

# Control of quantum magnets by atomic exchange bias

Shichao Yan, Deung-Jang Choi, Jacob A. J. Burgess, Steffen Rolf-Pissarczyk  
and Sebastian Loth

## 1. Spin Hamiltonian for the Fe trimer

The spin states of the Fe trimer were modelled with an effective spin Hamiltonian,  $\hat{H}_{Trimer}$ , similar to previous work<sup>15,18,19</sup>

$$\hat{H}_{Trimer} = \sum_{i=A,B,C} \hat{H}_{(i)} + J_1 (\vec{S}_{(A)} \cdot \vec{S}_{(B)} + \vec{S}_{(B)} \cdot \vec{S}_{(C)}) \quad (S1)$$

The spin operators  $\vec{S}_{(A)}$ ,  $\vec{S}_{(B)}$ , and  $\vec{S}_{(C)}$  describe each Fe atom as a spin with magnitude  $S = 2$ . The atoms couple by Heisenberg exchange interaction. The coupling strength,  $J_1$ , has been determined in previous work<sup>15</sup>. We account for minor variation of  $J_1$  due to the local environment of the studied Fe trimer within the error bars given in ref. 15. The single spin anisotropy Hamiltonian  $\hat{H}_{(i)}$  describes the magnetic anisotropy and the Zeeman effect of an external magnetic field  $\vec{B}_{ext}$  for each spin:

$$\hat{H}_{(i)} = -g_{(i)}\mu_B\vec{B}_{ext} \cdot \vec{S}_{(i)} + D_{(i)}\hat{S}_{(i)}^z{}^2 + E_{(i)}(\hat{S}_{(i)}^x{}^2 - \hat{S}_{(i)}^y{}^2) \quad (S2)$$

where  $g_{(i)}$  is the Landé  $g$ -factor and  $\mu_B$  the Bohr magneton and  $S_{(i)}^{x,y,z}$  the spin operators for each spin. To minimize free fit parameters we use the  $g$ -value of the isolated Fe atom  $g = 2.1$ , see ref. 18. The transverse anisotropy ( $E_{(i)}$ ) was previously found to vary minimally compared to its isolated-atom value and was set to  $E_{(i)} = 0.31$  meV<sup>18,19</sup>. The uniaxial anisotropy ( $D_{(i)}$ ) was found more sensitive to the local environment than the transversal anisotropy<sup>19</sup>. Supplementary figure S1 shows a comparison of measured and fitted spectra. The best fit yields  $D_{(A,C)} = -2.1$  meV (side atom) and  $D_{(B)} = -3.6$  meV (centre atom). The spin excitation spectra were calculated using the same spin-dependent scattering Hamiltonian as in ref. 28 and reproduce measured spectra including the difference between side and centre atoms well (see also *Methods* of the main text).

## 2. Exchange interaction with magnetic tip

The magnetic cluster on the tip (3-4 Fe atoms) can be assumed to be paramagnetic with a large magnetic moment. This magnetic moment then aligns to the external magnetic field. In this limit Heisenberg-type exchange interaction between the tip spin and atoms of the Fe trimer can be simplified to Ising-type interaction, because  $S^+$ ,  $S^-$  terms of the Heisenberg exchange become negligible,  $\hat{H}_{Couple} = J_{ts}\hat{S}_t \cdot \hat{S}_a = J_{ts} \left[ \frac{1}{2}(\hat{S}_t^+ \cdot \hat{S}_a^- + \hat{S}_t^- \cdot \hat{S}_a^+) + \hat{S}_t^z \cdot \hat{S}_a^z \right] \approx J_{ts}\hat{S}_t^z \cdot \hat{S}_a^z$ . The spin

vector operators of the tip spin and the spin of the coupled Fe atom in the trimer are represented by  $\hat{S}_t^z$  and  $\hat{S}_a^z$  respectively, and  $J_{ts}$  is the Heisenberg exchange coupling strength, see ref. 25. The simplification to Ising-type interaction permits treatment of the tip interaction without explicit inclusion of possible quantum states of the tip magnetic moment. By including this exchange interaction with the magnetic tip, the total spin Hamiltonian,  $\hat{H}_{Total}$  can be written as:

$$\hat{H}_{Total} = \hat{H}_{Trimer} + J_{ts} \hat{S}_t^z \cdot \hat{S}_a^z. \quad (S3)$$

