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Shang-Da Jiang

jiangsd@scut.edu.cn

South China University of Technology <https://orcid.org/0000-0003-0204-9601>

Jia-Yue Yuan

South China University of Technology

Peng-Xiang Fu

Peking University

Yao-Sheng Zhang

National University of Defense Technology

Ye-Xin Wang

South China University of Technology

Si-Yuan Wang

National University of Defense Technology

Bing-Cai Chen

National University of Defense Technology

Jian-Yu Liu

National University of Defense Technology

Song Gao

Peking University <https://orcid.org/0000-0002-0039-6346>

Tian Jiang

National University of Defense Technology <https://orcid.org/0000-0003-3343-5548>

Shen Zhou

National University of Defense Technology <https://orcid.org/0000-0001-5682-2589>

Article

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A Hybrid High-Spin Molecular Magnet for an Integrated Sensing–Storage Quantum Register

Jia-Yue Yuan^{a,b,e#}, Peng-Xiang Fu^{a,c,d#}, Yao-Sheng Zhang^a, Ye-Xin Wang^b, Si-Yuan Wang^a, Bing-Cai Chen^a, Jian-Yu Liu^a, Song Gao^{b,c,d}, Tian Jiang^{a,*}, Shen Zhou^{a,*}, Shang-Da Jiang^{b,*}

[a] College of Science, College of Advanced Interdisciplinary Studies, Hunan Key Laboratory of Mechanism and Technology of Quantum Information, National University of Defense Technology, Changsha, 410000, China.

[b] Spin-X Institute, School of Chemistry and Chemical Engineering, State Key Laboratory of Luminescent Materials and Devices, Guangdong-Hong Kong-Macao Joint Laboratory of Optoelectronic and Magnetic Functional Materials, South China University of Technology, Guangzhou, 511442, China.

[c] Beijing National Laboratory of Molecular Science, Beijing Key Laboratory of Magnetoelectric Materials and Devices, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China.

[d] Key Laboratory of Bioinorganic and Synthetic Chemistry of Ministry of Education, School of Chemistry, LIFM, IGCME, GBRCE for Functional Molecular Engineering, Sun Yat-Sen University, Guangzhou, 510275, China.

[e] Guangdong HUST Industrial Technology Research Institute, Dongguan, 523808 China.

Abstract: Hybrid quantum molecular systems combining high-spin electrons and nuclear spins possess enlarged Hilbert spaces that can encode multiple qubits within a single molecule and therefore hold great promise for constructing quantum registers. However, the full potential of their multilevel spin manifolds remains underexplored. Herein, we synthesize P@C₆₀ (electron spin $S = 3/2$, nuclear spin $I = 1/2$), a representative hybrid high-spin molecular magnet, via an improved, hazard-free synthetic route and systematically investigate its full electron–nuclear spin manifold. All ten spin transitions within an eight-dimensional Hilbert space, separated by hyperfine coupling and zero-field splitting, are individually addressed using pulsed electron paramagnetic resonance (EPR). We demonstrate coherent control across multiple electron-spin levels, quantitatively characterize the multi-quantum coherence times of the high-spin electron system, and reveal that such coherence enhances sensing of the surrounding magnetic environment, increasing the signal-to-noise ratio by a factor of 2.4. We further demonstrate integrated quantum sensing and storage by transferring electron-spin sensing information to the ³¹P nuclear spin, where it is preserved beyond the electron-spin coherence time. Finally, we quantify nuclear-spin storage by transferring coherence from the electron spin to the ³¹P nuclear spin, obtaining a phase-memory time of 20.8 ms, approximately 1,300 times that of the electron spin. These results establish an electron–nuclear molecular spin register in which quantum sensing and storage are integrated within a single molecule.

Keyword: Molecular spin qubits; Hybrid quantum system; Multi-quantum coherence; Quantum sensing; Quantum storage

Introduction

Quantum registers are controllable quantum systems composed of multiple qubits, typically realized in solid-state platforms such as spin defects in diamond^{1–3}, rare-earth-doped crystals⁴, superconducting circuits^{5–7}, semiconductor quantum dots^{8–10}, and low-dimensional materials^{11–13}. In most architectures, each unit hosts only one qubit, so scalable operation requires multiple units, whereas increasing internal dimensionality allows a single unit to support a Hilbert space with the dimensionality of multiple qubits.

Magnetic molecules are naturally suited to this strategy. Organic radicals^{14,15}, metal complexes^{16–18}, and paramagnetic endohedral fullerenes^{19–23} possess electron and nuclear spin manifolds engineerable at sub-Ångström precision and addressable by multi-frequency magnetic resonance. Within one molecule, the two spin species offer complementary resources. The nuclear spin is weakly coupled to the environmental noise and provides a long-lived quantum memory, whereas the electron spin couples strongly to magnetic fields, supporting fast manipulation and high sensitivity to the magnetic

environment. To date pure nuclear-spin systems^{24–26} have demonstrated multi-quantum coherence²⁷ and algorithm implementation^{28,29}, and pure electron-spin systems have extended coherence times^{22,23,30–34} and achieved a range of preliminary quantum applications^{35–44}. Combining the two within a single molecule would therefore unite fast, addressable sensing on the electron spin with long-lived storage on the nuclear spin, enabling a functional integration beyond the reach of either spin species alone.

However, realizing such an integrated register in molecules has been impeded by two obstacles. First, exploiting the enlarged electron-spin manifold for sensing requires multi-quantum coherences, which are superpositions connecting more than two spin levels and possess enhanced effective magnetic moments that increase sensitivity to weak magnetic environments. In molecular electron-spin systems, the lifetimes of these coherences have remained extremely short (20–300 ns)^{37,45,46}, precluding functional applications. Second, although nuclear spins can serve as long-lived quantum memories, information acquired through electron-spin sensing has not yet been transferred to the nuclear spin within the same molecule. The two spin species have thus far been exploited in parallel rather than in series.

