Supplementary Material
Tuning the coupling of an individual magnetic impurity to a superconductor: quantum phase transition and transport

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(Dated: September 18, 2018)

THEORETICAL CONSIDERATIONS

In this section, we summarize relevant theoretical considerations to understand the experimental results, including considerations of relevant parameters for driving the quantum phase transition, new analytical results on the effect of self-consistency on the local gap parameter $\Delta(\mathbf{r})$, and the energy ϵ of the YSR state.

Relation between experimental and model parameters

A minimal model for the scattering of substrate electrons by a magnetic impurity is the $s-d$ model ($\mathcal{H} = (V + J\mathbf{S}\cdot\boldsymbol{\sigma})$) which includes the hybridization between the impurity orbitals and the substrate through the exchange coupling J and the potential scattering V (as obtained by a Schrieffer-Wolff transformation from the Anderson model). Treating the impurity spin $\mathbf{S}$ as classical, the energies of the YSR states are given by

$$\epsilon = \pm\Delta \left(\frac{1 - \alpha^2 + \beta^2}{\sqrt{(1 - \alpha^2 + \beta^2)^2 + 4\alpha^2}} \right) \tag{S1}$$

with $\alpha = \pi\rho_0 SJ$ and $\beta = \pi\rho_0 V$. Here, ρ_0 is the normal-state density of states of the superconductor. As shown in the main manuscript, the approach of the STM tip to the FeP molecule shifts the YSR states substantially within the superconducting gap. Specifically, it shifts the YSR energies across the Fermi level, corresponding to the quantum phase transition. While according to Eq. S1, the YSR energies depend on several parameters, we argue that the exchange coupling strength J is the most relevant parameter for driving the quantum phase transition. In the following we explain why the other parameters are expected to affect the YSR energies only slightly, and cannot drive the quantum phase transition by themselves.

Exchange coupling J: The tip approach towards the molecule locally modifies the molecule-substrate distance as a result of tip-molecule forces. This changes the molecule-substrate hybridization and hence the exchange coupling J. As can be seen from Eq. (S1), J is essential for changing the sign of the YSR energy and, hence, the quantum phase transition. Moreover, all qualitiative features of our experimental data can be captured by the variation of this parameter in response to the force field of the STM tip, which induces conformational changes of the molecule.

Potential scattering V: The molecule-substrate hybridization also induces the potential scattering amplitude V. As V (and hence β) depends on the relative position of the singly and doubly occupied orbitals with respect to the Fermi level, V also accounts for changes in the charge transfer between impurity and substrate. However unlike J, the potential scattering V does not grow under renormalization group transformations of the $s-d$ model, so that V is generically expected to be weaker than J.

Normal density of states ρ_0 and gap parameter Δ: One can safely assume that ρ_0 cannot drive the quantum phase transition as it is a bulk parameter. Self-consistent calculations predict a J-dependent change in Δ at the impurity site. However, we show explicitly in the next section that this modification of Δ causes only minimal shifts of the YSR state energy which are substantially below the energy resolution of the experiment.

Impurity spin S: The tip approach may also modify the magnetic moment and thus the effective spin. However, we expect that the spin state is only changed by a small fraction of the total spin moment. If the spin magnetic moment changed by more than $\Delta S = 1/2$, we would expect more substantial changes in the subgap spectrum such as a variation in the number of YSR states. A small change is insufficient to explain the substantial shift in the YSR state energy.

While some of these additional parameters may thus be relevant for explaining quantitative details of the experiment, it suffices to focus on the exchange coupling J to understand the qualitiative features of the experimental data. This is the approach which we take in the main manuscript.

Gap parameter and YSR state energy near the quantum phase transition

In the absence of the magnetic impurity, the superconducting ground state involves an even number of electrons (even fermion number parity). Excited states with odd numbers of electrons (odd fermion parity) have a continuous spectrum with an excitation energy larger than the superconducting gap Δ. A magnetic impurity induces a localized quasiparticle state at subgap energies [1].

