Realizing Solution-Phase Room Temperature Quantum Coherence in a Tetrathiafulvalene-Based Diradicaloid Complex

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ABSTRACT: Molecular electron spins are promising candidates as scalable and tunable qubits but often suffer from air sensitivity or other undesirable decomposition pathways. Furthermore, significant spin–lattice relaxation and nuclear spin-mediated decoherence limit their applications. While significant advances in the synthesis of new molecular electron spin qubit candidates have led to improved coherence lifetimes, one key question is whether coherence can be maintained under conditions relevant for employment as quantum sensors, for instance in solution and at room temperature for sensing in biological systems. Here we report a tetrathiafulvalene-based molecular qubit candidate with spin centered on a nuclear spin-free bridging ligand. This unique air and water-stable scaffold exhibits a long spin decoherence time of hundreds of nanoseconds at ambient temperatures and in nuclear spin-rich protonated solvents. These results distinguish this system as a promising candidate for the development of novel room temperature, solution-phase quantum sensing technologies, and suggest that molecular electron spin qubits can be ideal candidates for these applications.

Introduction

Quantum information science (QIS) promises to revolutionize the fields of computation, cryptography, and sensing.1–3 Qubits, or quantum bits, form the basis for QIS; they are two-level systems that exist either in one of two states or a superposition of both.4 Electron spin qubits, particularly those which have coupled optical transitions, are especially promising due to optical addressability.5,6 The current state-of-the-art qubits which exhibit these properties are negatively charged solid-state defects in diamond called nitrogen–vacancy (NV) centers.7 NV centers are ground-state electron spin triplets. They display long spin decoherence times, or $T_2$, at room temperature, and can be initialized and read out optically; hence, they are featured in some of the most exciting applications of QIS, such as nanoscale magnetic resonance imaging, quantum metrology in living cells, and quantum networks.8–12 Paramagnetic molecules offer an alternative platform for QIS with potential advantages in site selective labeling, scalability, and tunability. However, molecular spins have historically suffered from poor quantum coherence, a key aspect of DiVincenzo’s criteria for qubit viability.5,13 Most paramagnetic molecules can therefore only be used as electron spin qubits at cryogenic temperatures where they exhibit sufficiently long $T_2$.14 This limits some applications such as quantum sensing in biological systems.15 The field has been actively working to improve $T_2$, with remarkable advances arising from nuclear spin-free ligands, molecular dilution, and clock-like spin state engineering.16–21 Meanwhile, various molecular design strategies, e.g. rigid ligands and reduction of orbital angular momentum, have been used to improve spin–lattice relaxation time, or $T_1$, which sets the upper limit of $T_2$ ($T_{2,max} = 2T_1$).22–24 While most of these advances have focused on metal-based qubits due to metal center spin-state and ligand field tunability, organic electron spin qubits offer possible advantages.25–30 Organic qubits typically consist of light elements which exhibit inherently weak spin-orbit coupling that reduces spin–lattice relaxation and increases $T_1$. Furthermore, C, O, and S all have >98% abundance of nuclear spin-free isotopes, so organic electron spin qubits composed of these elements have the potential for relatively long $T_2$ in ambient conditions. Peripheral H atoms provide nuclear spin which can cause decoherence, but strategies that minimize these moieties have led to spin qubits with excellent microsecond $T_2$ even at room temperature.31 This suggests
serve as spin qubits with are addressable electron spin qubit like could be optically excited and support a unique diradicaloid singlet ground state. Variational two-electron reduced density matrix (V2RDM) calculations predict a low-lying triplet state, with a small singlet-triplet gap. These calculations also predict that nearly all the ground and excited state spin density is centered on the central TTF core with slight diffusion to Pt (Figure 1B). Experimental data support a small singlet-triplet gap; the solution-phase magnetic moment of PtTTF is 1.37 μB at room temperature. Similarly, continuous-wave (CW) electron paramagnetic resonance (EPR) spectroscopic studies show decreasing signal with decreasing temperature, but persistent signals at temperatures as low as 15.2 K, consistent with thermal population of a low-lying triplet state (Figure S4).

We attempted to acquire magnetic susceptibility measurements on solid PtTTF, but the data is convoluted by aggregation and solid-state packing effects. Instead, we conducted variable-temperature Evans method measurements (Figure S11; see discussions in SI). The magnetic moment of PtTTF increases with temperature, similar to the CW EPR behavior. These data are limited by the liquid phase temperature window of the solvent (40 °C to −97 °C), but fits to the data suggest a singlet-triplet gap of <0.5 kcal/mol. With this evidence for a low-lying thermally populated triplet state in hand, we turned towards evaluating its viability as a qubit.