Herein, we demonstrate that the hybrid high-spin molecule, phosphorus endohedral fullerene (P@C₆₀) (S = 3/2, I = 1/2), serves as an electron–nuclear molecular spin register with integrated quantum sensing and storage. A hazard-free solid-state precursor route produces the P@C₆₀-containing crude material at gram scale per day; subsequent HPLC purification affords P@C₆₀ with 78.4% purity. The long coherence times of this molecular magnet enable reliable addressing of transitions within its hybrid high-spin manifold using standard pulsed electron paramagnetic resonance (EPR), electron–electron double resonance (ELDOR), and electron–nuclear double resonance (ENDOR). Coherent control across multiple electron-spin levels is achieved, and multi-quantum electron-spin coherences are prepared, with their coherence times systematically characterized. The unique advantages of the hybrid high-spin system are demonstrated: multi-quantum electron coherences enhance the signal-to-noise ratio of electron-spin-echo envelope modulation (ESEEM), enabling sensing of weakly coupled magnetic environments. ESEEM sensing information is transferred to the ³¹P nuclear spin and retained beyond the electron-spin coherence time,

demonstrating integrated quantum sensing and storage. Quantum information storage with a memory time exceeding the bare electron-spin phase-memory time (T_m) by over three orders of magnitude is achieved. Together, these results demonstrate that P@C₆₀ functions as a versatile molecular quantum register combining electron-spin sensing with nuclear-spin storage.

Synthesis and spin characterization

The magnetic molecule studied here is phosphorus endohedral fullerene (P@C₆₀). Its carbon cage provides a clean magnetic environment, enabling exceptionally long coherence times of the electron spin. Compared to ¹⁴N@C₆₀⁴⁷, P@C₆₀ features a ³¹P nuclear spin having a 5.6-fold larger gyromagnetic ratio. The higher hyperfine coupling constant and larger nuclear Rabi frequencies facilitate faster nuclear-spin quantum manipulations. Nevertheless, P@C₆₀ remains much less explored than its nitrogen analogue⁴⁸, primarily due to the hazardous synthetic protocols: earlier preparations followed the ion-implantation method developed for N@C₆₀, replacing the nitrogen source N₂ with the highly toxic phosphorus precursor PH₃^{49–51}.

A safer route for synthesizing P@C₆₀ was developed. Non-toxic red phosphorus⁵² was homogeneously mixed with a polymeric binder (thermoplastic polyurethane, TPU; 10–20 wt%), cured at 120 °C for 1 h, and shaped into a solid, stable target. The red phosphorus was ionized via magnetron sputtering (90–120 W) with Ar⁺ ions, and the resulting P⁺ beam was co-deposited with C₆₀ vapor (500–650 °C) onto a cooled copper substrate (–20 °C) (Fig. 1a). The toluene-soluble film contains ~80 ppm P@C₆₀, with a yield comparable to the best PH₃-based reports in the literature^{49–51}. No PH₃ byproducts were detected using a gas safety sensor mounted on the vacuum chamber, demonstrating that this method effectively eliminates phosphine hazards. Using a roll-to-roll deposition substrate for continuous collection (Supplementary Note 1-1), the productivity of the crude sample was managed to reach the gram scale per day. The crude material was then automatically purified by high-performance liquid chromatography (HPLC) with BuckyPrep-M and PBB columns⁵³, yielding approximately 78.4% pure P@C₆₀ dispersed in C₆₀ (Supplementary Note 1-2). The mass spectrum of the purified P@C₆₀ product (monoisotopic m/z = 751, Fig. 1b) confirmed the encapsulation of a single phosphorus atom inside C₆₀.

The purified sample was used for the following spin qubit experiments.

The room-temperature continuous-wave EPR spectrum of the as-prepared product in toluene- d_8 was measured to further confirm the desired spin structures (Fig. 1c). The encapsulated phosphorus atom generates an electron spin $S = 3/2$, which splits into four levels under an external magnetic field. These levels are coupled via hyperfine interaction to the P nuclear spin ($I = 1/2$), yielding $(2S + 1) \times (2I + 1) = 8$ hybrid spin levels that form a single spin center with a Hilbert-space dimension equivalent to that of three qubits. The spin Hamiltonian is

$$\hat{H} = \mu_B B_0^T g_e \hat{S} - \mu_n B_0^T g_n \hat{I}_P + \hat{I}_P^T A \hat{S} + \hat{S}^T \bar{D} \hat{S}$$

where μ_B and μ_n are the Bohr and nuclear magnetons, B_0 is the external magnetic field, $\hat{S}$ is the electron spin operator, $\hat{I}_P$ is the P nuclear spin operator, g_e and g_n are the isotropic Landé g-factor of the electron and P nuclear spin, respectively, A is the

isotropic hyperfine-coupling constant, and $\bar{D}$ is the zero-field splitting (ZFS) tensor, which vanishes when the P@C₆₀ structure preserves I_h symmetry. In the high-field limit, energy levels can be calculated (Supplementary Note 2-1).

As expected, the measured spectrum exhibits two sets of P hyperfine lines⁵⁴. The large ³¹P hyperfine coupling constant, determined from the splitting to be $A = 137.82$ MHz (Fig. 1c inset), enables clear resolution of the detailed peak shapes. In agreement with the simulated spectrum, each hyperfine line is further split into three components due to the second-order hyperfine effect, corresponding to the three allowed electron spin transitions within the $S = 3/2$ manifold. The three sub-peaks are evenly spaced by the second-order hyperfine shift $\Delta \approx A^2 \hbar / 2g\mu_B B_0 \approx 1.00$ MHz. A detailed derivation based on the Taylor expansion to the 2nd order of the frequency shift is provided in Supplementary Note 2-2.