For weak exchange coupling between impurity and electrons in the superconductor, this YSR state is unoccupied in the ground state so that the ground state remains fully paired (even fermion parity). But there is now a discrete excited state with odd fermion parity at an excitation energy ϵ below Δ in which the YSR state is occupied by a quasiparticle.

The excitation energy of this odd fermion parity state reduces with increasing exchange coupling until it reaches zero at a critical coupling J_c. Beyond the critical coupling, the bound quasiparticle state becomes occupied in the ground state and empty in the excited state, i.e., the ground state is now an odd fermion parity state while the excited state has even parity. This level crossing between states with even and odd fermion parity at the critical coupling is a true level crossing as it is protected by fermion parity conservation [1].

At zero temperature, tunneling into superconductors at subgap energies proceeds via Andreev processes which transfer Cooper pairs into the superconductor. At finite temperatures, inelastic processes open an additional tunneling channel in which single electrons are transferred. An electron tunnels into the superconductor occupying a subgap quasiparticle state and is subsequently excited inelastically into the quasiparticle continuum (or recombines inelastically into a Cooper pair with another subgap excitation). This single-particle tunneling dominates over Andreev processes when the tunneling rate is slow compared to the inelastic relaxation rate. This is the case in STM experiments at sufficiently low tunneling conductance [2].

We start from a 4×4 Bogoliubov-deGennes (BdG) Hamiltonian

$$\mathcal{H} = \xi_{\mathbf{p}}\tau_z + (V\tau_z + J\mathbf{S}_i \cdot \boldsymbol{\sigma})\delta(\mathbf{r}) + \Delta\tau_x. \tag{S2}$$

in the basis in which the four-component Nambu operator takes the form $\Psi = [\psi_\uparrow, \psi_\downarrow, \psi_\downarrow^\dagger, -\psi_\uparrow^\dagger]$ in terms of the electronic field operator $\psi_\sigma(\mathbf{r})$ and, for definiteness, consider a classical magnetic impurity. Here, $\xi_{\mathbf{p}} = \mathbf{p}^2/2m - \mu$ with the chemical potential μ, V the strength of the potential scattering by the impurity, and J denotes the strength of the exchange coupling between the magnetic impurity with spin S and the electrons in the superconductor. The Pauli matrices σ_i (τ_i) operate in spin (particle-hole) space. Choosing the impurity spin $\mathbf{S}$ to point along the z direction, the 4×4 Hamiltonian separates into independent 2×2 Hamiltonians

$$\mathcal{H}_\pm = \xi_{\mathbf{p}}\tau_z(V\tau_z \pm JS)\delta(\mathbf{r}) + \Delta\tau_x. \tag{S3}$$

A standard calculation [3] shows that H_+ (H_-) has one subgap solution $[u_\epsilon(\mathbf{r}), v_\epsilon(\mathbf{r}]$ ($[u_{-\epsilon}(\mathbf{r}), v_{-\epsilon}(\mathbf{r})]$), whose energy we denote by ϵ ($-\epsilon$). Since the BdG formalism doubles the degrees of freedom, it is sufficient to consider only the solutions of one of these Hamiltonians, say H_-. Its subgap (YSR) state starts out at positive energies at small exchange couplings and crosses to negative energies for strong coupling. Keeping only the contribution of the subgap state with Bogoliubov operator

$$\gamma_\epsilon = \int d\mathbf{r}[u_\epsilon^*(\mathbf{r})\psi_\downarrow(\mathbf{r}) - v_\epsilon^*(\mathbf{r})\psi_\uparrow^\dagger(\mathbf{r})], \tag{S4}$$

we can write the electron operators as

$$\psi_\downarrow(\mathbf{r}) = u_\epsilon(\mathbf{r})\gamma_\epsilon + \dots \tag{S5}$$

and

$$\psi_\uparrow(\mathbf{r}) = -v_\epsilon^*(\mathbf{r})\gamma_\epsilon^\dagger + \dots, \tag{S6}$$

where the ellipses indicate the contributions of above-gap quasiparticles. The even parity state satisfies $\gamma_\epsilon|\text{even}\rangle = 0$ and the odd-parity state is $|\text{odd}\rangle = \gamma_\epsilon^\dagger|\text{even}\rangle$. Note that $\gamma_\epsilon^\dagger$ removes an electron spin of $1/2$ from the electron system, so that the spin of the odd parity state is lower by $1/2$ compared to the (spinless) even parity state.