We assume the tip spin is aligned by the external magnetic field, and that it will not change its spin alignment significantly during the measurements. Magnetic interaction between Fe atoms across a vacuum gap is dominated by direct exchange interaction and features an exponential dependence with tip-sample distance<sup>12,14</sup>:

$$J_{ts} \hat{S}_t^z = J_{ts}^0 \hat{S}_t^z (\exp(-\gamma z) - 1) \quad (S4)$$

Diagonalization of the total spin Hamiltonian yields the spin state distribution of the Fe trimer modified by the exchange interaction with the tip. We calculated the spin relaxation time of the trimer,  $T_1$ , for different exchange interaction strengths (see Section 6). The decay constant,  $\gamma$ , of the exchange coupling is found to be 60 pm±2 pm by fitting the calculated evolution of  $T_1$  to the measured tip-sample distance dependence of  $T_1$  (Fig. 2a). The fit value for  $J_{ts}^0 \hat{S}_t^z$  was found to be  $4.86 \times 10^{-3}$  meV.

### 3. Spin relaxation time calculation

We measure the spin relaxation time of the Fe trimer,  $T_1$ , by electronic pump-probe spectroscopy. In this method a pump pulse excites the spin and a weaker probe pulse measures the state of the system after a time delay  $\Delta t$ . The resulting decay curve of the probe pulse induced tunnel current,  $I(\Delta t)$ , describes the average relaxation of the Fe trimer in the absence of tunnel current as no voltage is applied between pump and probe pulses. Hence,  $T_1$  is determined by the spontaneous relaxation rate,  $r_{ge}^{s \leftarrow s}$ , from excited state,  $|\varphi_{-}\rangle$ , to ground state,  $|\varphi_{+}\rangle$ , due to the spin-dependent scattering of electrons from the Cu substrate that interact with the atoms of the Fe trimer and return to the substrate. The same relaxation process is possible for tip electrons, but for the tip-sample separations and tunnel junction conductances used in this work, it is negligible<sup>22</sup>.

To calculate the relaxation rate, we use a previously published model for magnetic atoms adsorbed on the Cu<sub>2</sub>N surface<sup>22,28</sup>. The relaxation rate,  $r_{ge}^{s \leftarrow s}$ , is determined by the number of electrons,  $N$ , available for scattering and the transition probability,  $\tilde{P}_{eg}^{s \leftarrow s}$ , for electron scattering between  $|\varphi_{-}\rangle$  and  $|\varphi_{+}\rangle$ ,

$$r_{ge}^{s \leftarrow s} = N \cdot \tilde{P}_{eg}^{s \leftarrow s} \quad (S5)$$

The scattering process requires an occupied and an empty state with energy difference ( $E_e - E_g$ ) within Cu substrate's density of states.  $E_e$  and  $E_g$  are the energies of excited state and ground

state of the total spin Hamiltonian. Consequently, only electrons close to the Fermi energy contribute to the spin relaxation of the Fe trimer. Thermal occupation of electron states according to the Fermi-Dirac distribution has to be considered.  $\tilde{P}_{\text{eg}}^{s \leftarrow s}$  includes the quantum mechanical transition intensities between spin states and the scattering probability across the  $\text{Cu}_2\text{N}$  decoupling layer. Under the assumption of a constant density of states in the energy window of interest ( $\pm 2$  mV around the Fermi energy) the spin relaxation rate can be expressed as:

$$r_{\text{ge}}^{s \leftarrow s} = \frac{G_S}{e^2} \int_{-\infty}^{+\infty} F(E) [1 - F(E - E_e + E_g)] \cdot P_{\text{eg}}^{s \leftarrow s} dE \quad (\text{S6})$$

