Ultrafast entangling gates between nuclear spins using photoexcited triplet states

Vasileia Filidou1†, Stephanie Simmons3†, Steven D. Karlen1,2, Feliciano Giustino1, Harry L. Anderson2 and John L. Morton1,3* 

The representation of information within the spins of electrons and nuclei has been a powerful method in the ongoing development of quantum computers1,2. Although nuclear spins are advantageous as quantum bits (qubits) because of their long coherence lifetimes (exceeding seconds3), they exhibit very slow spin interactions and have weak thermal polarization. A coupled electron spin can be used to polarize the nuclear spin4-6 and create fast single-qubit gates7,8, however, the permanent presence of electron spins is a source of nuclear decoherence. Here we show how a transient electron spin, arising from the optically excited triplet state of C60, can be used to hyperpolarize, manipulate and measure two nearby nuclear spins. Implementing a scheme that uses the spinor nature of the electron9, we performed an entangling gate in hundreds of nanoseconds: five orders of magnitude faster than the liquid-state J coupling. This approach can be widely applied to systems comprising an electron spin coupled to multiple nuclear spins, such as nitrogen-vacancy centres in diamond10, while the successful use of a transient electron spin motivates the design of new molecules able to exploit photoexcited triplet states.

Different quantum systems possess different advantages as qubits, stimulating the use of so-called hybrid approaches to quantum computing11. Examples include interfacing superconducting qubits with spin ensembles12, optical photons with defects in solids13, and electron spins with nuclear spins14. Spins controlled by nuclear magnetic resonance (NMR) have played an important role in the development of much work in quantum information processing, showcasing high-fidelity control15, complex demonstrations of quantum algorithms16 and many-qubit decoupling strategies16. Nuclei in such systems are only weakly coupled: the indirect J-coupling interaction available in liquid-state NMR can be on the order of 100 Hz (ref. 15), although nuclear spin dipole couplings in the solid state can exceed 10 kHz.

This weak coupling places a lower limit on the duration of a quantum logic operation between two spins, and thus the computational speed of a nuclear spin-based quantum information processor. Furthermore, the weak magnetic moment of nuclear spins leads to a weak polarization in general (typically less than 0.01% for liquid state NMR), making the scaling-up of the initial polarization methods4,5, typical single-qubit gate times for electron spins are tens of nanoseconds and, given typical electron–nuclear couplings (in the range 1–100 MHz), it is possible to manipulate a nuclear spin on these timescales. For purely isotropic couplings, phase gates can be applied to nuclear spin qubits to perform dynamic decoupling7,17, whilst using anisotropic coupling, more general gates have been applied to single nuclear spins8,20,21, or, recently, two nuclear spins22.

A disadvantage of using coupled electron spin is that the nuclear spin coherence time can be strongly limited by electron spin relaxation or flip-flop processes1. A better strategy invokes an electron spin only at certain key times, for example to hyperpolarize the nuclear spins or to perform fast logic gates, so that there is minimal long-term impact on nuclear decoherence23.

To explore such possibilities, we synthesised the fullerene derivative dimethyl[9-hydro(C10H5)5,6(fulleren-1(9H)-yl)]phosphonate (DMHFP; ref. 24), illustrated in Fig. 1a, containing two nuclear spins (31P and 1H) which are directly bonded to a C60 fullerene cage. The molecule has a diamagnetic singlet ground state which can be photoexcited to populate the first excited singlet state. This state undergoes intersystem crossing (ISC) to a hyperpolarized, long-lived triplet state which is paramagnetic (S = 1) with electron spin density delocalized over the cage (Fig. 1b,c). This system provides all the ingredients to explore nuclear spin manipulations mediated by a transient electron spin using a combination of optical excitation, electron spin resonance (ESR) and NMR control.

We begin by characterizing the spin Hamiltonian, $\mathcal{H}$, of the DMHFP molecule:

$$\mathcal{H} = \mu_B S \cdot g_e \cdot B + S \cdot D \cdot S + \sum_{i=1}^3 S \cdot A_i \cdot I_i + J_{I_e} I_{e,z} + \gamma_e I_1 \cdot B$$  \hspace{1cm} (1)$$

where $S$ and $I$ are respectively the electron and nuclear spin operators, $B$ is the applied magnetic field, $\gamma_e$ the nuclear gyromagnetic ratio, $g_e$ the electron g-factor tensor, $\mu_B$ the Bohr magneton, $D$ the zero-field splitting (ZFS) tensor for the $S = 1$ triplet state, $A_i$ the hyperfine coupling tensor between the triplet and the nuclear spins $i$, and $J$ is the coupling between the nuclear spins. $I_{e,z}$ is the projection of $I$ along $z$. All terms involving $S$ vanish in the electronic ground state.