**Evidence of Room Temperature Coherence from EPR Spectroscopy**

We performed X-band (9-10 GHz) CW and pulse EPR measurements on a 0.05 mM/L dichloromethane solution of PtTTF at 296 K. The CW EPR spectrum displays significant hyperfine splitting (A) likely stemming from the 31P and 195Pt nuclear spins. The spectrum can be fit as an S = 1 diradical with g = 2.0046, D = 0, A(31P) = 1.1 MHz, A(195Pt) = 2.1 MHz (Figure 2A, Figure S3; see further discussions in SI). The g-factor is close to the free-electron value, 2.0023, consistent with an organic radical exhibiting weak spin-orbit coupling. This suggests a minimal orbital angular momentum contribution from Pt and the possibility of slow spin–lattice relaxation and long T1. The zero-field splitting is not well resolved at X-band frequencies which indicates negligible interaction between the two unpaired electrons. The hyperfine features are complicated by the 33.8% natural abundance of 195Pt (I = 1/2). As a result, there is a mixture of species with two, one, and zero 195Pt, respectively, all of which exhibit different hyperfine structures that contribute to a complex CW EPR spectrum.

**Results and Discussion**

**PtTTF Electronic Structure**

We have previously reported experimental and theoretical data on PtTTF that support a unique diradicaloid singlet ground state. Tetraphiafulvalene (TTF) systems, whose core is composed entirely of C and S, are exemplary candidates among nuclear spin-free organic qubits. They can be oxidized to form stable radicals, which have been used as electron spin qubits and even applied in CNOT quantum gates, a universal building block of quantum circuits. Previous studies have revealed 1.8-2.7 μs T2 for TTF radicals, albeit still at reduced temperatures and in the solid-state. Moreover, we have recently reported a set of bimetallic complexes featuring tetraphiafulvalene tetrathiolate (TTFt) as a bridging ligand which exhibit redox-activity, intense near-infrared absorption and emission, and air/water stability. Most importantly, transition metal complexes of TTFt support a formal TTF2+ oxidation state. This oxidation state exhibits a small ground-state singlet-triplet gap which could be optically excited and thus in principle act as an optically addressable electron spin qubit like an NV center. We rationalized that TTFt-based diradicaloids, whose electron spins are primarily localized on a nuclear spin-free TTF core, could serve as spin qubits with quantum coherence in solution and/or under ambient conditions. Here we report an in-depth study of the electronic spin properties of [[(dppe)Pt]2TTFt][BAR4]2: (PtTTFt, where dppe = 1,2-bis(diphenylphosphino)ethane and BAR4 = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, Figure 1A), which displays T1 of approximately 0.3 μs at room temperature in protonated solvents. These results demonstrate the applicability of molecular qubit candidates for room temperature and solution-phase quantum sensing applications.

**Figure 1.** A) Chemical structure of PtTTFt. B) Electronic structure of PtTTFt obtained from V2RDM calculations. Both the highest (HONO) and lowest (LUNO) natural orbitals of PtTTFt are shown. That an appropriately stable organic spin system would be an ideal candidate for application as a room temperature solution-phase qubit.

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Furthermore, we were able to obtain an X-band echo-detected field swept (EDFS) spectrum of PtTTF\textsuperscript{tt} (Figure 2B) with pulse EPR spectroscopy. The spectrum displays a single peak with a Gaussian line shape. The hyperfine features are not resolved due to the relatively large excitation bandwidth of pulses used, which causes additional line broadening. Importantly, the observation of a spin echo in solution at room temperature indicates coherence for PtTTF\textsuperscript{tt} under these conditions.

To confirm the diradicaloid character of PtTTF\textsuperscript{tt} and qualify it as a qubit, we performed nutation experiments at various microwave magnetic fields, $B_1$, for a 0.1 mmol/L dichloromethane solution at 288 K. By varying the length of the nutation pulse we observed Rabi oscillations at each $B_1$ (Figure 3A, Figure S5A) that demonstrate the coherent addressability of the system and the feasibility of implementing single-qubit quantum logic gates.\textsuperscript{14} The Rabi frequency, $\omega_{\text{Rabi}}$, increases linearly with increasing $B_{\text{out}}/B_{\text{in}}$ (normalized $B$, see SI for details) with a slope of 25.7 MHz (Figure 3B). We further performed nutation experiments for the 1 e\textsuperscript{−} reduced monoradical form of PtTTF\textsuperscript{tt} (PtTTF\textsuperscript{tt}+, see SI) at the same conditions which also displays a linear relationship between $\omega_{\text{Rabi}}$ and $B_{\text{out}}/B_{\text{in}}$ with a slope of 19.1 MHz (Figure S5), 1/1.35 times that of PtTTF\textsuperscript{tt} (Figure S6). The field dependence of the Rabi frequencies between two spin sublevels $m_s$ and $m_s \pm 1$ is described by the following relationship:\textsuperscript{49}

$$\omega_{\text{Rabi}} = \frac{g\mu_B B}{\hbar} \sqrt{S(S+1) - m_s(m_s \pm 1)}$$
The ratio between $\omega_{\text{Rabi}}/B$ of monoradical doublet ($S = 1/2$) and a diradicaloid triplet ($S = 1$) should be $1/\sqrt{2}$ which matches our experimental data. These experiments verify that PtTTF$^t_t$ is a diradicaloid system with an accessible triplet state at room temperature.