Where  $F$  is the Fermi function  $F(E) = (1 + \exp(E)/k_B T)^{-1}$ . The prefactor  $G_S$  characterizes the strength of the spontaneous relaxation channel and is an empirical parameter. Throughout this work, it is maintained as a constant,  $G_S = 3.1 \mu\text{S}$ , which suggests that it is an intrinsic property of the Fe trimer on this surface. The transition coefficient  $P_{\text{eg}}^{s \leftarrow s}$  relates the probability for spin-dependent scattering per unit time to the quantum-mechanical transition intensities<sup>7,22,28,29</sup>. We assume that the total transition intensity for electron scattering with the Fe trimer's states is given by the sum of the transition intensities for each atom of the trimer ( $A$ ,  $B$  and  $C$ ). The total transition coefficient is given by

$$P_{\text{eg}}^{s \leftarrow s} = \sum_{i=A,B,C} \frac{1}{P_0} \sum_{\sigma, \sigma'} |\langle \varphi_+, \sigma | \vec{S}_{(i)} \cdot \vec{\sigma} | \varphi_-, \sigma' \rangle|^2 \quad (\text{S7})$$

where  $\varphi_-$  and  $\varphi_+$  are the two low-lying spin states of the Fe trimer and  $\varphi_+$  has lower energy.  $\sigma, \sigma'$  represent the initial and final spin state of the scattering electron.  $|\varphi, \sigma\rangle$  is the product state of the Fe trimer spin  $|\varphi\rangle$  and tunneling electron spin  $|\sigma\rangle$ .  $\vec{S}_{(i)}$  and  $\vec{\sigma}$  are the spin vector operators for each atom of the Fe trimer and tunnelling electron spin respectively.  $P_0$  is a normalization constant, see ref. 22. We calculate the spin lifetime  $T_1$  for the excited spin state as

$$T_1 = (r_{\text{ge}}^{s \leftarrow s})^{-1} \quad (\text{S8})$$

#### **4. Linear dependence of $T_1$ on external magnetic field**

The energy difference ( $E_e - E_g$ ) between the two low-lying spin states increases with application of a magnetic field due to the Zeeman energy. For strong enough magnetic fields, this energy gap becomes proportional to the magnetic field strength. At low temperature ( $E_e - E_g$ ) also quickly exceeds the thermal energy. In this case, the number of substrate electrons,  $N$ , that contribute to the spin relaxation is proportional to the magnetic field,  $N \sim B_{\text{ext}}$ . All experiments of this work were carried out at 0.5 K where this simplification can be made for magnetic field in excess of  $B_{\text{ext}} > 0.2$  T.

The transition between the two low-lying spin states is induced by the transverse anisotropy. In strong enough external magnetic field ( $B_{\text{ext}} > 0.2$  T) the transition probability,  $\tilde{P}_{\text{eg}}^{s \leftarrow s}$ , becomes reciprocal to the square of the external magnetic field,  $\tilde{P}_{\text{eg}}^{s \leftarrow s} \sim B_{\text{ext}}^2$ . Consequently, the relaxation rate,  $r_{\text{ge}}^{s \leftarrow s}$ , becomes inversely proportional to the external magnetic field and  $T_1$  will respond

linearly to the external magnetic field (Fig. 3c):

$$T_1 = \frac{1}{N\tilde{P}_{eg}^{s\leftarrow s}} = \frac{\alpha}{B_{ext} \cdot \frac{1}{B_{ext}^2}} = \alpha B_{ext} \quad (\text{S9})$$

$\alpha$  is the rate of change of the spin relaxation time with external magnetic field. For the Fe trimer in Figs. 1, 2a, 3d, the calculated rate of change with external magnetic field is  $\alpha = |dT_1/dB_{ext}| = 1.32 \pm 0.08 \mu\text{s/T}$ .

