Readout and control of an endofullerene electronic spin

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Atomic spins for quantum technologies need to be individually addressed and positioned with nanoscale precision. C₆₀ fullerene cages offer a robust packaging for atomic spins, while allowing in-situ physical positioning at the nanoscale. However, achieving single-spin level readout and control of endofullerenes has so far remained elusive. In this work, we demonstrate electron paramagnetic resonance on an encapsulated nitrogen spin (¹⁴N@C₆₀) within a C₆₀ matrix using a single near-surface nitrogen vacancy (NV) center in diamond at 4.7 K. Exploiting the strong magnetic dipolar interaction between the NV and endofullerene electronic spins, we demonstrate radio-frequency pulse controlled Rabi oscillations and measure spin-echoes on an encapsulated spin. Modeling the results using second-order perturbation theory reveals an enhanced hyperfine interaction and zero-field splitting, possibly caused by surface adsorption on diamond. These results demonstrate the first step towards controlling single endofullerenes, and possibly building large-scale endofullerene quantum machines, which can be scaled using standard positioning or self-assembly methods.
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ding quantum technologies requires the constituent quantum elements to be precisely positioned and addressable.
Fullerene cages have demonstrated positioning with nanoscale precision. The cages can be dragged into position with a scanning tunneling microscope tip, or can be packed into one-dimensional arrays within carbon nanotubes (CNTs). Recent experiments have even demonstrated that C$_{60}$ can self-assemble on monolayer graphyne sheets. To address the fullerene system, an atomic spin is encapsulated within the diamagnetic enclosure of the C$_{60}$ cage (also known as an endofullerene). The encapsulated spin is created by ion implantation, and retains its free atomic electron configuration. Previous electron resonance experiments on the encapsulated spin have utilized ensemble techniques, involving $\sim$10$^6$ spins. However, electron paramagnetic resonance (EPR) on single endofullerenes demonstrating readout and control has remained elusive.

In this work, we focus on the endofullerene N@C$_{60}$. N@C$_{60}$ is formed by a single 14N atom sitting at the centrosymmetric $I_h$ position of a C$_{60}$ cage. The nitrogen atom retains its single-electron eigenvalues, in particular its electronic ground-state configuration. The ground state is formed by an electronic spin $S = 3/2$ system residing in the hyperfine field of a spin $I = 1$ nucleus. The experiment is performed at low magnetic fields ($B \approx 10$ mT), leading to second-order corrections to the N@C$_{60}$ energy-level scheme of order $A^2/(g_eB)^2 \approx 1$ MHz, where $A$ is the N@C$_{60}$ hyperfine constant and $g_eB$ is the electronic Zeeman shift. This is shown in Fig. 1a. We utilize the dipolar interaction of the N@C$_{60}$ electronic spin with a local readout sensor to demonstrate single-spin level endofullerene spin readout and control.

**Results**

**Sensor and system.** For the local readout sensor, we use single near-surface (3–8 nm deep) nitrogen vacancy (NV) centers in diamond. The NV center is ubiquitous as a quantum sensor whose robust solid-state packaging and unique energy level structure make it ideal as a noninvasive local magnetic field probe. Briefly, it consists of a substitutional nitrogen atom neighboring a vacancy site in the diamond lattice, creating a triple ground state that can be polarized and readout optically. Single NV centers were isolated using Hanbury Brown–Twiss measurements (Fig. 1b, see Supplementary Section 1.3). The single NV centers were located using standard confocal microscopy and are labeled to probe the same NV site at different experimental conditions (Fig. 1c). The optical collection efficiency of the NV centers was enhanced by guiding the emitted light using tapered nanowaveguides structured directly onto the diamond substrate.

The diamond surface was cleaned and oxygen-terminated by tri-acid boiling (see “Methods”). After cleaning, a disordered layer of empty (C$_{60}$) and filled (N@C$_{60}$) cages was created by drop-casting and air-drying N@C$_{60}$ solution on the surface. The filling factor of the cages (1.0(1) × 10$^{-4}$) and concentration in solution...
(1 μL·L⁻¹) was tuned for single N@C₆₀ spin detection within the NV center sensing radius of ~10 nm. From the filling factor and concentration, we calculate a probability of ~4.5% of coupling to a single N@C₆₀ spin (see Supplementary Section 1.4). In other words, on average only 1 in 22 NV centers will couple to an N@C₆₀ spin. The probability of coupling of more than a single spin falls rapidly, and is ~0.2% for coupling to two N@C₆₀ spins. However, we note that the statistical fluctuations in these values can be large for single-spin coupling.