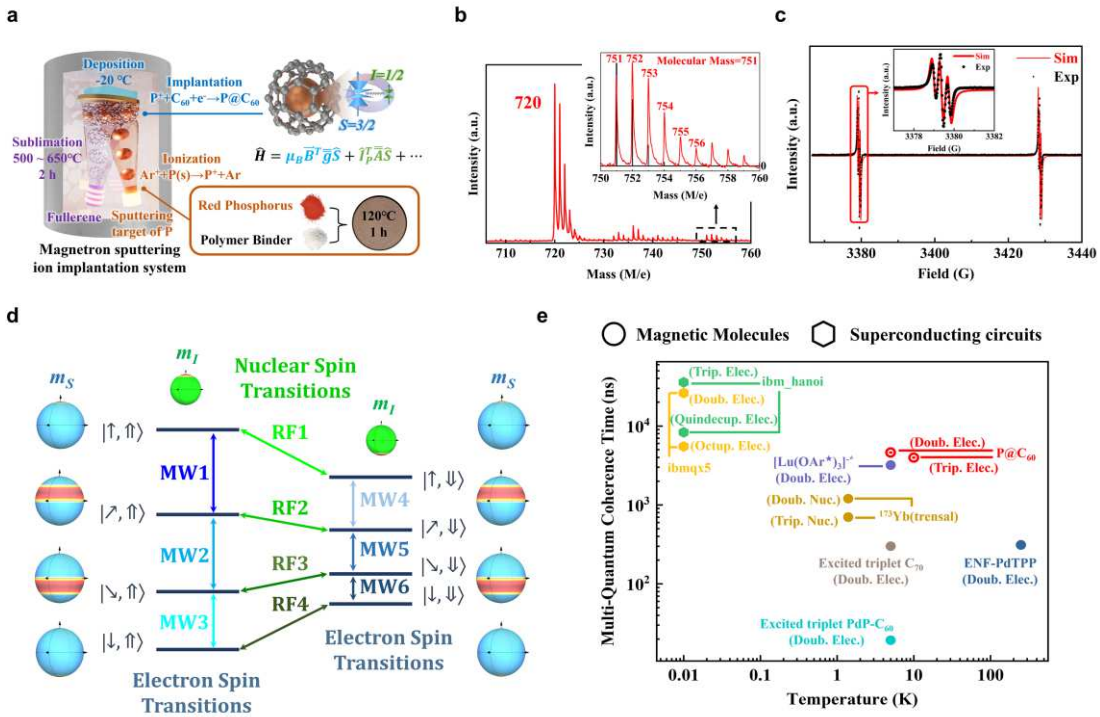


Fig. 1 | Synthesis and spin levels of P@C₆₀. **a**, Experimental setup for phosphorus implantation using magnetron sputtering. **b**, MALDI-TOF-MS (dithranol matrix, negative mode) of purified P@C₆₀. The main peak at M/z = 720 corresponds to C₆₀, and the zoom-in spectrum shows the monoisotopic mass peak of P@C₆₀ (m/z = 751). **c**, Continuous-wave EPR spectrum (black dots) and simulation (red solid line) of purified P@C₆₀ in toluene- d_8 at room temperature. The inset shows a zoom-in of the $m_I = +1/2$ transition, revealing details of the line shape. **d**, Energy-level diagram showing the corresponding transitions in a frequency-swept scheme, with MW1-MW6 and RF1-RF4 denoting the electron- and nuclear-spin transitions, respectively, together with visualization of the hybrid high-spin system using Q -distributions. **e**, Multi-quantum coherence times versus temperature for P@C₆₀ and other representative spin-qubit systems. Reference include ibm_hanoi⁵⁵, ibmqx5⁵⁶, [Lu(OAr⁺)₃]⁺⁴³, ¹⁷³Yb(trensai)²⁷, Excited triplet C₇₀⁴⁵, Excited triplet PdP-C₆₀⁴⁶ and ENF-PdTPP³⁷. Among these systems, [Lu(OAr⁺)₃]⁺, marked with *, was not measured via combined quantum controls; instead, its multi-quantum coherence was obtained through direct transition processes using parallel-mode excitation.

We mapped the complete magnetic energy-level diagram of the hybrid high-spin molecular magnet $P@C_{60}$ (Fig. 1d), with electron spin eigenstates $|\uparrow\rangle$, $|\nearrow\rangle$, $|\searrow\rangle$, and $|\downarrow\rangle$, and nuclear spin eigenstates $|\uparrow\rangle$ and $|\downarrow\rangle$. The 8-D Hilbert space is visualized via the Q -distributions^{57–60} on two Bloch spheres representing the electron spin (blue) and nuclear spin (green), respectively. Details of the visualization method of the Q -distribution is documented in Supplementary Note 2-3.

Based on this energy-level structure, we realized high-spin multi-quantum coherences in $P@C_{60}$. Their coherence times are compared with representative results from different quantum platforms, including magnetic molecules^{27,37,43,45,46} and superconducting qubits^{55,56} in Fig. 1e. Well-established superconducting qubit systems serve as a benchmark for multi-quantum coherence times (5–40 μ s)^{55,56}. However, reports of combined multi-quantum transitions spanning multiple spin levels in magnetic molecules remain rare, and the coherence times reported to date are extremely short (20–300 ns)^{37,45,46}. Even the pure nuclear spin in $^{173}\text{Yb}(\text{trens})$ molecule exhibits multi-quantum coherence times of only ~ 1 μ s²⁷. Special multi-quantum ($\Delta m_S > 1$) coherences achieved through parallel-mode excitation⁴³ are still direct processes, therefore not

fully comparable. In comparison, $P@C_{60}$ enables long multi-quantum coherence times at comparatively high operating temperatures. The prerequisites, preparation, characterization, and applications of these high-spin coherences are presented in the following sections.

Selective Spin Control

Addressability of individual transitions is a prerequisite for coherent control across the full electron-nuclear spin manifold of $P@C_{60}$. We individually addressed and coherently controlled all six electron-spin transitions (MW1–MW6) and four nuclear-spin transitions (RF1–RF4).

In the electron spin manifold, the three allowed transitions ($|\uparrow\rangle \leftrightarrow |\nearrow\rangle$, $|\nearrow\rangle \leftrightarrow |\searrow\rangle$, and $|\searrow\rangle \leftrightarrow |\downarrow\rangle$) within the $^4S_{3/2}$ manifold are degenerate to first order and therefore cannot be individually addressed. A Hamiltonian term beyond the Zeeman interaction is required to lift this degeneracy. At room temperature, the second-order hyperfine splitting partially resolves the three transitions (Fig. 1c, inset). However, at the low temperatures required for extended coherence times and high-fidelity quantum control, the EPR lines broaden, rendering these transitions indistinguishable (Supplementary Note 3-1).

