Electrically driven nuclear spin resonance in single-molecule magnets
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back into the membrane (36, 37). On the other hand, TM7 is in the middle of the 7-TM structure of BsYetJ, where it forms extensive interactions with other TM helices. These include the conserved di-aspartyl pH sensor between TM6 and TM7 and a derivative h1-BI-1 models provide substantial insights into the functioning of TMBIM proteins and other therapeutic prospects for intervention of anti-apoptotic functions in treatments of cancers.

REFERENCES AND NOTES

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SUPPLEMENTARY MATERIALS
www.sciencemag.org/content/344/6188/1131/suppl/DC1
Materials and Methods
Figs. S1 to S10
Table S1
References (41–63)
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REPORTS
QUANTUM INFORMATION
Electrically driven nuclear spin resonance in single-molecule magnets
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Recent advances in addressing isolated nuclear spins have opened up a path toward using nuclear-spin–based quantum bits. Local magnetic fields are normally used to coherently manipulate the state of the nuclear spin; however, electrical manipulation would allow for fast switching and spatially confined spin control. Here, we propose and demonstrate coherent single nuclear spin manipulation using electric fields only. Because there is no direct coupling between the spin and the electric field, we make use of the hyperfine Stark effect as a magnetic field transducer at the atomic level. This quantum-mechanical process is present in all nuclear spin systems, such as phosphorus or bismuth atoms in silicon, and offers a general route toward the electrical control of nuclear-spin–based devices.

The realization of a functional quantum computer is currently one of the most ambitious technological goals. Among existing concepts (7–3), devices in which the quantum bits (qubits) are encoded by spins are very attractive, as they benefit from the steady progress in nanofabrication and allow for electric readout of the qubit states (4–6). Nuclear-spin–based devices are better isolated from the environment than their electron spin counterparts (7), but their detection and manipulation remain challenging.

Operating nuclear spin qubits have been demonstrated with devices based on nitrogen vacancy centers (8), single-molecule magnets (9–11), and silicon (12). Yet, their integration remains limited by the on-chip microcoils (13) used to manipulate the spin. The parasitic crosstalk to neighboring spin qubits and the large currents necessary to perform quantum operations are serious limiting factors. Using electric fields instead of magnetic fields to manipulate the spin would alleviate this problem, as only small displacement currents are required; in addition, electric fields can be easily focused and shielded within a small volume. The coupling of the spin to the electric field is established by the hyperfine Stark effect, which transforms the electric field into a local magnetic field. Moreover, the static hyperfine Stark effect can be used

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A nuclear spin qubit transistor and its detection scheme. (A) Artist’s view of a nuclear spin qubit transistor based on a single TbPc2 molecular magnet. The molecule, consisting of a Tb3+ ion (pink) sandwiched between two Pc-ligands (white), is coupled to source, drain, and gate (not shown) electrodes. The four anisotropic nuclear spin states of the Tb3+ (colored circles) can be manipulated with an electric field pulse. (B) Three coupled subsystems of the transistor: (i) The four-level nuclear spin qubit is hyperfine (HF) coupled to (ii) an Ising-like electronic spin, which in turn is antiferromagnetically exchange (Ex) coupled to (iii) a readout quantum dot.

Fig. 2. Zeeman diagram and nuclear spin detection procedure. (A) Zeeman diagram of the TbPc2 molecular magnet, showing the hyperfine split electronic spin ground state doublet |↑⟩ and |↓⟩ as a function of the external magnetic field \( H_z \) parallel to the easy-axis of magnetization. The ligand-field–induced avoided level crossings (colored rectangles) allow for tunneling of the electron spin. (B) The jumps of the conductance \( g \) of the readout quantum dot during magnetic-field sweeps are nuclear-spin dependent. (C) Histograms of the positions of about 75,000 conductance jumps, showing four nonoverlapping Gaussian-like distributions; each conductance jump can be assigned to a nuclear spin state.
Fig. 3. Rabi oscillations of a single nuclear spin qubit. (A) Time-dependent external magnetic field \( H_z \) and pulse sequence. The nuclear spin is first initialized in the lower \(|3/2\rangle\) state (init sequence). A subsequent MW pulse of frequency \( v_z \) and duration \( \tau \) induces an effective oscillating magnetic field resulting in coherent manipulation of the two lower states of the nuclear spin qubit. Finally, \( H_z \) is swept back to probe the final state of the nuclear spin qubit. (B and C) Rabi oscillations between \(|3/2\rangle\) and \(|1/2\rangle\) states obtained by repeating the above sequence 100 times at each \( \tau \), for two different MW powers, (B) \( P_{\text{MW}} = 1 \) mW and (C) \( P_{\text{MW}} = 1.58 \) mW.