In the regime of single-electron tunneling, the differential conductance at $eV = \pm(\Delta_t + \epsilon)$ (for a superconducting tip with gap Δ_t) provides access to the Bogoliubov-deGennes wave function of the YSR bound state (energy ϵ) at the tip position $\mathbf{r}$ [2]. Consider first a positive bias voltage with electrons tunneling into the superconducting substrate.

- For $J < J_c$, the tunneling electrons excite the system from the even parity ground state to the odd parity excited state. In view of the spin polarization of the YSR state, the differential conductance is proportional to $|\langle \text{odd}|\psi_\downarrow^\dagger(\mathbf{r})|\text{even}\rangle|^2$ (Fermi's Golden Rule). We therefore deduce that the differential conductance is proportional to $|u(\mathbf{r})|^2$ in terms of the electron component of the YSR state.

- For $J > J_c$, the differential conductance involves the matrix element $|\langle \text{even}|\psi_\uparrow^\dagger(\mathbf{r})|\text{odd}\rangle|^2$, since $|\text{odd}\rangle$ ($|\text{even}\rangle$) is now the ground (excited) state. The differential conductance is thus proportional to $|v(\mathbf{r})|^2$ involving the hole wave function of the bound state.

As the electron and hole wave functions are generically different, one expects a discontinuous change in the differential conductance at the critical coupling J_c.

Now consider negative bias voltages where electrons are tunneling out of the superconducting substrate. The differential conductance is then proportional to $|\langle \text{odd}|\psi_\uparrow(\mathbf{r})|\text{even}\rangle|^2$ for $J < J_c$ and $|\langle \text{even}|\psi_\downarrow(\mathbf{r})|\text{odd}\rangle|^2$ for $J > J_c$. Consequently, the roles of u and v invert relative to positive bias voltages.

This picture of the quantum phase transition must be amended when effects of self-consistency are taken into account. Both the local gap parameter and the energy of the YSR state have discontinuities at the critical coupling. This has been investigated repeatedly by numerical simulations [4–6], but to the best of our knowledge, there are no analytical estimates for the magnitudes of these discontinuities in the literature. Such estimates are provided in the following.

The jump in the local gap parameter can be understood when writing the (zero-temperature) gap equation in terms of the Bogoliubov-deGennes wave functions $u_n(\mathbf{r})$ and $v_n(\mathbf{r})$ of, say, H_-,

$$\Delta(\mathbf{r}) = g \sum_n u_n(\mathbf{r}) v_n^*(\mathbf{r}), \tag{S7}$$

where the sum is over positive-energy eigenstates within an energy band about the Fermi energy whose width is given by the Debye frequency ω_D. The parameter $g > 0$ denotes the coupling constant of the attractive interaction. As the system passes through the quantum phase transition, the positive energy subgap state crosses to negative energies and no longer contributes to the sum on the right hand side of the gap equation. Thus, we find

$$\delta\Delta(\mathbf{r}) = -g u_\epsilon(\mathbf{r}) v_\epsilon^*(\mathbf{r}). \tag{S8}$$

for the jump in the gap parameter. Here, we assume that the effect of the discontinuity on the other Bogoliubov-deGennes eigenstates is weak. We will confirm below that this is indeed the case. For a classical magnetic impurity and uniform gap parameter, one finds that u_ϵ and v_ϵ can be chosen real and have the same sign at the impurity position [3]. Thus, this indeed describes a local suppression of the order parameter.