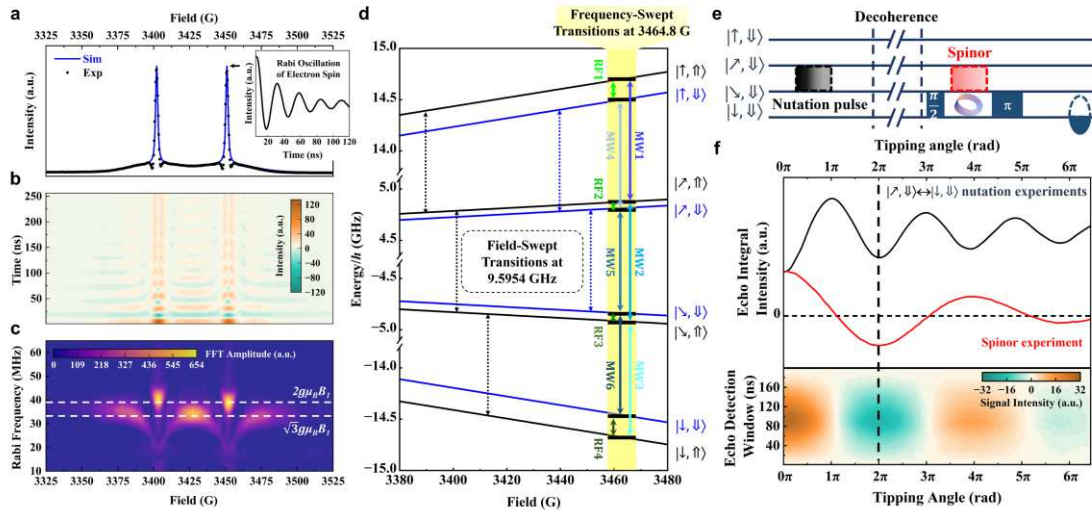


Fig. 2 | Addressability of spin transitions in $P@C_{60}$. **a**, Field-swept electron-spin-echo (ESE) signal (black), and simulation (blue) of $P@C_{60}$ in toluene- d_8 at 8 K. The inset shows Rabi oscillations of the electron-spin. **b–c**, Field-swept Rabi oscillation experiment and its Fourier transform. The dashed lines indicate the ratio of the Rabi frequencies for different transitions. **d**, Energy-level diagram showing the corresponding transitions under a field-swept scheme at a resonance frequency of 9.5954 GHz and a frequency-swept scheme at a resonance field of 3464.8 G. MW1–MW6 and RF1–RF4 denote the electron- and nuclear-spin transitions, respectively. **e**, Pulse sequences for the multilevel Rabi oscillation (black) and spinor experiment (red). **f**, Corresponding results for the multilevel Rabi oscillation (black line) and spinor experiment (red line) at 8 K, showing doubled periodicity; the spinor transient signal is shown in the contour map.

A stronger degeneracy-lifting interaction is therefore required for selective electron-spin control. Our previous work demonstrated that the symmetry of the $^4S_{3/2}$ endohedral electron spin manifold can be broken via molecular engineering, including chemical functionalization^{35,39,61} and co-crystallization⁶². These approaches have been applied to N@C₆₀ to generate ZFS, enabling selective electron spin control. In P@C₆₀, the phosphorus atom is substantially larger than the nitrogen atom in N@C₆₀, making P@C₆₀ is sensitive to strain from the surrounding glassy solvent. After rapid cryogenic quenching, inhomogeneously broadened ZFS peaks were observed in the field-swept electron-spin-echo (ESE) spectrum (Fig. 2a). Quantitative line-shape simulation yields an average zero-field parameter $|\bar{D}|$ of 58 MHz. ZFS was also observed in the field-swept ESE spectrum of P@C₆₀ powder, showing that strain-induced ZFS is not limited to the frozen-solution environment (Supplementary Note 3-2).

Field-dependent Rabi nutation experiments performed under the same conditions (Fig. 2b) allowed us to assign the individual electron-spin transitions between adjacent m_S levels. Fourier transform of the Rabi oscillations (Fig. 2c) yielded frequency ratios of $\sqrt{3} : 2$ between the satellites and main peaks, in exact agreement with the $S = 3/2$ prediction:

$$\Omega^{m_S \leftrightarrow m_{S+1}} = \mu_B g B_1 \sqrt{S(S+1) - m_S(m_S + 1)}$$

where B_1 is the microwave field in the rotating frame. This observation indicates that these satellite peaks arise from zero-field splitting, which lifts the degeneracy of the electron-spin transitions.

Therefore, solvent-strain-induced ZFS enables individual addressing of all six electron-spin transitions. With the magnetic field fixed at 3464.8 G, these transitions can be selectively driven using different microwave frequencies (MW1–MW6; Fig. 2d). Such individual addressing requires selective pulses because of the distribution of D values in the frozen solution^{35,39,61}.

We next extended coherent control beyond individual transitions to multiple spin levels. By employing an ELDOR setup with two independent microwave sources (Supplementary Note 5-1), we performed three-level Rabi oscillation and spinor experiments (Fig. 2e, f).

First, the three-level Rabi experiment demonstrated population manipulation. Starting

from the thermal state of the $S = 3/2$ system, a variable-length pulse applied to the $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$ transition (black pulse in Fig. 2e) drove Rabi oscillations, thereby modulating the population difference between $|\downarrow, \downarrow\rangle$ and $|\downarrow, \uparrow\rangle$. This population difference was subsequently detected using a Hahn-echo sequence (blue pulses in Fig. 2e). Whereas the conventional two-level Rabi signal oscillated between positive and negative values, initially decreasing (Fig. 2a, inset), the three-level Rabi signal initially increased and remained positive throughout the oscillation (black curve in Fig. 2f), effectively amplifying the initial thermal population imbalance.