By performing pulsed ESR immediately following a 532 nm laser pulse we examine the properties of the triplet state. Figure 1d shows the intensity of an electron spin echo as a function of the applied magnetic field in the X-band (9.7 GHz microwave frequency). By comparing the spectrum to simulations25, we obtain the $g_e$-tensor

---

1Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK; 2Department of Chemistry, University of Oxford, Oxford OX1 3TA, UK; 3CAESR, The Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, UK. †These authors contributed equally to this work.

*E-mail: john.morton@materials.ox.ac.uk.
bandwidth enables high-fidelity control on these transitions. Corresponding to the nuclear Larmor frequencies of the 31P spectra, shown in Fig. 1e, show narrow peaks around 6 and 14 MHz to select different molecular orientations within the sample. The electron-nuclear double resonance (ENDOR) method indicating hyperpolarization well above the thermal polarization. Spect to the applied magnetic field; however, typical values are p = 0.6 and p = 0.2 as the initial populations of T, T0 and T, indicating hyperpolarization well above the thermal polarization.

The hyperfine coupling between the triplet electron spin and the 1H and 31P nuclear spins can be measured using the Davies electron–nuclear double resonance (ENDOR) method, applied to select different molecular orientations within the sample. The spectra, shown in Fig. 1e, show narrow peaks around 6 and 14 MHz corresponding to the nuclear Larmor frequencies of the 31P and 1H spins, and arising from nuclear transitions in the T0 subspace, where the hyperfine coupling is negligible (see Fig. 1c). The narrow linewidth of these peaks compared to the pulse excitation bandwidth enables high-fidelity control on these transitions.

The other peaks in the ENDOR spectra arise from the (orientation-dependent) hyperfine coupling in the T subspace. Fitting yields the isotropic hyperfine coupling terms A(1H) = 6.0 MHz and A(31P) = 11 MHz, consistent with density functional theory (DFT) modelling (see Supplementary Information). This hyperfine coupling allows conditional electron/nuclear spin operations to be performed; however, the breadth of these peaks (arising from the randomly oriented solid) results in poor fidelity nuclear spin control in the T subspace. Nevertheless, we will show that it is possible to apply entangling operations to states within the T0 subspace, where there is negligible coupling between the nuclear and electron spins.

NMR experiments in the absence of optical excitation reveal the ground-state J-coupling between 31P and 1H to be 30 Hz, which leads to a nuclear controlled-NOT (CNOT) operation time of 17 ms. In the solid state, the dipolar coupling can be measured using the spin echo double resonance (SEDR) pulse sequence, shown in Fig. 2a. SEDOR can be interpreted as a standard NMR CNOT operation modified to allow for initialization and readout by the electron spin. The timing of the refocussing pulses is swept to identify the optimum CNOT time of 160 μs,
corresponding to a 3 kHz nuclear coupling. By comparing this coupling time to the lifetime of the triplet state (approximately 0.5 ms) and nuclear $T_2$ times (0.20(4) and 1.9(4) ms for $^{1}{}$H and $^{31}{}$P, respectively), we see that shorter entangling gate times are needed for higher fidelity operations. This can be achieved by using a triplet electron spin transition to apply an Aharonov–Anandan (AA; refs 7,28) controlled-phase (CPHASE) gate to the nuclear spins, as proposed in ref. 10.

If a quantum state is taken through a closed-loop trajectory in Hilbert space, it acquires a geometric phase equal to half the solid angle mapped out by that trajectory. A simple manifestation of this is a $2\pi$ pulse applied to a spin, which results in a global phase shift to the eigenstate associated with the chosen electronic rotation. The eigenstates $|i\rangle$ and $|j\rangle$ differ from $|4\rangle$ by a $^{1}{}$H and $^{31}{}$P spin flip, respectively, and $|1\rangle$ differs from $|4\rangle$ by a flip of both nuclear spins. The relationship between these states $|1\rangle\cdots|4\rangle$ and a particular nuclear spin configuration (for example $|↑↑\rangle$) varies according to the molecular orientation (see Supplementary Information).

The duration of the CPHASE operation is limited only by the hyperfine coupling strength, which determines the minimum bandwidth of a selective microwave pulse, such that a CPHASE gate on a timescale of hundreds of nanoseconds can be performed. To illustrate how this phase gate can be applied to the individual nuclear spins, we applied $2\pi$ microwave pulses while driving nuclear Rabi oscillations (Fig. 2d). We verified that this CPHASE behaviour was conditional by observing uninterrupted Rabi oscillations on the $^{1}{}$H spin at points marked with arrows. Uninterrupted nuclear Rabi oscillations are shown in black.

