methodology derived in this work suggest 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.$^{18}$ Adapting this methodology to lower-frequency EPR measurements, where the microwave permittivity of strongly polar solvents is much higher,$^{58}$ 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 pulsed EPR techniques. Ultimately, single ion/molecule sensitivity may be achieved by addressing single molecular electron spin qubits with optically or electrically detected magnetic resonance.$^{28,59}$

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is free of charge on the ACS Publications website.

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, pulsed EPR characterization results, and theoretical analysis for quantitative sensing by CP-ESEEM (PDF)

Accession Codes

The crystallographic information has been deposited in the Cambridge Crystallographic Data Center (CCDC) under accession code 2103823.

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Notes

The authors declare no competing financial interest.

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