Second, the spinor experiment demonstrated coherent phase manipulation. A variable-length pulse applied to the $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$ transition (red pulse in Fig. 2e) was inserted into the delay τ of the Hahn-echo sequence (blue pulses in Fig. 2e), enabling observation of the spinor effect. Owing to the intrinsic spin-1/2 nature of the electron, the spinor response exhibited a 4π periodicity, repeating every two complete Rabi cycles, analogous to a Möbius band³⁵. Accordingly, after a 2π rotation, the spinor signal reached its most negative value rather than returning to its initial value (red curve in Fig. 2f). The pronounced phase variation in the transient signal (Fig. 2f) provides direct evidence of coherent superpositions spanning more than two levels, the prerequisite for the multi-quantum coherences in the next section.

The coupling of the nuclear spin of ^{31}P to an $S=3/2$ electron spin generates four allowed nuclear spin transitions ($|\uparrow, \uparrow\rangle \leftrightarrow |\uparrow, \downarrow\rangle$, $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$, $|\downarrow, \uparrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$, and $|\downarrow, \downarrow\rangle \leftrightarrow |\downarrow, \uparrow\rangle$) corresponding to four distinct NMR resonance frequencies (RF1–RF4 in Fig. 2d). To first order, the spin Hamiltonian gives $\nu_{\text{RF1}} = 3A/2 - \gamma_P B_0$, $\nu_{\text{RF2}} = A/2 - \gamma_P B_0$, $\nu_{\text{RF3}} = A/2 + \gamma_P B_0$, and $\nu_{\text{RF4}} = 3A/2 + \gamma_P B_0$ (Supplementary Note 2-1). Electron–nuclear double resonance (ENDOR) measurements using Davies and Mims sequences resolved all four lines at the predicted frequencies (Supplementary Note 3-3). Field-swept Davies ENDOR measurements revealed distinct magnetic-field distributions for the four nuclear-spin transitions, indicating an approximately even distribution of positive and negative D values, consistent with random oblate and prolate distortions of the fullerene cage induced by solvent strain (Supplementary Note 3-4).

Each transition (RF1–RF4) can be used for coherent nuclear-spin manipulation. As a

representative example, nuclear-spin Rabi oscillations were obtained by varying the length of the RF2 pulse in a Davies ENDOR sequence (Supplementary Note 3-3).

Multi-quantum coherence of High spin

Quantum coherence of molecular magnets is mainly studied based on allowed transitions (Fig. 3a). It is crucial to demonstrate that different allowed transitions can be combined coherently to generate multi-quantum coherence. After initialization to a pseudo-pure spin state (Supplementary Note 4), we quantified the multi-quantum coherence times associated with the forbidden transitions. As shown in Fig. 3b, we developed a modified Hahn-echo sequence that refocuses the quantum-phase evolution of forbidden transitions. The double-quantum coherence time of $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$ was measured over

the temperature range of 5~80 K. The effectiveness of the refocusing was demonstrated via experimental comparison and theoretical analysis in Supplementary Note 5-2. Compared with the single-quantum coherence times of the $|\uparrow, \downarrow\rangle \leftrightarrow |\uparrow, \uparrow\rangle$, $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \uparrow\rangle$, and $|\downarrow, \downarrow\rangle \leftrightarrow |\downarrow, \uparrow\rangle$ transitions, the double-quantum coherence time was comparable to those of the ZFS-related transitions, namely $|\uparrow, \downarrow\rangle \leftrightarrow |\uparrow, \uparrow\rangle$ and $|\downarrow, \downarrow\rangle \leftrightarrow |\downarrow, \uparrow\rangle$. This suggests that fluctuations in the ZFS dominate the decoherence of the double-quantum coherence, as further supported by their similar temperature dependence. In contrast, the single-quantum coherence time associated with the non-ZFS-related $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$ transition exhibited a temperature dependence attributed to the flip-flop dynamics of the surrounding toluene molecules^{23,63}, whereas this behavior was not observed for the double-quantum coherence time.