Figure 2 | Two different ways to implement nuclear spin entangling gates using the triplet electron spin. a, A technique based on the SEDOR sequence can be used to measure the dipolar coupling between spins. The sequence resembles a Hahn-echo experiment on one spin ($^{1}{}$H), however both spins are flipped during the refocussing pulse such that the sign of their coupling remains unchanged. Microwave pulses before and after are used to prepare and measure the $^{1}{}$H nuclear spin coherence. b, The SEDOR sequence produces an oscillation in the nuclear coherence as $\tau$ is swept, corresponding to a nuclear coupling of 3 kHz. c, An alternative implementation of a CNOT gate consists of two Hadamard gates ($\pi/2$ pulses) and a CPHASE gate created by applying a selective $2\pi$ pulse to the electron spin. d, An ultrafast nuclear phase gate (created by a $2\pi$ microwave pulse) is applied during nuclear spin Rabi oscillations on the $^{1}{}$H spin at points marked with arrows. Uninterrupted nuclear Rabi oscillations are shown in black. e, Comparison of the speed of the entangling operations. From the liquid state to the photoexcited solid state with the application of CPHASE gates there is an improvement of the entangling speed of five orders of magnitude.
Figure 3 | Density matrix tomography results. a, General pulse sequence for the extraction of the $|1\rangle\langle 4|$, $|4\rangle\langle 1|$ elements of the density matrix, beginning with transfer of spin polarization from the triplet to the nuclear spins. The CNOT representations correspond to the entangling gates as represented by the shaded areas of Fig. 2a,b. The pulses mapping a density matrix element to the observable change depending on the density matrix element. b, Density matrix obtained using the entangling gates based on nuclear spin dipole coupling. The slow coupling leads to a fidelity of the operations of 34%. c, Density matrix obtained using CPHASE-based entangling gates. The ultrafast CPHASE gate entangles the nuclear spins in 220 ns and the fidelity increases to 65%. Uncertainties due to signal noise account for less than 0.005 and 0.002 on each density matrix element for the SEDOR- and CPHASE-based matrices, respectively (see Supplementary Information).
consistent with simulations incorporating a 4% error on each nuclear gate in the sequence.

The lifetime of the double quantum coherence is $T_{2,2QC} \approx 100 \mu$s and the lifetime of the zero quantum coherence is $T_{2,0QC} \approx 200 \mu$s, which indicates that they are limited by the hydrogen $T_2$ in the photoexcited state. Both nuclear coherence lifetimes in the liquid state are longer by orders of magnitude, which motivates the controlled removal of the electron spin in place of the stochastic decay process. Further improvements to the fidelity of the entangling gates and the polarization of the triplet state could be expected by using single-crystal samples allowing better orientation selection.

The approach demonstrated here can be readily applied to other systems where a transient electron spin can be coupled to multiple nuclear spins. Photoexcited triplet states offer the advantages of hyperpolarization, although methods for controlled de-excitation require further study. This could be achieved with the application of a second excitation to a higher order triplet state which undergoes reverse ISC to a singlet state25. Alternatively, charge separated states could be used to optically create a spin-1/2 electron on part of a molecule, and multiple excitations/chromophores could offer routes to controllably remove the spin. Finally, an electron spin may be controllably added and removed through electrostatic means in different systems, for example by ionizing/neutralizing a donor in silicon26, which can couple to several $^{29}$Si nuclear spins in addition to the donor nuclear spin.

Methods

Dimethyl[9-(hydroxyl)-5,6]fullerene-1(9H)-yl]phosphonate was prepared following the procedure reported in ref. 24, Scheme 1. Mono-functionalization of $C_60$ was performed using dimethyl phosphate in a solution of toluene and HMPA at 120 °C in the presence of oxygen. The product was purified by silica column chromatography (toluene, ramped to 10% ethyl acetate in toluene).

Pulsed electron spin resonance experiments were performed using an X-band (9–10 GHz) Bruker Elexsys680 spectrometer equipped with a low-temperature-helium-flow cryostat (Oxford CF395). The arbitrary phase RF pulses were generated using a pulse using a Rohde and Schwarz AFQ100B together with an Amplifier Research (910 GHz) Bruker Elexsys680 spectrometer equipped with a low-temperature-probehead.

Microwave pulse lengths were 128 ns for π/2 pulses, and 220 ns for both π and 2π pulses. The duration of RF pulses (both π/2 and π) was 17 μs. The samples were prepared in toluene-d8 with a concentration of 4 x 10$^{-4}$ M, deoxygenated and flame-sealed under vacuum, and flash-frozen in liquid nitrogen.