Dipolar interaction model. Denoting the interacting spins as $S_{nv}$ (NV electronic spin), $S_{ef}$ (endofullerene electronic spin), and $I_{ef}$ (endofullerene nuclear spin), and applying a static magnetic field $B_0 = B_{0x,0y,0z}$ aligned to the NV quantization axis, the spin Hamiltonian in units of $\hbar$ of the system reads as:

$$
\mathcal{H} = \mathcal{H}_{nv} + \gamma_{el} B_{0x} S_{el} + A_{el} S_{el} I_{el} + D_{el} S_{el} I_{el} + J_{el} S_{el} I_{el}.
$$

Here, $\gamma_{el} = g\mu_B/\hbar = 28$ GHz/T is the gyromagnetic ratio of the endofullerene electronic spin, $|A| = 15.87$ MHz is the isotropic hyperfine coupling of the encapsulated ¹⁴N, and $|D|$ is the zero-field interaction strength appearing in the absence of perfect icosahedral cage symmetry. The interaction Hamiltonian $\mathcal{H}_{nv,el}$ assumes higher external fields $B_0$ relative to the hyperfine interaction $A$ and dipole–dipole interactions $J$, i.e., $\gamma_{el} B_0 \gg A \gg J$. The dipole–dipole coupling strength $|J| = \mu_0 \mathcal{H}_{coy} \gamma_{el} (2r^3) = 52$ MHz/(r/nm) varies with NV and endofullerene separation $r$ (in nm).

**Single-spin EPR.** The dipole–dipole interaction was probed at several single NV centers using pulsed electron–electron double resonance (PELDOR or DEER) spectroscopy. DEER spectroscopy utilizes periodic microwave (MW) pulses in a spin-echo sequence to preserve the phase coherence and enhance the magnetic field sensitivity of the NV center. The central spin-flip of the NV center is synchronized with a radio-frequency (RF) spin-flip pulse in a lock-in scheme. When the frequency of the RF pulse matches the transition frequency of an external spin, the NV center basis states pick up a relative phase proportional to the magnetic field of the external spin. To increase the net phase pickup and suppress common mode noise, we chose the $\Omega_t = \{\pm 1\}$ NV electronic spin sublevels as sensor basis states. This double-quantum (DQ) pulse scheme is shown in Fig. 2a.

Figure 2b shows the single-spin EPR spectrum of N@C₆₀ at 4.7 K under an external magnetic field of 9.697 mT. The spectrum is obtained on averaging many individual single-shot experiments, and therefore represents a temporal average in which the N@C₆₀ spin system assumes all allowed configurations with a probability given by the temperature, and possibly by saturation effects due to finite shot repetition times. Three resonance peaks at 251.5(5), 271.4(1), and 288.7(7) MHz mark the hyperfine splitting of the endofullerene nitrogen. Note that after cleaning the diamond surface, the signal disappeared completely, indicating that the signal stems from the surface and not from impurities within the diamond itself.

Comparing single-endofullerene EPR (Fig. 2b) with ensemble measurements (Fig. 2d) on the same sample reveals good agreement between the central and upper hyperfine components. However, the single-endofullerene EPR spectrum shows two additional features—(i) the lowest-energy hyperfine transition is shifted downward by ~4 MHz, and (ii) the EPR linewidths are broadened. Both of these experimental features can be modeled using second-order perturbation theory (see Supplementary Section 2), and the result of the simulation is shown in Fig. 2b as a solid blue line. Firstly, the position of the three peaks can be best reproduced by using an isotropic hyperfine constant of 19 MHz for the spin-3/2 species instead of the usual 15.85 MHz, and an axial zero-field splitting (parameterized as $D$ in Eq. (1)) of 1.52 MHz. The former shifts the frequency of the hyperfine satellites relative to the central peak and the latter leads to an additional splitting within each hyperfine line. The apparent enhancement of these parameters may be due to either covalent or non-covalent chemical interactions between the fullerene and the diamond surface. Secondly, the simulation uses an overall line broadening of 4 MHz, which is in agreement with the typical experimental power broadening expected from Fourier transformed 100 ns RF pulses $1/(r \times 100$ ns) ≈ 3.3 MHz. The peak intensities are modeled considering a weak coupling to a spin-bath ($g = 2.03$), which may originate from electronic spins in the drop-coated solution. Another possible interpretation of the single-endofullerene EPR peak intensities can be made by invoking nonthermal spin distributions, potentially caused by the NV intersystem crossings during laser excitation (see Supplementary Section 2.4).