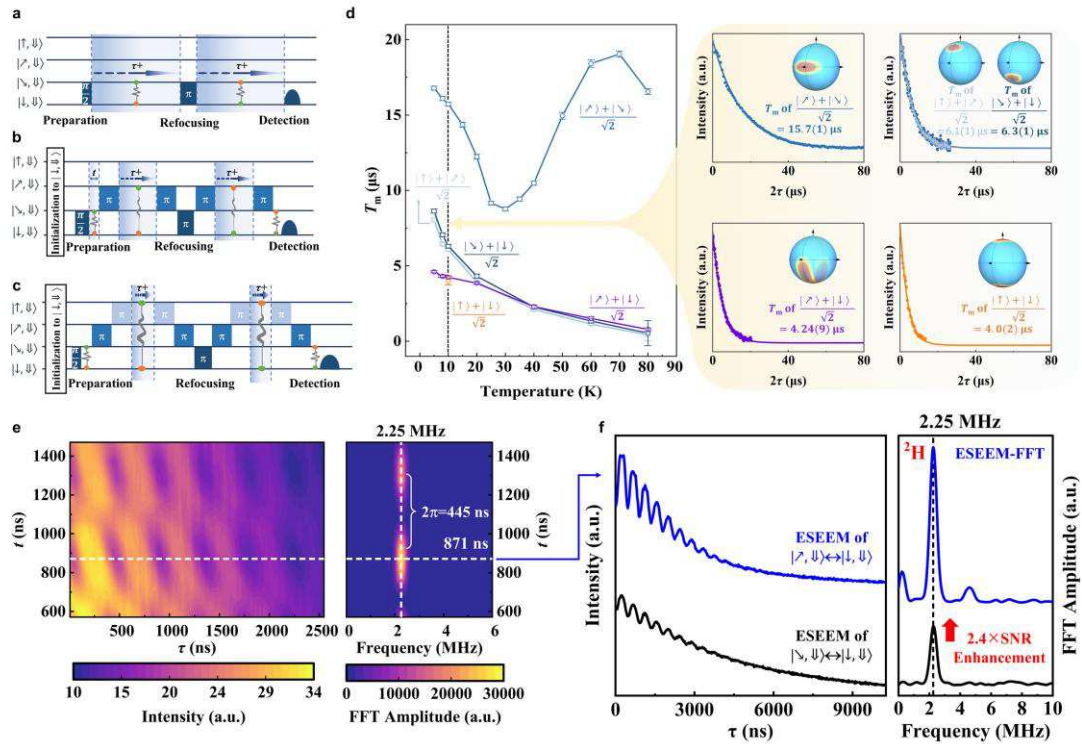


Fig. 3 | Electron spin multi-quantum coherence and enhanced quantum sensing. **a-c**, Pulse sequences used to generate single-, double- and triple-quantum coherence and to measure the corresponding coherence times. **d**, Coherence time T_m as a function of temperature for single- (blue), double- (purple) and triple- (orange) quantum coherence. along with echo decay curves measured at 10 K for each coherence type. **e**, Two-dimensional ESEEM maps showing the signal intensity as a function of τ (left) and the corresponding Fourier-transformed frequency (FFT, right) at 5 K. The vertical axis represents t (571-1471 ns, 50 ns steps), and the color scale indicates echo intensity ((left) or FFT amplitude (right)). A spectral feature at 2.25 MHz corresponds to the ^2H Larmor frequency. **f**, ESEEM traces recorded at $t=871$ ns for the double- (blue) and single- (black) quantum transitions, with the corresponding Fourier-transformed spectra highlighting the enhanced signal at the ^2H Larmor frequency (2.25 MHz).

Moreover, we extended coherent control to all four electron spin levels by integrating a home-built arbitrary waveform generator (AWG) pulse module (Supplementary Note 6), enabling the simultaneous generation of more than two frequency channels. Starting from the three-level superposition state, a four-level superposition $(|\uparrow, \downarrow\rangle + |\downarrow, \downarrow\rangle)/\sqrt{2}$ can be readily prepared by applying a π pulse (MW4), which transfers the coherence from $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$ to $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$. A combined sequence of five π pulses involving MW6, MW5, and MW4 was applied to refocus the triple-quantum coherence. The spin echo became detectable after the coherence was transferred back to the allowed-transition channel (Fig. 3c). At 10 K, the triple-quantum coherence time was measured to be 4.0(2) μ s (Fig. 3d, orange dot), comparable to the double-quantum coherence time, indicating that the coherence transfer introduces no additional decoherence. To the best of our knowledge, this is the first experimental demonstration of triple-quantum coherence in a molecular electron spin system. Compared with the widely studied three-level NV center ($S = 1$)⁶⁴⁻⁶⁷, P@C₆₀ ($S = 3/2$) offers four electron-spin levels, providing a higher-dimensional state space for quantum control.

Applications of the electron-spin multi-quantum coherence were further explored. Multilevel superposition states possess large effective magnetic moments, which present both a challenge and an advantage. On the one hand, they are more susceptible to magnetic-field inhomogeneities, resulting in shorter coherence times (Supplementary Note 5-2), a challenge that we successfully addressed using the refocusing pulse sequences described above. On the other hand, these large effective magnetic moments make them highly sensitive to the magnetic environment, enabling applications in quantum metrology, such as the detection of external magnetic fields⁶⁸ or magnetic nuclei⁶⁷.

Here, we employ the electron-spin-echo envelope modulation (ESEEM) effect to detect the ²H nuclear spins in the toluene-*d*₈ solvent. The standard 2-pulse ESEEM experiment uses the same sequence as the Hahn-echo ($\pi/2$ - τ - π - τ -echo, Fig. 3a). The interactions are probed by recording the amplitude modulations in the electron spin echo signal. Fourier transformation of these modulations reveals the characteristic frequencies of the magnetic environments, and the sensitivity depends on the intensities of the FFT peaks. We exploit multi-

quantum coherence to enhance sensitivity to the magnetic environment. The larger effective magnetic moment of these states strengthens the ESEEM modulation and increases the FFT signal. Similarly, the double-quantum ESEEM sequence is based on the double-quantum Hahn echo (Fig. 3b). The two-level superposition $|\downarrow, \downarrow\rangle \leftrightarrow |\uparrow, \downarrow\rangle$ first evolves for a time t , after which coherence is transferred to and remains in the three-level superposition $|\uparrow, \downarrow\rangle \leftrightarrow |\downarrow, \downarrow\rangle$ for a time τ , and the electron spin echo is measured as a function of τ (Supplementary Note 7-1). At $B_0 = 3464.8$ G, both 2-pulse and double-quantum ESEEM experiments yielded a ²H Larmor frequency of 2.25 MHz, corresponding to a period of 445 ns. We observed that double-quantum ESEEM was deterministically enhanced or suppressed depending on the evolution time t when t was an integer multiple of the ²H Larmor period, the modulation was enhanced, producing constructive interference; when t was a half-integer multiple, the modulation was suppressed or vanished (Fig. 3e, Supplementary Note 7-2), demonstrating controllable interference in the ESEEM effect. The enhancement and suppression observed in double-quantum ESEEM were exactly opposite to that predicted for 3-pulse ESEEM ($\pi/2$ - t - $\pi/2$ - τ - $\pi/2$ - t -echo), in which adjusting t can similarly modulate the echo along τ . This contrast likely arises from the transfer of environmental modulation between the two- and three-level electron spin manifolds. At $t = 871$ ns, approximately twice the ²H Larmor period, double-quantum ESEEM enhanced the FFT signal-to-noise ratio by factors of 2.4 relative to conventional 2-pulse ESEEM (Supplementary Note 7-3). Notably, the enhancement of higher harmonics of the ²H Larmor frequency was more pronounced in the double-quantum ESEEM experiment (Fig. 3f).