### 5. Local magnetic field

The Ising-type exchange interaction between the tip spin,  $\vec{S}_t$ , and the spin of the coupled Fe trimer atom,  $\vec{S}_a$ , can be modelled as a local magnetic field by assuming that the tip spin is rigid and does not change during the measurements. The local magnetic field only acts on the atom of the Fe trimer under the magnetic tip. Because of the antiferromagnetic nature of the exchange coupling between the magnetic tip and Fe trimer atom, the local magnetic field is always pointing opposite to the direction of the external magnetic field.

$$\hat{H}_{ts} = J_{ts} \hat{S}_t^z \cdot \hat{S}_a^z = -g\mu_B \left( -\frac{J_{ts}}{g\mu_B} \hat{S}_t^z \right) \cdot \hat{S}_a^z = -g\mu_B B_{loc} \hat{S}_a^z \quad (\text{S10})$$

By comparing equations (S4) and (S10), we can arrive at the tip-sample distance dependence of the local magnetic field stated in equation (1) of the main text:

$$B_{loc} = B_0(\exp(-\gamma z) - 1) \quad (\text{S11})$$

### 6. Dependence of $T_1$ on the local magnetic field ( $B_{loc}$ )

The local magnetic field can act on each atom of the Fe trimer depending on which atom the tip is positioned. Supplementary figure S3 shows the calculated evolution of the trimer's spin states for local magnetic field applied on a side atom (Fig. S3a) and the centre atom (Fig. S3b) in the absence of the external magnetic field. The two low-lying spin states show the same Zeeman splitting independent of where the local magnetic field is applied. In contrast the higher excited states at  $>7$  meV energy differ when the local magnetic field is applied to side or centre atom.

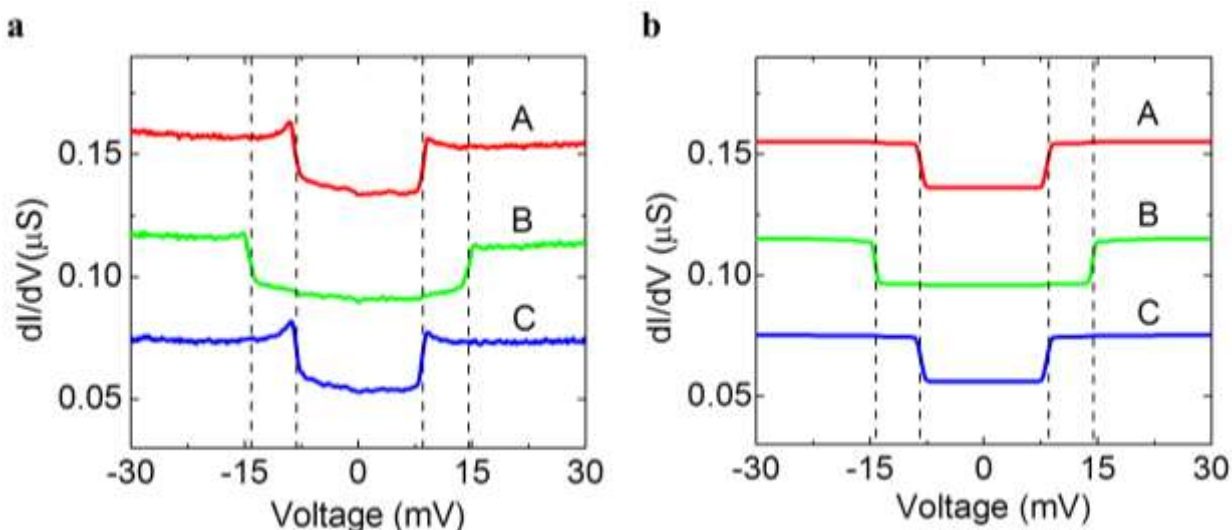
Pump-probe spectroscopy is sensitive to the spin relaxation between the two low-lying states. Close inspection of these two states shows that the difference in excitation energy is less than 1% when the local magnetic field is applied to the centre atom as compared to a side atom, Fig. S3 a, b. Furthermore, the spin state composition of the first excited spin state also differs by less than 1%, Fig. S3 c, d. Consequently the response of the spin relaxation time to application of the local magnetic field on either the centre or a side atom is almost identical. The reason for the similar behaviour lies in the large energy gap between the two low-lying states and the fact that all constituent atoms of the trimer have equal spin.