At 4.7 K, we could observe the single-spin EPR signal over weeks, and N@C₆₀ itself is known to be thermally stable up to 550 K. However, when placing N@C₆₀ under the exposure of strong laser irradiation, ensemble experiments have demonstrated that it can undergo thermo-optical decay at temperatures well ~550 K (ref. 28). To test this, we raised the temperature of the system to 300 K and repeated the DEER measurement. We observe a complete suppression of any discernible side peaks along with the formation of a broad featureless central dip (Fig. 2c). This behavior is consistent with previous attempts at room temperature endofullerene spin readout under laser irradiation. Ensemble EPR measurements have attributed the decay mechanism to the formation of a radical species in an adiabatic photoreaction. Another possibility is the thermally assisted rapid dephasing of an intact N@C₆₀ spin.

**N@C₆₀ spin relaxation and control.** The sensor relaxation times can provide crucial information about the environment, such as the distance to a dipolar-coupled spin. To determine the distance of the endofullerene from the NV center, we make a direct comparison of the temporal evolution of the NV phase pickup with and without a spin-flip on the central N@C₆₀ spin transition (Fig. 2f and see Supplementary Section 1.5). The spin-echo sequence on the NV center shown in Fig. 2e mainly refocuses the phase imprinted by nearby spins (i.e., a strongly coupled spin-bath), and the simple decoupling sequence does not affect the dephasing caused by farther spins (i.e., a weakly coupled spin-bath). Hence the long-time behavior is unaffected by the $\pi$-pulse. As we start to flip the N@C₆₀ spin, depending on the timescale of the phase evolution, the NV center either dominantly dephases due to its coupling to the N@C₆₀, or to the weakly coupled spin-bath. This behavior is seen in Fig. 2g, where a strong initial dephasing due to the NV–N@C₆₀ interaction slowly relaxes to the dephasing caused by the spin-bath. Hence, the difference between the two dephasing curves should display the expected behavior, i.e., a transition from a faster dephasing caused by external spins toward a slower dephasing from the local spin-bath. Using a simple rate equation model (for full analysis see Supplementary Section 1.5 and ref. 19), we extract an NV–N@C₆₀ coupling strength of $\approx 0.29$(2) MHz from the initial linear dephasing, corresponding to an NV–N@C₆₀ separation $\approx 5.6(1)$ nm. Considering the possibility of the additional presence of a finite number ($<10$) of unknown bath spins, the uncertainty in distance measurements is slightly affected with an additional error bar of ±1 nm.
Fig. 2 Electron spin resonance of endofullerenes. a Single-spin electron paramagnetic resonance (EPR) realized using double electron-electron resonance (DEER) in the double-quantum (DQ) basis. Brown pulses (dotted lines) and red pulses (continuous lines) address 0 → +1 and 0 → −1 nitrogen vacancy (NV) transitions, respectively. b Low-temperature DEER-DQ spectroscopy on a single NV center in diamond. The solid brown and purple lines indicate the simulated spectrum of a single N@C60, and weakly coupled spin-bath (g = 2.03), respectively (linewidths reduced to 1 MHz for clarity). The solid blue line indicates the combined simulation with experimental linewidth. The simulated endofullerene has an isotropic hyperfine constant α = 19 MHz, axial zero-field splitting D = 1.52 MHz and a static magnetic field B0 = 9.697 mT (see Supplementary Section 2). Dotted vertical lines indicate positions of ensemble EPR hyperfine components. Error bars depict photon shot noise. c Spectrum decays under room-temperature (RT) thermo-optical load, solid line indicates fit to single Lorentzian model. Dotted lines indicate positions of ensemble EPR hyperfine components. Error bars depict photon shot noise. d Ensemble solution EPR data on the same N@C60 sample measured across ~100 spins. e Pulse sequence comparing NV center Hahn-echo decoherence in presence (first RF sequence) and absence (second RF sequence) of an NF spin-flip on N@C60. f Direct comparison of the temporal evolution of the NV Hahn-echo signal with and without an spin-flip on the coupled N@C60. g Difference in NV center decoherence at short evolution times versus longer evolution times reveals the clear separation of timescales at which the NV-N@C60 interaction is dominant.

The dephasing and relaxation times of N@C60 were long enough to generate and measure spin coherence, as shown by the Rabi oscillations (pulse sequence Fig. 3a). The Rabi nutation of the endofullerene spin is demonstrated in Fig. 3b, c. Rabi oscillations are recorded by fixing the RF frequency at the central (mJ = 0) and upper (mJ = +1) peaks in Fig. 2b, and varying the pulse duration time τ. The Rabi frequency displays the characteristic square-root scaling with driving power (Fig. 3d). The Rabi control allows for rapid pulsed control of the endofullerene spin-level populations, with spin-state switching rates tunable up to νR = 12.47(1) MHz.