Integrated quantum sensing and storage

Quantum control can be extended to the hybrid electron-nuclear spin manifold. As demonstrated above, electron spins are well suited for quantum sensing, whereas nuclear spins often exhibit much longer coherence times and are attractive for quantum storage. This extension allows the complementary properties of the two spin species to be jointly exploited.

Here, we demonstrate this capability in an experiment integrating quantum sensing and storage. An electron-spin ESEEM measurement was first performed (MW5 $\pi/2$) with a sensing interval τ_E to

probe the ^2H nuclear spins in the toluene- d_8 solvent. This sensing information was then transferred to the ^{31}P nuclear spin (RF2 π -MW5 π), stored for a total evolution time $2\tau_N$, and subsequently transferred back to the electron spin for readout using the reverse pulse sequence (MW5 π -RF2 π). During this process, refocusing pulses were applied to the nuclear-spin coherence (second RF2 π) and the electron-spin coherence (first and fourth MW5 π), thereby suppressing dephasing in both spin manifolds (Fig. 4a). The retrieved ESEEM signal showed no appreciable attenuation beyond the electron-spin coherence time (Fig. 4b), indicating that the sensing information was preserved in the nuclear spin and demonstrating the integration of quantum sensing and storage within P@C₆₀.

We further evaluated the storage capability by directly measuring the storage time of electron-spin

coherence. The pulse sequence was therefore slightly different: an electron-spin superposition was prepared without varying τ_E ; its coherence was then transferred to the nuclear spin for storage and later transferred back for readout (Supplementary Note 8-1). The resulting quantum storage time reached 20.8(8) ms (Fig. 4c), approximately 1,300 times the electron-spin coherence time of 16.1(1) μs , and was limited by the nuclear-spin coherence time. Compared with widely adopted and well-established strategies for extending coherence time, such as dynamical decoupling^{69–72} using a Carr-Purcell-Meiboom-Gill (CPMG) sequence, which extended the electron-spin coherence time from ~ 10 μs with CPMG-1 to ~ 57 μs with CPMG-32 (Fig. 4c and Supplementary Note 8-2), transferring coherence to the nuclear spin achieved a much greater enhancement.

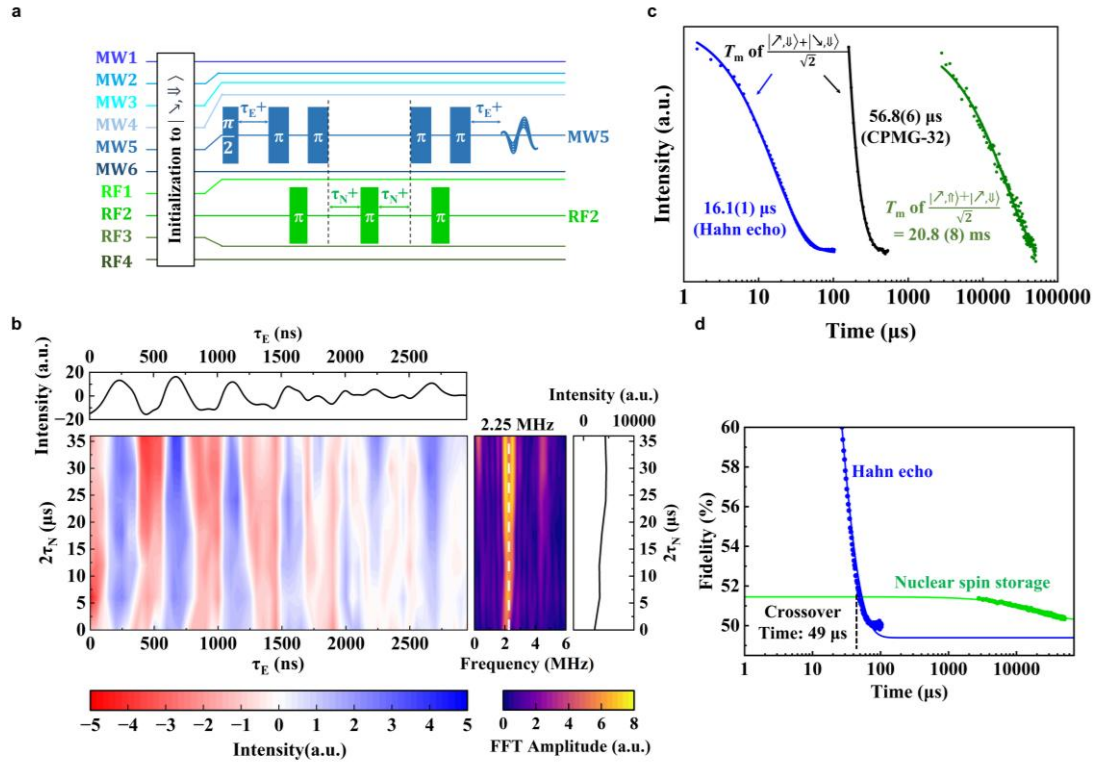


Fig. 4 Quantum sensing and nuclear-spin storage. **a**, Pulse sequence for electron-spin sensing followed by transfer to nuclear-spin storage. **b**, Corresponding result for electron-spin sensing followed by transfer to nuclear-spin storage. Two-dimensional ESEEM maps showing the signal intensity as a function of τ_E (left) and the corresponding Fourier-transformed frequency (FFT, right) at 5 K. The vertical axis represents $2\tau_N$ (0–36 μs , 6 μs steps), and the color scale indicates the echo intensity (left) or FFT amplitude (right). A spectral feature at 2.25 MHz corresponds to the ^2H Larmor frequency. The upper inset shows the ESEEM signal intensity summed over τ_N as a function of τ_E , while the right inset shows the summed FFT peak intensity as a function of τ_N . **c**, T_m of coherence stored in the original electron-spin superposition (Hahn echo and CPMG-32) and in the nuclear-spin superposition at 5 K. **d**, Corresponding fidelity decays derived from the Hahn-echo and nuclear-spin-storage data in **c**. Their intersection marks the crossover time of 49 μs .

