Gate tuning and universality of Two-stage Kondo effect in single molecule transistors

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Abstract
Using single molecule transistor incorporating individual Manganese phthalocynine (MnPc) molecules, we studied two-stage Kondo effect involving a multi-level impurity. Utilizing extreme confined molecular structure, we have achieved gate tuning of Kondo temperatures for single channel two-stage Kondo process. Single gate in our devices can significantly change the Kondo temperature $T^*$ representing the internal correlation between different molecular levels. A linear relationship was obtained between the $T^*$ and effective interaction of two electrons, and exchange energy of electrons in this molecule device could be extracted accordingly. Moreover, the two-stage Kondo resonance behaves almost identical to small excitations in electric field, magnetic field and thermal change, showing a clear universality. Messages learned in this study not only fill in missing experimental knowledge of evolution in two-stage Kondo resonance toward the quantum phase transition point, but also help in understanding sophisticated molecular electronic spectroscopy in strong correlation regime.

Strong correlated many-body effects are among the most intriguing topics in modern solid state physics, crucial for understanding fundamental mechanism of exotic phenomena such as non-Fermi liquid behaviors of heavy fermion, formation of Mott insulator, unconventional superconductivity and Kondo physics$^{1,2}$. Although origins of many correlation effects of complex materials are quite different and in debate, Kondo effect has risen to be a powerful paradigm to understand strong correlations processes in many fields involving strong Fermion or Bosonic impurity scatterings, mainly due to the advances in constructing confined nanostructures$^{3,4}$. Kondo effect is a strong resonance at low temperature first discovered and understood in diluted magnetic metals$^{1,5}$ and confined nanostructures$^{6,7}$, where itinerant electrons coherently couple to local magnetic impurities. Later Kondo effect has found widely in multiple fields where orbital$^8$, charge$^9$, topological$^{10}$ and most recently spinon$^{11}$, phonon$^{12}$ degree of freedom form degenerate impurities.

The most studied Kondo process is single level single channel spin 1/2 Kondo resonance$^{6,13,14}$, correlation problems in reality could be more complicated$^{15}$. Two-stage Kondo effect$^{13,15-17}$, describing Kondo correlation with two quantum levels via one or two conduction channels, is the
simplest multi-level multi-channel Kondo phenomenon. It was observed in artificial quantum dots\textsuperscript{16,17}, carbon nanotube\textsuperscript{18} and molecules\textsuperscript{19}. However, due to the difficulties in constructing good multi-level Kondo systems\textsuperscript{17}, in which multiple parameters can be well controlled\textsuperscript{20}, controlling and systematic studies of two-stage Kondo effect is not yet achieved.

Here we report the observation and control of two-stage Kondo effects in a single molecule transistor incorporating individual Manganese phthalocyanine (MnPC, insert of Fig. 1a) molecules. By choosing orbital degenerate molecules, we achieved a multi-level Kondo system. In this system, the correlation between itinerant electrons and localized impurities competes with correlation between localized impurities, leading to single channel two-stage Kondo effect, characterized by two Kondo temperatures, $T_K$ and $T'_K$, respectively. Gate control of two stage Kondo resonance reveals a linear relationship between $T'_K$ and effective interaction of two electrons. Exchange energy of 1.4meV could be obtained for electrons in the corresponding orbitals for such a structure. In the low temperature range, the resonance could be described by a universal quadratic power law function against electrical field, magnetic field or temperature, scaled by $T'_K$. The information learned from this transport study also shine lights on molecular configuration in the devices.

Results

Device fabrication and measurement. Our devices were prepared by electromigration techniques\textsuperscript{4} (details in Supplemental Material) and a schematic diagram is depicted in Fig. 1a. Fig. 1b shows the scanning electron microscopy (SEM) image of a represented junction. Transition metal phthalocyanine molecules benefit from high coupling to metal substrate, and their near degenerate molecular orbitals (HOMOs) mainly occupied by d orbital electrons of the metal ion. By changing the transition metal ion, the orbital structure and spin ground state could be easily changes\textsuperscript{21}, making them ideal for studying exotic Kondo phenomena.

Electrical measurement was taken from 280mK to 20K, above which the molecule is less stable. A bias voltage $V_{sd}$ between source and drain electrodes was applied to adjust the energy of electrons passing through the device. While a gate voltage $V_g$ was applied to an aluminum electrode to change chemical potential of the molecule. The excited states arising from the internal vibration of the molecules help us to identify whether the measured signals come from individual MnPc molecules (see Supplemental Material).