In the experiment a minimum external magnetic field of 0.5 T was applied to obtain spin polarization of the tip. This adds to the local magnetic field. Due to the antiferromagnetic order of the Fe trimer  $dT_1/dB_{\text{loc}}$  can have a different sign for  $B_{\text{loc}}$  applied to the different atoms but the rate of change  $|dT_1/dB_{\text{loc}}|$  remains almost identical, Fig. S4. The rate of change of  $T_1$  with local magnetic field is  $1.28 \pm 0.04 \mu\text{s/T}$  on the side atom and  $1.31 \pm 0.04 \mu\text{s/T}$  on the centre atom. This difference is smaller than the uncertainty of the fit to the experiment ( $\pm 0.04 \mu\text{s/T}$ ).

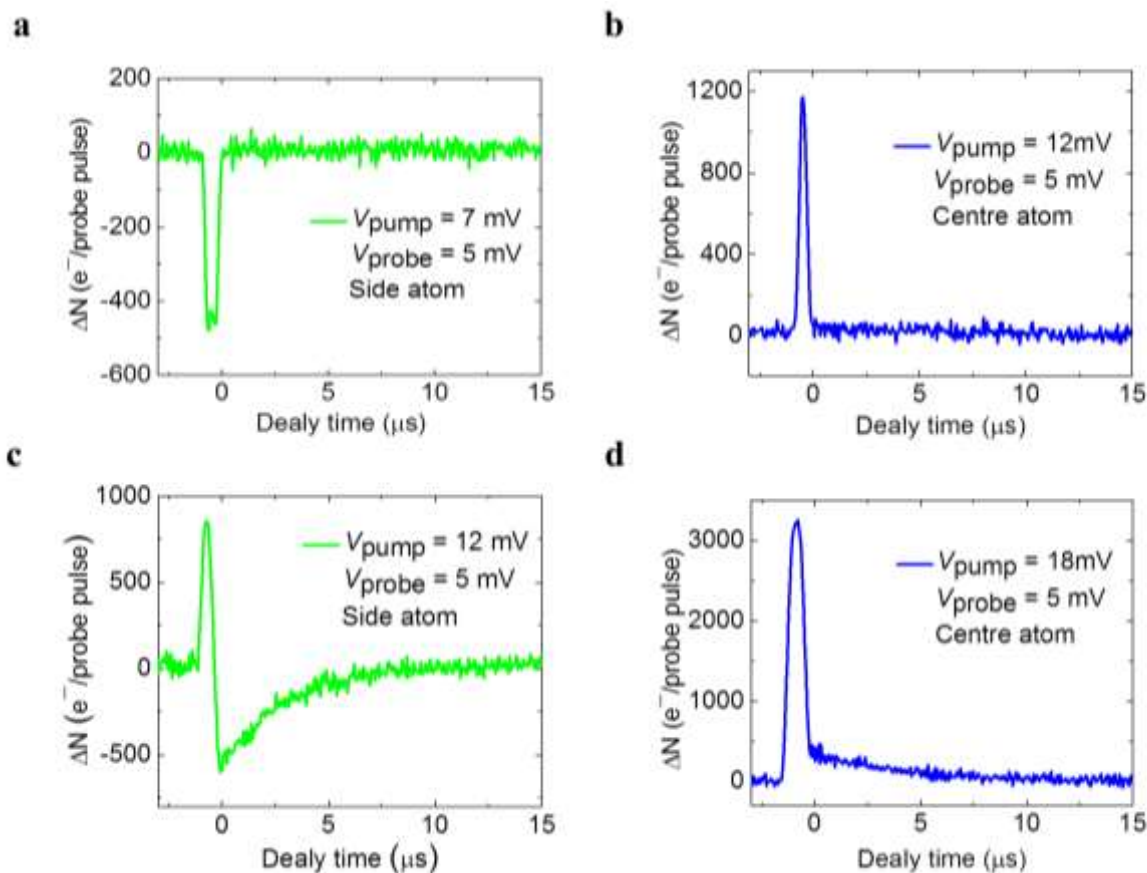
We also note that close to the avoided level crossing, in the range where  $|B_{\text{ext}} + B_{\text{loc}}| < 0.2 \text{ T}$  ( $B_{\text{ext}}$  is the strength of the external magnetic field), the linear dependence of  $T_1$  on  $B_{\text{loc}}$  breaks down because the thermal occupation of the electron states in the Cu substrate as well as the detailed spin-state mixing become significant Fig. S4.