Received 23 January 2012; accepted 25 May 2012; published online 1 July 2012

References

1. Cory, D. G., Fahmy, A. F. & Havel, T. F. Ensemble quantum computing by

2. Simmons, S. et al

3. Morton, J. J. L. & Lovett, B. W. Hybrid solid-state qubits: The powerful role of

4. Kubo, Y. et al. Hybrid quantum circuit with a superconducting qubit coupled to a spin ensemble.

5. Barrett, S. D. & Kok, P. Efficient high-fidelity quantum computation using

6. Ryan, C. A., Emerson, J., Poulin, D., Negnevitsky, C. & Laflamme, R. Characterization of complex quantum dynamics with a scalable NMR information processor.

7. Vandersypen, L. M. K. et al. Experimental realization of Shor’s quantum factorization algorithm using nuclear magnetic resonance.

8. Jones, J. A. Quantum computing with NMR. Proc. Natl. Acad. Sci. USA. 108, 325–360 (2001).

9. Ryan, C. A., Moussa, O., Baugh, J. & Laflamme, R. Spin based heat engine: Demonstration of multiple rounds of algorithmic cooling. Phys. Rev. Lett. 100, 140501 (2008).

10. Davies, E. R. A new pulse ENDOR technique. Phys. Lett. A 47, 1–2 (1974).

11. Tyryshkin, A. M. et al. Coherence of spin qubits in silicon. J. Phys. 18, 5783–5794 (2006).

12. Khaneja, N. et al. Shortest paths for efficient control of indirectly coupled qubits. Phys. Rev. A 75, 012322 (2007).

13. Mitrakis, G., Sanakis, Y. & Papavassiliou, G. Ultrafast control of nuclear spins using only microwave pulses. Towards switchable solid-state quantum gates. Phys. Rev. A 81, 020305 (2010).

14. Zhang, Y., Ryan, C., Laflamme, R. & Baugh, J. Coherent control of two nuclear spins using the anisotropic hyperfine interaction. Phys. Rev. Lett. 107, 170503 (2011).

15. Gauger, E. M., Rohde, P. P., Stoneham, A. M. & Lovett, B. W. Strategies for entangling remote spins with unequal coupling to an optical active mediator. New J. Phys. 10, 073027 (2008).

16. Isobe, H., Chen, A.-J., Solin, N. & Nakamura, E. Synthesis of hydrophosphorylated fullerene under neutral conditions. Org. Lett. 7, 5633–5635 (2005).

17. Stoll, S. & Schweiger, A. EasySpin, a comprehensive software package for spectral simulation and analysis in EPR. J. Magn. Reson. 178, 42–55 (2006).

18. Emswiller, M., Hahn, E. & Kaplan, D. Pulsed nuclear resonance spectroscopy. Phys. Rev. 118, 414–424 (1960).

19. Schweiger, A. & Jescake, G. Principles of Pulse Electron Paramagnetic Resonance (Oxford Univ. Press, 2001).

20. Aharonov, Y. & Anandan, J. Phase change during a cyclic quantum evolution. Phys. Rev. Lett. 58, 1593–1596 (1987).

21. Kamata, Y., Akiyama, K., Tero-Kubota, S. & Tabata, M. Two-laser two-color time-resolved EPR study on higher, excited-state triplet-singlet intersystem crossing of porphyrins and phthalocyanines. Appl. Magn. Res. 23, 409–420 (2003).

22. Morello, A. et al. Single-shot readout of an electron spin in silicon. Nature 467, 687–691 (2010).

Acknowledgements

We thank B. Lovett, M. Schaffry, E. Gauger, C. Kay, A. Ardavan, A. Briggs and D. Cereso for helpful discussions. This work was supported by the Engineering and Physical Sciences Research Council (EPSRC) through the Centre for Advanced Electron Spin Resonance (CAESR) (EP/D048559/1) and the Materials World Network (EP/I035536/1), as well as by the European Research Council (ERC) under the European Community’s Seventh Framework Programme (FP7/2007-2013)/ERC grant agreement no. 279,781. We thank the Violette and Samuel Glasstone Fund, Clarendon Fund, John Templeton Foundation, St John’s College, Oxford, and the Royal Society for support.

Author contributions

V.F. and S.D.K. designed and synthesised the molecule. All authors discussed the results and manuscript.

Additonal information

The authors declare no competing financial interests. Supplementary information accompanies this paper on www.nature.com/naturephysics. Reprints and permissions information is available online at www.nature.com/ reprints. Correspondence and requests for materials should be addressed to J.J.L.M.