Fig. 4. Stark shift of the hyperfine coupling and Ramsey fringes. (A) Rabi oscillations visibility measured at different MW frequencies for three different gate voltages \( V_g \). (B) Rabi frequencies \( \Omega_r \) corresponding to the visibility of (A). The continuous lines are fit to the experimental points following the theoretical expression of the Rabi frequency dependence (see text). (Inset) The relative change \( \Delta A/A \) with respect to the applied \( V_g \). (C) Time-dependent external magnetic field \( H_z \) and pulse sequence. Initialization and probe of the nuclear spin qubit are performed by using the identical protocol as in Fig. 3A. The MW sequence consists of two \( \pi/2 \) pulses, with an increasing interpulse delay \( \tau \). (D) Ramsey interference fringes obtained by repeating the procedure of (C) 100 times. \( V_g = 2.205 \) V, corresponding to a Rabi frequency \( \Omega_r = 1.136 \) MHz and a resonant frequency \( v_z = 2.449 \) MHz of the nuclear spin qubit. The measured coherence time \( T_2^* = 64 \) \( \mu \)s.

We turn now to the electrical manipulation of a single nuclear spin. The hyperfine Stark effect describes the change of the hyperfine constant \( A \) in the Hamiltonian \( H_{\text{HF}} = A I \) as a function of an external electric field (21, 22). Writing the Hamiltonian as \( H_{\text{HF}} = E_z \mu_0 \mathbf{I} \cdot \mathbf{B}_{\text{HF}}(A, J) \), we demonstrate that the modification of \( A \) is converted into a change of the effective magnetic field \( \mathbf{B}_{\text{HF}}(A, J) \) at the center of the nucleus. Given a HF constant of \( A = 24.9 \) mT (23) and \( J = 6 \), we obtain an effective static field of 329 T. Thus, a periodic modulation of \( A \) by 1/1000 of its value is sufficient to generate local magnetic field oscillations of \( \pm 329 \) mT. Because the orientation of the quantization axis of the molecule with respect to the electric field is not well determined, the effective magnetic field will have components in the \( x \) and \( z \) direction. However, in terms of oscillating fields, only the component in the \( x \) direction can rotate the nuclear spin, whereas the \( z \) component induces additional decoherence. Moreover, even moderate electric field amplitudes of 1 mV/nm are sufficient to induce a controlled fine tuning of the HF constant, which is on the order of 1% (15).

For the experimental demonstration of the single–nuclear-spin manipulation, we focused on the nuclear qubit subspace of \(|+3/2\rangle\) and \(|+1/2\rangle\) whose eigenstates are separated by \( \Delta v_0 = 2.45 \) GHz (the exact value is device dependent (23, 24)). We initialize the nuclear spin qubit by sweeping the external magnetic field and forth between \( \pm 60 \) mT at 80 mT/s (Fig. 3A) until a QTM transition is measured at \( \approx 38 \) mT, which is the signature of the \(|+3/2\rangle\) qubit state (Fig. 2C). We then apply a microwave (MW) pulse of duration \( \tau \) and a local field amplitude on the order of \( \approx 1 \) mV/nm while keeping the external magnetic field constant (Fig. 3A); the pulse modulates the hyperfine constant \( A \) at the MW frequency. Finally, we detect the resulting state by sweeping back the external magnetic field on a time scale faster than the measured relaxation times of both nuclear spin states. The entire sequence is repeated when the final state is not detected because of a missing QTM transition. Repeating this procedure resulted in coherent Rabi oscillations (Fig. 3B and C). The visibility of the Rabi oscillations as a function of the applied MW frequency (Fig. 4A) has a maximum at the resonant frequency \( v_0 \) and decreases for increasing detuning \( \Delta v = |v - v_0| \). In addition, a clear dependence of the nuclear-qubit resonance frequency on the gate voltage is observed in Fig. 4A. This effect can be attributed to the static HF Stark shift, owing to the additional electric field induced by the gate voltage, which shows our ability to tune the HF constant \( A \) between the electronic spin and the nuclear spin qubit. Only the \( z \) component of the effective magnetic field will modify the level splitting. Applying a static gate voltage offset of 16 mV shifts the resonant frequency of the nuclear spin qubit by \( \Delta v_0 \approx 7 \) MHz, corresponding to \( \Delta A / A \approx 0.23\% \) (Fig. 4B, inset).