## References

28. Loth, S., Lutz, C. P. & Heinrich, A. J. Spin-polarized spin excitation spectroscopy. *New J. Phys.* **12**, 125021 (2010).
29. Lambe, J. & Jaklevic, R. C. Molecular vibration spectra by inelastic electron tunneling. *Phys. Rev.* **165**, 821–832 (1968).

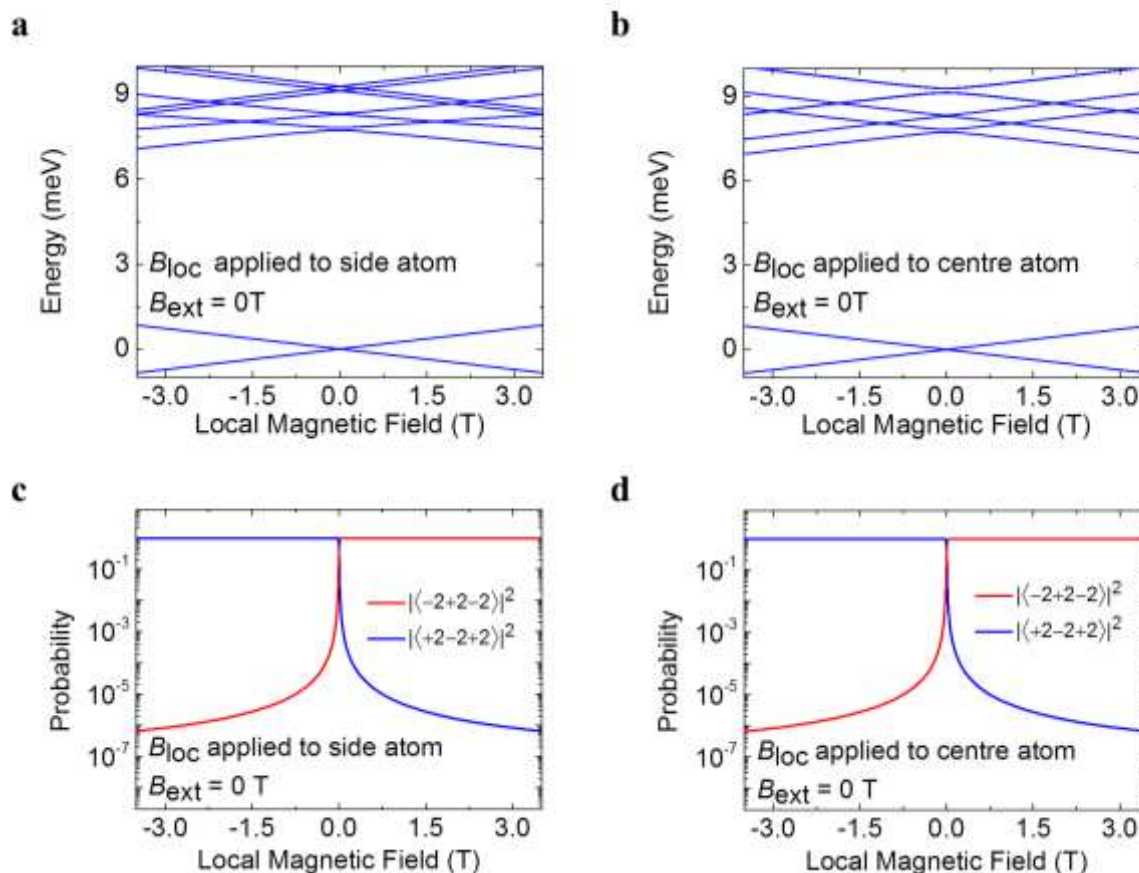


**Supplementary Figure S1 | Measured and calculated spin excitation spectra of the Fe trimer.** **a**, Experimental spectra acquired at the tunnel junction setpoint 30 mV, 2 nA with a non-magnetic tip. Magnetic field of 2 T was applied along the magnetic easy axis of the Fe atoms in the trimer. Temperature was 0.5 K. A and C were measured on the two side atoms of the Fe trimer and B on the centre atom. The dashed lines indicate the threshold voltages for the spin excitations on the side (8.5 mV) and centre (14.5 mV) atoms of the Fe trimer. **b**, Calculated spin excitation spectra using the spin Hamiltonian and parameters outlined in Supplementary Section 1 and in *Methods* of the main text.



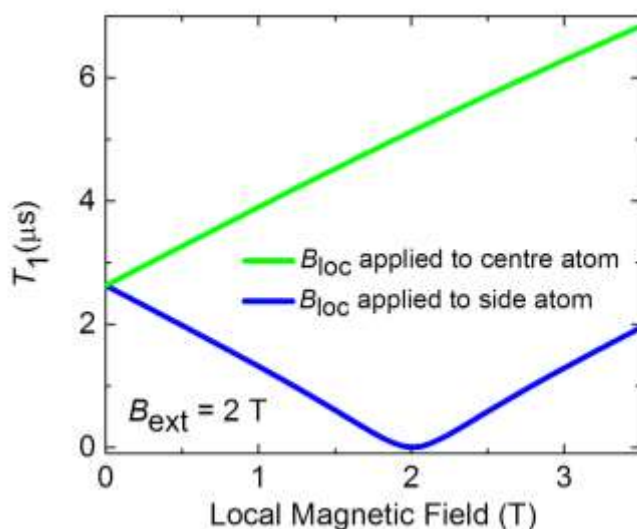
**Supplementary Figure S2 | Determination of the threshold pump voltage for the side and centre atoms of the Fe trimer.** **a, b**, Pump-probe measurements with the STM tip positioned on a side atom of the Fe trimer with pump voltage amplitude 7 mV and 12 mV. The onset of the pump-probe signal was observed between 7 mV and 12 mV and lies at the threshold voltage for spin excitations  $V_{\text{thr}} = 8.5$  mV. **c, d**, Pump-probe