Rate equations
The theoretical simulations are based on (1), and summarized here for completeness. To model the differential conductance we have used rate equations up to third order in the coupling between the conduction electrons and the Co atoms. The transition probability for an electron tunneling from tip to sample from a collective initial state (i) to a final state (f) is given by

$$W_{if} = \frac{2\pi}{\hbar} \left| H'_{if} \right|^2 + \sum_m \left( \frac{H'_{im} H'_{mf} H'_{fi}}{E_i - E_m + c.c.} \right) \delta(E_i - E_f)$$

where $H'$ represents the (isotropic) interaction between the Co atoms and the conduction electrons in the tip and substrate. We assume that the only non-negligible current flows through the atom directly situated under the tip, indicated with an index $l$ for the spin exchange operators hereafter. The interaction Hamiltonian is thus given by

$$H' = \sum_{\alpha, \alpha'} \sum_{k, k'} J^{\alpha\alpha'} \left[ S_i^\alpha \left( c_{wkl}\alpha c_{atk'} - c_{wkl}\alpha c_{akt} \right) + S_i^{\alpha'} c_{atk}^{\dagger} c_{ak}\alpha + S_i^{-\alpha'} c_{atk}^{\dagger} c_{ak}\alpha \right] + \sum_{\alpha, \alpha'} \sum_{k, k'} \sum_\sigma T^{\alpha\alpha'} c_{wkl}\alpha c_{ak}\sigma$$

where the indices $\alpha$ and $\alpha'$ represent either the tip or substrate, such that $T^{k\alpha}$ and $J^{k\alpha}$ are the coupling constants for potential scattering and spin flip exchange processes respectively involving electrons from both the tip and the substrate. The second order contribution to the differential conductance then yields

$$\frac{\partial I}{\partial V}^{(2)} = \frac{2\pi e^2}{\hbar} \rho' \rho^* \left( 2 \langle T^{ks} \rangle^2 + \langle J^{ks} \rangle^2 \sum_{if} p_i(T) \left[ \langle \epsilon_f | S_i^+ | \epsilon_i \rangle \rangle^2 + \langle \epsilon_f | S_i^- | \epsilon_i \rangle \rangle^2 + 2 \langle \epsilon_f | S_i^z | \epsilon_i \rangle \langle \epsilon_f | S_i^z | \epsilon_i \rangle \right] \right) \times \Theta(eV + \Delta_{if}, T) + \Theta(-eV + \Delta_{if}, T)$$

with the usual temperature broadened step function

$$\Theta(\omega) = \frac{1 - (\omega/k_BT + 1) \exp(-\omega/k_BT) + 1 - \exp(-\omega/k_BT)}{\left(1 - \exp(-\omega/k_BT)\right)^2}$$
and $\Delta_{if} = \varepsilon_i - \varepsilon_f$ the energy difference between the eigenstates $i$ and $f$ of $H_{3/2}$ in the manuscript. The parameters $\rho^t$ and $\rho^s$ are the density of states of the tip and substrate electrons at the Fermi energy. We have assumed the thermal equilibrium solution for the stationary level occupations $p_i(T)$, justified by the fact that the measurements are performed with a large distance between the tip and sample.

The largest third order contribution to the differential conduction arises due to interference between electrons tunneling from tip to substrate and spin exchange processes between the substrate electrons and the Co atoms, yielding

$$
\frac{\partial I^{(3)}}{\partial V} = \frac{4\pi e^2}{h}\rho^t \rho^s \left( f^{fs} \right)^2 \sum_{if} p_i(T) \sum_{\alpha,\beta,\gamma = \pm, \pm, \pm} \varepsilon_{\alpha\beta\gamma} \langle \varepsilon_i | S^\alpha_i | \varepsilon_f \rangle \langle \varepsilon_f | S^\beta_m | \varepsilon_m \rangle \langle \varepsilon_m | S^\gamma_i | \varepsilon_i \rangle \times \\
\left( \Theta(eV + \Delta_{if}) [F(eV - \Delta_{fm}) + F(eV - \Delta_{mi})] + \Theta(-eV + \Delta_{if}) [F(-eV - \Delta_{fm}) + F(-eV - \Delta_{mi})] \right)
$$