The discontinuity in the gap parameter is limited to the region in which the YSR bound state is localized. At its center, say $\mathbf{r} = 0$, and at the critical exchange coupling J_c, the YSR bound state has an amplitude of $|u(0)|^2 \sim |v(0)|^2 \sim \nu_0\Delta$ [3], where ν_0 is the (normal-state) density of states of the superconductor at the Fermi energy. Inserting this into the expression for the jump in the gap parameter, we have $\delta\Delta(0) \sim -g\nu_0\Delta$. Using the relation

$$\Delta \sim \omega_D e^{-1/g\nu_0}, \tag{S9}$$

we therefore obtain

$$\delta\Delta(0) \sim -\frac{\Delta}{\ln(\omega_D/\Delta)} \tag{S10}$$

for the local and discontinuous reduction in the gap parameter at the critical coupling.

As the gap is locally suppressed at the quantum phase transition, it can even change sign. This happens when the discontinuity is larger than the value of the local gap parameter just before the quantum phase transition. For $J < J_c$, the magnetic impurity suppresses the gap parameter continuously and this suppression of the gap parameter has been previously estimated within perturbation theory [6], yielding a suppression by $\alpha^2\Delta$ for small exchange coupling $\alpha = \pi\nu_0 JS$. As $\alpha \sim 1$ at the quantum phase transition, the value of $\Delta(\mathbf{0})$ just before the quantum phase

transition may indeed be smaller than the magnitude $\delta\Delta(0)$ of the jump, so that the gap parameter changes sign across the transition.

Since the jump in $\Delta(\mathbf{r})$ is associated with the bound state contribution to the gap equation, it is localized in the vicinity of the impurity. To provide an estimate for the associated jump in the energy of the YSR state, we approximate the jump in $\Delta(\mathbf{r})$ by a δ-function [6],

$$\delta\Delta(\mathbf{r}) = a^3\delta\Delta(0)\delta(\mathbf{r}). \tag{S11}$$

Here, a is the linear dimension of the region over which the gap parameter is suppressed, which can be estimated as [5] $a \approx 2/k_F$ in terms of the Fermi wave vector of the superconductor. The associated jump in the energy of the YSR state can then be obtained from first-order perturbation theory which yields

$$\delta\epsilon \sim \frac{\Delta^2}{E_F \ln(\omega_D/\Delta)}. \tag{S12}$$

In deriving this expression, we have again used the magnitude of the YSR wave function at the position of the impurity. This expression shows that the effect of the gap reduction on the Shiba states is small in the parameter Δ/E_F which is of order 10^{-5} for conventional superconductors.

Clearly, this predicts a discontinuity in the energy of the Shiba state which is below experimental resolution by orders of magnitude. Moreover, in the regime of single electron tunneling, STM experiments are sensitive to the change in the local gap parameter only via the associated change in the bound state wave function which is negligible.

ADDITIONAL EXPERIMENTAL DATA

Fe(III)-porphine-chloride molecules

As mentioned in the main text, Fe(III)-porphine-chloride molecules are evaporated on a Pb(111) sample held below room temperature, followed by annealing the preparation to 370 K. We show in Fig. S1a a topography image obtained on a sample before annealing. There, we observe the formation of ordered islands in which a few molecules ($\leq$ 1%) exhibit a pronounced protrusion above their center. As shown in Fig. S1b, the apparent height of such a molecule is approximately 0.7 Å larger than the one of molecules with a clover shape. A similar elevation has been observed for Cl ligands on other Fe porphin derivatives, e.g., Fe-octaethylporphyrin-chloride (Fe-OEP-Cl) on Au(111) [7] and Pb(111) [8]. The dI/dVspectra on these bright protrusions reveal the presence of sharp peaks outside the superconducting energy gap at bias voltages of $\pm$4 mV and $\pm$5.4 mV (see Fig. S1c). These peaks reflect inelastic excitations of the molecule on a superconductor [8], which can be assigned to spin excitations of the Fe center. In the presence of the Cl ligand the Fe center lies in +3 oxidation state with $S = 5/2$. The anisotropic environment lifts the degeneracy of the d levels. Together with spin-orbit coupling, this introduces magnetocrystalline anisotropy to the Fe states. The inelastic peaks in the dI/dVspectrum arise from transitions between these anisotropy-split levels. The absence/presence of these excitations thus indicates the absence/presence of the Cl ligand. All molecules discussed in the main text have lost their Cl ligand after annealing the deposited molecules to 370 K

Quantum phase transition in molecules in different surroundings

The results presented in the main text are acquired above a molecule at the border of an island. Here, we show that the same observations can be made for molecules in different surroundings.