measurements with the STM tip positioned on the centre atom of the Fe trimer with pump voltage amplitude of 12 mV and 18 mV. The tip-sample distance was fixed at a tunnel junction setpoint 10 mV, 1 nA for all the measurements.





**Supplementary Figure S3 | Response of Fe trimer to local magnetic field.** **a, b**, Energy levels of the Fe trimer in the absence of the external magnetic field,  $B_{ext}$ , calculated for local magnetic field applied to a side atom (**a**) and the centre atom (**b**). **c, d**, Variation of the composition of the excited spin state showing the probability distribution of  $|+2 -2 +2\rangle$  and  $|-2 +2 -2\rangle$  calculated as a function of the local magnetic field applied to a side atom (**c**) and the centre atom (**d**) for the parameters of (**a, b**).





**Supplementary Figure S4 | Dependence of  $T_1$  on the local magnetic field.** Calculated dependence of  $T_1$  as a function of local magnetic field applied to the side (blue line) and center (green line) atoms. External magnetic field,  $B_{\text{ext}}$ , was set to 2 T. For fields  $|B_{\text{ext}} + B_{\text{loc}}| > 0.2$  T the rate of change  $|dT_1/dB_{\text{ext}}|$  is  $1.31 \mu\text{s/T}$  as  $B_{\text{loc}}$  is applied to a side atom and  $1.28 \mu\text{s/T}$  for the center atom. The parameters for the calculation (see Supplementary Section 3 and 4) are extracted by fitting the spin excitation spectra (Fig. S1) and the intrinsic lifetime (Fig. 3d) of the Fe trimer.