Notably, both nuclear-spin storage and CPMG involve relatively long pulse sequences, inevitably reducing fidelity because of decoherence and pulse imperfections. Storage time and fidelity should therefore be considered together. By comparing the fidelity decay of coherence retained in the electron spin (Hahn-echo measurement) with that after transfer to the nuclear spin for storage, we identify a crossover time of 49 μ s, at which the two fidelities are equal (Fig. 4d and Supplementary Note 8-3).

Below the crossover at 49 μ s, the lower fidelity of nuclear spin storage reflects the initial transfer loss, as the phase-cycle selection retains only the coherence successfully transferred to the ^{31}P nuclear spin. Nuclear spin coherence decays on a timescale more than three orders of magnitude longer than electron spin coherence (20.8 ms versus 16.1 μ s; Fig. 4c), whereas the electron spin coherence rapidly approaches complete dephasing. The initial transfer loss is therefore offset within approximately three electron spin coherence times, beyond which nuclear spin storage provides higher fidelity.

Conclusion

In summary, we have realized the hybrid high-spin molecule P@C_{60} , which combines long-lived spin coherence with an eight-dimensional electron–nuclear spin manifold. By developing a solid-state precursor and employing magnetron sputtering, we achieved scalable production of high-purity P@C_{60} samples. Advanced EPR techniques enabled full addressability and coherent control of all spin levels, allowing the preparation of multi-quantum superpositions, which exhibit long coherence times exceeding those reported for other molecular spin systems. By exploiting double-quantum ESEEM and the nuclear spin, we achieved enhanced quantum sensing and extended quantum storage, respectively, and further demonstrated the integration of quantum sensing and storage. These advances provide a versatile framework for constructing electron–nuclear molecular spin registers.

Further chemical tailoring could enable site-directed spin labeling of proteins for highly localized and in situ biosensing in complex environments⁷³, for example in living cells⁷⁴ and in vivo⁷⁵. Magnetic-resonance-based control is also compatible with superconducting qubit integration and on-chip miniaturization^{76,77}. Future incorporation of quantum error correction could enable fully integrated molecular quantum registers capable of sensing,

storage, and computation, further advancing molecular magnets for quantum information processing.

Methods

Chemicals and Reagents

C_{60} (Xiamen Funan Material Technology Co., Ltd., 99.9%), red phosphorus (Anhui Senrise Technologies Co., Ltd, 98.5%), toluene (Thermo Fisher Scientific, HPLC grade), toluene- d_8 (Cambridge Isotope Laboratories, Inc, 99.5% D), and dithranol (Sigma-Aldrich, >90%) were used as received without further purification.

Preparation of P@C_{60}

P@C_{60} was synthesized via ion implantation using C_{60} as the starting material and red phosphorus as the phosphorus source. For target preparation, 3.6 g of non-toxic red phosphorus was homogeneously mixed with 0.4 g of TPU, pressed into a copper holder, and cured at 120 °C for 1 h to form a solid, mechanically stable target.

Separately, 200 mg of C_{60} was sublimed under a pressure of 10^{-1} – 10^{-2} Pa by gradually heating from 500 °C to 650 °C over 1.5 h. During sublimation, the phosphorus target was magnetron-sputtered (90–120 W) using argon plasma, generating P^+ ions that reacted with C_{60} molecules during flight and were co-deposited onto a water-cooled copper substrate maintained at -20 °C.

The deposited film was subsequently dissolved in toluene and filtered to yield crude P@C_{60} (approximately 80–100 ppm). The crude product, containing a large excess of unreacted C_{60} , was purified by high-performance liquid chromatography (HPLC, Aunotech LC-2000). The HPLC system was operated in two separation modes: repeat injection and recycling. For the initial separation, 3 mL aliquots of the crude solution were injected at fixed intervals in repeat injection mode to remove the bulk of unreacted C_{60} (BuckyPrep-M columns, 12 mL/min, toluene). After this step, the sample volume was reduced to ≤ 3 mL and further purified in recycling mode, in which a single injection was circulated repeatedly through the columns to achieve complete separation of P@C_{60} from residual C_{60} (PBB columns, 12 mL/min, toluene). Fractions exhibiting spin signals were collected, yielding P@C_{60} with a purity of 78.4%. The toluene was removed by rotary evaporation, replaced with toluene- d_8 , and the P@C_{60} solution was transferred into a 3 mm EPR

tube.

MALDI-TOF MS

Measurements were performed using a Bruker autoflex maX. Approximately 0.2 μL of the P@C₆₀ and dithranol solutions (both in toluene) were mixed, spotted onto a MALDI target plate, and, after solvent evaporation, introduced into the ion source for measurement. Mass spectra were acquired in the range of 700–1000 Da using the negative-ion reflectron mode.

EPR

Measurements were performed using an X-band CIQTEK EPR 100 equipped with pulsed electron–nuclear double resonance (ENDOR) and electron–electron double resonance (ELDOR), and an arbitrary waveform generator (AWG) from SpinQ. Microwave pulses were applied through a 450 W high-power amplifier with 12 dB attenuation, with π pulses of 64 ns. Radio-frequency pulses were applied through a 175 W high-power amplifier, with π pulses of 10,000 ns. For EPR measurements, the P@C₆₀ solution in a 3 mm tube was degassed, sealed under an argon atmosphere, and rapidly cooled to 5–10 K in a liquid-helium cryostat to form a glassy solid solution. The electron spin echo (ESE) spectrum was simulated using the EasySpin MATLAB toolbox.

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Author contributions

S. Zhou and S.-D. Jiang initiated the idea and supervised the project. J.-Y. Yuan synthesized the samples and performed the measurements with the help of P.-X. Fu and B.-C. Chen. Y.-S. Zhang and S.-Y. Wang performed the calculations and simulations. B.-C. Chen and J.-Y. Liu participated in

the synthesis of the samples. S. Zhou and J.-Y. Yuan wrote the manuscript with contributions from Y.-X. Wang. S. Gao, T. Jiang, S. Zhou, and S.-D. Jiang conceived the project. All authors participated in discussions of the research.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information

Correspondence and requests for materials should be addressed to Shen Zhou and Shang-Da Jiang

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