Encouraged by the suggestion of room temperature coherence from the EDFS and nutation experimental results, we probed $T_1$ and $T_2$ of PtTTF$^t_t$ in a 0.05 mmol/L dichloromethane solution at 296 K. Employing inversion recovery and Hahn echo pulse sequences revealed a $T_1$ of 1.44 $\mu$s and a $T_2$ of 0.34 $\mu$s, respectively (Figure 4). These are comparable to other organic radicals with long spin relaxation lifetimes, and generally longer than most metal-based molecular qubits that only operate at cryogenic temperatures. The room temperature quantum coherence of PtTTF$^t_t$ likely stems from the spin density being centered on the rigid and nuclear spin-free TTF$^t_t$ linker with weak spin-orbit coupling. While there are $^{31}\text{P}$ and $^{195}\text{Pt}$ nuclear spins that are hyperfine-coupled to the electron spins on TTF$^t_t$, they are likely within the nuclear diffusion barrier and do not cause decoherence. 21-53

**Variable Temperature EPR Measurements**

The remarkable room temperature spin coherence of PtTTF$^t_t$ prompted us to investigate spin dynamics of this molecule at low temperatures. We performed inversion recovery and Hahn echo measurements on frozen (20 K to 140 K) and fluid solution (220 K to room temperature) samples; solvent melting occurs at 150 – 210 K that causes loss of coherence and precludes pulse EPR measurements (Figure 5, Figure S7–9, Table S1). In the frozen solution, $T_1$ decreases rapidly with increasing temperature from 6.11 ms at 20 K to 10.5 $\mu$s at 140 K. Fitting suggests that the spin–lattice relaxation in this regime likely proceeds via the Raman process (Figure S10). The slow spin–lattice relaxation indicates that $T_2$ is not $T_1$-limited. Indeed, the spin decoherence in this regime is complex. $T_2$ remains relatively temperature-independent at approximately 6 $\mu$s from 20 K to 70 K, likely limited by hyperfine interactions. It begins decreasing at 80 K, potentially due to enhanced thermal motion of solvent such as methyl group rotation. Above 100 K, the decoherence from the hyperfine interaction is overridden by other effects, such as increased motion as the solvent approaches the melting point. Indeed, $T_2$ plummets to 0.53 $\mu$s at 110 K and eventually to 0.37 $\mu$s at 140 K.

In the fluid-solution regime, $T_1$ gradually decreases from 3.56 $\mu$s at 220 K to 1.44 $\mu$s at 296 K. The spin–lattice relaxation may be attributed to local vibrational modes and molecular tumbling. In contrast, $T_2$ gradually increases from 0.14 $\mu$s at 220 K to 0.34 $\mu$s at 296 K. This behavior can be rationalized by an increasing rate of motional processes in the solution as temperature rises: these processes become so fast that they effectively average out inequivalent environments around the electron

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**Figure 4.** A) Inversion recovery measurement of PtTTF$^t_t$, in blue, fit to a monoexponential decay, in red. B) Hahn echo decay measurement of PtTTF$^t_t$, in blue, fit to a monoexponential decay, in red. All experiments performed on a 0.05 mmol/L dichloromethane solution at 296 K.

**Figure 5.** Spin lattice relaxation ($T_1$) and decoherence ($T_2$) times of a 0.05 mmol/L dichloromethane solution of PtTTF$^t_t$ across various temperatures.
spins which enables longer spin coherence. Similar trends have been observed in solutions of endohedral fullerenes and other organic radicals. T$_1$ should be limited by T$_2$ as these two values approach each other at higher temperatures. These data indicate that the slow spin–lattice relaxation in PtTTFtt stemming from its organic diradicaloid character is crucial to enable spin coherence at room temperature in solution.

Conclusions

We report a nuclear spin-free organic diradicaloid scaffold, TTFtt, with weak spin-orbit coupling that allows for the realization of long spin–lattice relaxation times in electron spin-based molecular qubits. These long relaxation times enable room temperature coherence, even in dynamic nuclear spin-rich environments. The robust coherence and overall stability of the PtTTFtt system distinguish it as a promising candidate for quantum sensing under ambient conditions, as might be required for biological studies. Furthermore, the bright near-infrared emission unique to this scaffold suggests the possibility of using these systems as optically addressable qubits.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(25) Mao, H.; Pazera, G. J.; Young, R. M.; Krzyaniak, M. D.; Wasielewski, M. R. Quantum Gate Operations on a Spectrally
Complexes