The evolution of the junction conductance above the center and ligand of such a molecule within an island shows a reversible contact formation similar to the molecule in the main text [Fig. S2(ii)]. A set of spectra recorded at different tip–sample distances is shown as a false 2D color plot in Fig. S2(iii). At far tip distance, a pair of YSR states is observed at $\pm$2.5 mV at both the center and the ligand of the molecule. At both locations the YSR states first shift toward zero energy upon tip approach, indicating a screened spin ground state and negative YSR energy. Above the center, the YSR state crosses zero energy and reverses its asymmetry around $\Delta z = -200$ pm [see Fig. S2a (iv and v)] indicating that the system undergoes the quantum phase transition. In contrast, above the ligand, the YSR energy remains negative and a reversal of the YSR asymmetry only occurs at high junction conductance ($G \geq 0.1 \times G_0$) when Andreev reflections dominate the transport through the junction [see Fig.S2b (iv and v)].

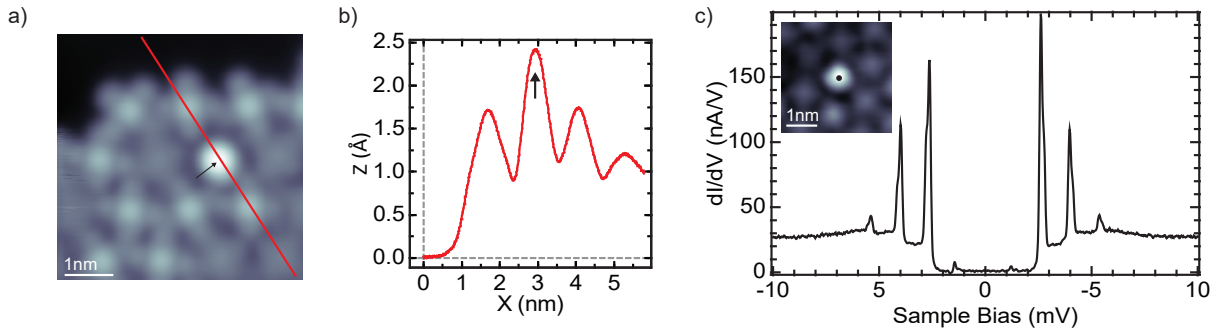

Figure S1. a) STM topography image ($V = -45$ mV, $I = 100$ pA) after deposition of FeP-Cl on a sample held below room temperature. A few molecules kept their Cl ligand and show a protrusion above their center. b) Line profile along the red line shown in a) showing the larger apparent height of the molecule indicated by an arrow. c) dI/dVspectrum acquired above the center of such a molecule (feedback opened at $V = -45$ mV, $I = 100$ pA, $V_{\mathrm{rms}} = 50$ μV) showing the presence of inelastic spin excitations in accordance with [8].