To extract the Stark shift–induced effective ac magnetic driving field at the nuclei, used to
coherently manipulate the nuclear spin quibt, we measured the Rabi frequency $\Omega_R$ evolution as a function of the applied MW frequency for the three different gate voltages (Fig. 4B). The horizontal shift of the minimum is again induced by the static gate voltage, whereas the vertical evolution indicates an increasing effective ac field in the direction, which is probably caused by the nonlinearity of the HF Stark effect. The solid lines are fits to $\Omega_R = \sqrt{\Delta^2 + \left(\sqrt{3}\tilde{B}_N + B_0\right)^2}$, with $g_N$ being the nuclear $g$-factor [1.354 for Tb (25)], $\tilde{B}_N$ the nuclear magneton, and $B_0$ the effective magnetic field in the $x$ direction. The equation gives $B_0 = 62, 98$, and $183$ mT for $V_g = 2.205, 2.215$, and $2.221$ V, respectively, up to two orders of magnitude higher than magnetic fields created by on-chip microcoils. The electric driving field is induced along the source-drain direction, and only the $x$ component of the corresponding effective magnetic field is responsible for the nuclear spin rotation.

We turn now to the measurements of the Ramsey fringes to asses the dephasing time $\tau_\phi$ of the nuclear spin quibt, which is tantamount to the average duration over which the coherence of the quantum superposition is preserved. As shown by the pulse sequence presented in Fig. 4C, the nuclear spin quibt is first initialized in the $|3/2\rangle$ state. Subsequently, two $\pi/2$ MW pulses are generated with an interpulse delay $\tau$. Finally, the readout of the final state is probed with the same procedure as explained previously. Repeating this procedure results in the Ramsey fringes shown in Fig. 4D. The data follow an exponentially decaying cosine function revealing a coherence time $\tau_\phi \approx 64$ $\mu$s. Detailed studies suggest that the major contribution to the decoherence was caused by charge noise, which induced magnetic field fluctuations of about $10$ mT via the HF Stark effect. Therefore, we expect that more stable gate oxides would increase $\tau_\phi$ by one or two orders of magnitude. Our results show the general feasibility of establishing an all-electrical control of a single nuclear spin through use of the hyperfine Stark effect and should be transferable to other spin quibt devices with a large hyperfine interaction.

REFERENCES AND NOTES
15. Materials and methods are available as supplementary materials on Science Online.

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INTERFACIAL CHEMISTRY

Liquid flow along a solid surface reversibly alters interfacial chemistry

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In nature, aqueous solutions often move collectively along solid surfaces (for example, raindrops falling on the ground and rivers flowing through riverbeds). However, the influence of such motion on water-surface interfacial chemistry is unclear. In this work, we combine surface-specific sum frequency generation spectroscopy and microfluidics to show that at immersed calcium fluoride and fused silica surfaces, flow leads to a reversible modification of the surface charge and subsequent realignment of the interfacial water molecules. Obtaining equivalent effects under static conditions requires a substantial change in bulk solution pH (up to 2 pH units), demonstrating the coupling between flow and chemistry. These marked flow-induced variations in interfacial chemistry should substantially affect our understanding and modeling of chemical processes at immersed surfaces.

The chemistry taking place at the interface between a solid material and an aqueous solution is relevant for a variety of disciplines, including geology, environmental sciences, and catalysis (1–3). The local chemical composition at the interface strongly influences the reactivity of the system, as has been demonstrated, for example, in geological studies of weathering (4). Similarly, the abra-sion and dissolution of materials immersed in aqueous solutions is at the heart of environmental concerns. Dissolution of ocean organisms’ shells and skeletons stemming from increasing acidification of water could lead to potentially devastating consequences for marine life (5). Accurate knowledge of the composition of both the solid material and the aqueous solution locally at the surface is essential to understand, model, and predict these interfacial chemical processes.

Previous studies have shown that the structure of liquid water at a solid interface is different from that of the bulk phase (6–8) and can resemble the ice structure (9) because of the specific physico-chemical properties of the surface (e.g., charge, morphology, wetting properties). Generally speaking, interfacial water possesses a more structured hydrogen bonding network than bulk water. Among various factors, the solid surface holding a net electric charge acts to align the static dipole of water molecules at the surface (Fig. 1A, top). The length over which the electric field extends into the solution from the surface is referred to as the Debye length ($\lambda_D$) and correlates with the distance from the surface that water retains its preferential alignment (~1 to 10 nm). In addition to causing water alignment at the surface, the charge present at the interface also attracts ions from the solution to the interface, causing surface-charge screening and leading to the formation of the so-called electrical double layer ($\lambda_D$). Accordingly, the composition, as well as the structure, of the fluid adjacent to the surface can vary substantially compared with the bulk ($\lambda_D$–14). Molecular dynamics simulations have shown, for instance, that the interfacial pH can be quite different from the bulk ($\lambda_D$). Although substantial progress regarding interfacial composition and molecular organization has been achieved, in nearly all of these studies on solid-liquid