where the Levi-Civita symbol $\varepsilon_{\alpha\beta\gamma}$ has the value $+1$ for $\varepsilon_{+\pm\pm}$ and all cyclic permutations, and the value $-1$ for all anti-cyclic permutations. The function $F(\omega)$ is defined as

$$
F(\omega) = -\int \int d\varepsilon d\varepsilon' \frac{\partial}{\partial \omega} f(\varepsilon - \omega) \frac{f(\varepsilon')}{\varepsilon' - \varepsilon} \approx \log \left| \frac{E_0 + |\omega|}{\omega + i\alpha k_B T} \right|
$$

where the last approximation is valid at low temperatures. The parameter $\alpha$ represents the thermal broadening of the Fermi Dirac distributions $f(\varepsilon)$ and is set to 1.5 throughout the computations. The value of the dimensionless parameter $\rho^t \rho^s f^t$ was previously estimated (2) to be equal to $\rho^t \rho^s \approx 0.15$, and as such is used in the theoretical modeling.

Throughout the paper we have used an effective temperature of 800 mK, which is higher than the base temperature of the STM due to the voltage modulations present in the experiment. All theoretical calculations of the differential conductance have been normalized by their value at 7.8 mV. We have furthermore set the ratio between the spin exchange constant and the potential scattering coupling to $J^s / T^s \approx 0.47$ in order to match the zero bias $dI/dV$ approximately with the experimental values.

For the calculation of the differential conductance in the effective spin-1/2 model, the Schrieffer-Wolff transformation yields the effective Hamiltonian describing the spin-1/2 multiplet of the Co chain. However, it is worth noting that the Kondo exchange interaction also changes due to the projection onto the spin-1/2 sector of the Co atoms. In contrast to the expansion of the Hamiltonian describing the Co chain, where we have expanded up to first order in $1/D$, we have for simplicity only taken into account the zeroth order expansion in $1/D$ for the exchange with the conduction electrons, leading to an extra factor of 2 in front of the $S^+$ and $S^-$ terms in $H'$. The effective spin-1/2 Kondo exchange thus becomes anisotropic. Finally, the spin-1/2 $dI/dV$ curves are normalized by the $dI/dV$ values at 7.8 mV of the spin-3/2 computations.
**Supplementary figures**

**Fig. S1.** a—i. Total magnetization calculations along the field direction (blue) for chains \( N = 1 \) to 9 as calculated from the \( H_{3/2} \) model. Below: lowest excitation energy calculations (red) following from the same model.
Fig. S2. a—i. Calculated magnetization ($<S^z>$) for the $H_{3/2}$ model along the field direction per site for $N = 1$ to 9 chains. Each magnetization plot is accompanied with the $H_{3/2}$ lowest excitation energy curve (red). Changes in local magnetization correspond to the experimentally observed field evolution of $dl/dV$ features per site shown in Figs. 3 and S3.
**Fig. S3.** Experimental results on chains of 1 to 9 atoms – comparison with $H_{3/2}$ taking into account next-nearest neighbor (nnn) interaction. ±3 mV IETS spectra from 0 T to 9 T transverse field (in 200 mT increments) obtained on each atom of every chain up to a length of 9 atoms (up to 8.6 T for $N = 7$). Red dashed lines indicate positions of expected ground state crossings calculated from the $H_{3/2}$ model with antiferromagnetic nn coupling $J$ only (same as in Fig. 3b). Orange dashed lines come from the same model but accounting for ferromagnetic nnn coupling of 0.05 $J$. Same color coding applies to the energy calculations below each chain data set. Due to normalization, scaling of individual spectra may differ by ~20% from values listed at the color bars.
**Fig. S4.** IETS spectra on a single Co atom on Cu$_2$N in a 3 T magnetic field oriented perpendicular to the surface, taken with the same spin-polarized tip as used in Fig. 4 (blue) and with a spin-unpolarized tip (grey).

**Fig. S5.** a—c. Spin-polarized IETS spectra taken at 1 T, 4.5 T and 5.5 T transverse field in an $N = 7$ chain (blue curves). Corresponding spectra taken with an unpolarized tip are shown in grey. d—e. IETS spectra taken on a single Co atom at the same field values as in a—c with the same spin-polarized tip (blue) and with a spin-unpolarized tip (grey). Dashed spin-unpolarized curves were taken on a different instance of the chain/atom than the corresponding spin-polarized curves.

**References**