Performing more general control sequences demands phase coherence (T2). To measure this, we performed a spin echo on the endofullerene within half of the free evolution time in the NV spin echo (Fig. 3e). The result is a characteristic Hahn decay in Fig. 3f, with an observed decay time of T2 ≥ 1 μs. For NV centers with a spin-echo coherence of T2^N@C60 ~ 2.5 μs, this leads to a maximum measurable coherence time of T2^N@C60/2 ~ 1.25 μs. Thus, the time represents a lower limit on N@C60 coherence due to the measurement being constrained to a single branch of the NV spin echo. The maximum measured ensemble endofullerene coherence time is ~190 μs (ref. 29), and thus probing and controlling such spins requires near-surface NV centers with significantly longer coherence times. This can be achieved through the chemical surface modification of diamond, or by doping the diamond with n-type impurities30.

Discussion

In conclusion, we have demonstrated electron spin resonance with readout and control on the endofullerene 14N @C60 using a near-surface nitrogen vacancy center in diamond. The surface adsorption on to the diamond surface appears to enhance isotropic hyperfine constants and zero-field splitting of the fullerene cage. The use of fullerenes, such as 31P@C60, which has hyperfine interactions an order of magnitude larger than 14N@C60, may permit spin control without strong surface effects. The current results represent the first steps toward controlling single endofullerenes and combining our result with recent advances in C60 self-assembly, or fullerene packed CNTs, opens a path for scaling endofullerene systems3. Furthermore, the nuclear spin of the encapsulated atom allows for nuclear quantum interfaces interfaced with electron spin “buses”31,32. This can be realized with pulse schemes, such as Hartman-Hahn, which transfer polarization from the NV center to the endofullerene electronic and nuclear spins (see Supplementary Section 3).
techniques together open up incredibly exciting possibilities of building large-scale endofullerene quantum machines.

Methods

Experimental setup. The single-spin EPR measurements on N@C60-coated diamond samples were performed with a home-built low-temperature (4.7 K) and ultrahigh vacuum (10^{-10} mbar) setup capable of confocal microscopy and pulsed MW/RF control. The ensemble EPR measurements were performed on an X-band cw-EPR spectrometer (see Supplementary Section 1.1).

Diamond preparation and characterization. All experiments were performed on a 30 μm thick electronic grade [100] diamond made, using chemical vapor deposition by Element Six, Inc. The diamond was implanted with 14N at an energy of 5 keV and subsequently annealed at 975 °C for 2 h. Nanopillar waveguides (base diameter 700 nm, tip diameter 400 nm, and height 1 μm) were etched into the diamond to increase optical collection efficiency. The diamond surface was cleaned and oxygen terminated by boiling in a tri-acid mixture (1:1:1, HNO3:H2SO4:HClO4) at 200 °C for 5 h.

The magnetic field at NV center was calculated using the ODMR spectrum and NV Hamiltonian. The DEER Hamiltonian is represented by the electron Zeeman interaction, and the perturbation by the hyperfine and zero-field interactions.

Data availability

The data that support the findings of this study are available from the corresponding author on reasonable request.

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Fig. 3 Relaxation and coherence of an endofullerene spin. a Pulse scheme for driving Rabi oscillations on endofullerene spins and probing with a single nitrogen vacancy (NV) center. b, c Rabi oscillations on the endofullerene central (mI = 0) and upper (mI = +1) hyperfine components. Solid line is fit to an exponentially decaying sinusoid. Error bars indicate photon shot noise. d Characteristic square-root behavior of Rabi frequency with RF driving power. e Pulse scheme for probing endofullerene spin–echo phase coherence. f Spin–echo measurements place a lower limit of T2 ≥ 1 μs on the phase coherence times. Solid line indicates exponentially decaying sinusoidal fit, error bars indicate photon shot noise.
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Author contributions

J.W. and K.K. supervised and directed this project. R.W. under the supervision of W.H. synthesized the N@C60 samples and performed ensemble EPR measurements. D. Pinto, D. Paone, and B.K. performed the single-spin EPR measurements. D. Pinto, D. Paone, D.D., T.D., R.W., A.S., A.F., W.H., J.W., and K.K. performed the analysis. D.D. and T.D. performed theoretical calculations and simulations. D. Pinto drafted the manuscript with contributions from all authors.

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Competing interests

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