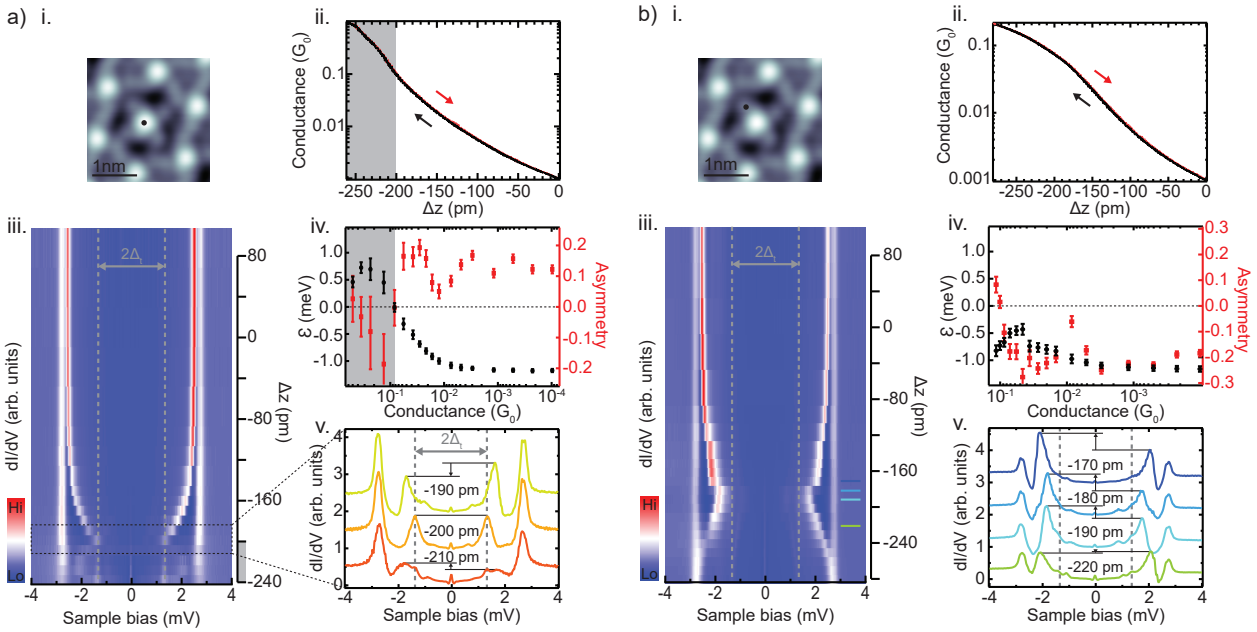

Figure S2. Evolution of the spectroscopic features above the center a) and ligand b) of a molecule within an island. i. STM topography image showing the tip location (black dot). ii. Dependence of the junction conductance upon tip approach. iii. Set of dI/dVspectra normalized to their conductance at 5 mV recorded at different tip height. iv. Extracted YSR energy and asymmetry as a function of the junction conductance. v. Selected spectra (offset for clarity) showing that the system goes through the quantum phase transition on the center of the molecule (a), and does not go through the quantum phase transition by approaching on the ligand (b).

As shown in Fig. S3, resonances within $V = \pm\Delta_t$ build up upon further tip approach. In addition to a zero-bias peak due to Cooper pair tunneling, resonances are observed at $V = \pm\frac{\Delta+\Delta_t}{2}$ and $V = \pm\frac{\Delta+\epsilon}{2}$ (see Fig.S3c) arising from multiple Andreev reflections, as discussed in the main text.

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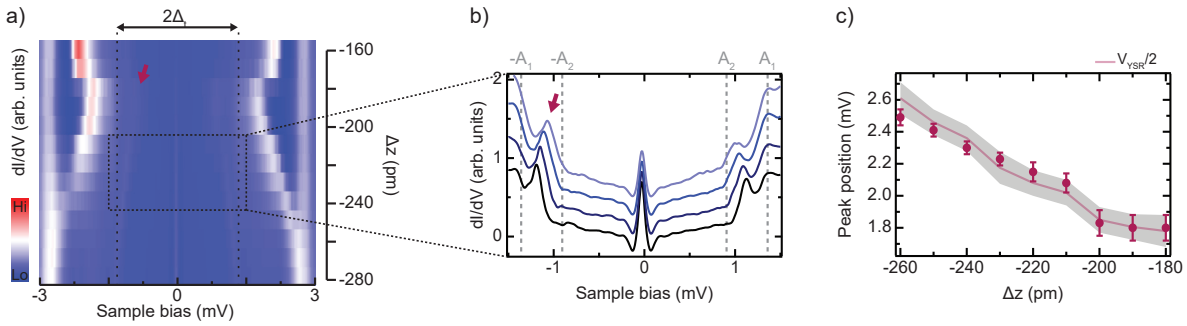

Figure S3. a) Close-up view of the approach set of Fig. S2b highlighting the presence of resonances due to multiple Andreev reflections. b) Four spectra of this approach set (offset for clarity) showing a peak shifting upon tip approach. c) Extracted peak position as well as the expected position of the Andreev process according to the position of the YSR state.

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