Two stage Kondo effect. Fig.1c and 1d show differential conductance (dI/dV) plots of two representative molecular devices, (1 and 2) as a function of bias voltages ($V_{sd}$) and gate voltages ($V_g$). Typical coulomb blockade behaviors were observed in both devices, with differential conduction peaks defining two electron blocking regions, I and II, associated with two adjacent charge states of the molecule. A sharp zero-bias peak was observed in region I while a zero-bias split peak was observed in region II for both devices. Study of these zero-bias peaks forms the central topics of this work, and as we will see they are different Kondo processes corresponding to different conditions in different charge states of MnPc molecules. For simplicity, further discussions are mainly based on device 1, although all the features are shared by device 1 and 2.
Temperature, electrical and magnetic study of the zero bias conductance peak in region I prove a single channel spin 1/2 Kondo resonance (see Supplemental Material), with a single Kondo temperature $T_{K,1/2}=3.21\pm0.02$K (at $V_g=2$V) and a $g$ factor of 1.79. In region II, a pronounced sharp dip is observed within a large broad peak (Fig.2a), forming a split peak feature. The dip become shallower and disappears when temperature increases from 0.3K to 3K. As the temperature increase further, the broad peak decreases, and eventually vanishes. The zero bias conductance shows a distinct nonmonotonic temperature dependence(Fig.2b). These features, combining together, demonstrate a clear two stage Kondo resonance in single MnPc transistors.

The spin state in region II could be either 0 or 1 with two-electron occupation. And two stage Kondo effect can appear with either spin singlet or triplet impurity states. A magnetic field was applied perpendicular to the substrate to determine the ground state of the device(shown in Fig. 2c). The splitting of the peak diminishes first, then splits further with the increasing field. This crossing and linear dependence behavior of split peak is in consistent with spin singlet being ground state and the finite bias peak is associated with excitations into spin triplet. At zero field, energy of triplet state is 0.45meV higher than that of singlet state at $V_g=-2$V. The critical field of singlet to triplet (S-T) ground state transition is at 3.2T. Device at higher field has triplet ground state. $g$ factor is calculated to be 1.76, very close to the value obtained in region I.
Singlet two-stage Kondo effect is predicted to associate with single conduction channel and to be near a Kosterlitz-Thouless (KT) type quantum phase transition point. The fact that no significant enhancement of resonance was observed at the critical field (Fig. 2c in Supplemental Material), demonstrates two stage Kondo effect in our molecular devices is a single channel process. The small energy difference between singlet and triplet (0.45 mV at 0T and V_g at -2V) also indicate ground state of our single molecular devices is close to quantum phase transition point. Thus the scenario is in consistent with the proposed theory for single channel two stage Kondo effect.

**Fig. 2** Two stage Kondo effect. a Plot of differential conductance dI/dV against V_sd at V_e=-2V (region II) of device 1 at various temperatures. b Temperature dependence of the zero-bias conductance G(T) at V_e=-2V. The green and blue lines are fitting result to spin 1/2 fully screened Kondo model (equation S2 in Supplemental material) and inverted spin 1/2 Kondo model (equation 1) respectively. c Differential conductance dI/dV as a function of B and V_sd at V_e=-2V and temperature T=280mK (bottom). Energy level sketch of magnet induced singlet to triplet transition process (top). B_0 =3.2T is the critical point where transition occurs.

The observed nonmonotonic singlet two stage Kondo could be explained by competition between molecular internal binding correlation and the correlated spin screening process by itinerant electrons via a single conduction channel. At finite temperature, spin singlet state could dissociate into two independent spin due to quantum criticality near the KT quantum phase transition. At higher temperature, itinerant electrons in the electrodes screen one of the two spins in the molecule, leading to a broad Kondo peak, characterized by T_k, described by a spin 1/2 Kondo resonance model (equation S1 in Supplemental Material). At lower temperature, the singlet binding energy cause the second spin to destroy screening cloud of the first stage Kondo resonance, forming a Kondo scattering in the second stage, described by an inverted spin 1/2 Kondo resonance form of

$$G(T) = G_0 - G_0/[1 + (2^{1/2} - 1)(T/T^*)^2]^s + G_c$$ (1)

at lower temperature, where T* is the second Kondo temperature, G_0 is a typical conductance value, G_c is the background conductance. T_k and T* can thus be extracted accordingly. T_k=13.3±2.7K and T*=4.1±0.1 K are extracted at V_e=-2V, much higher than previous molecular and quantum dots studies.

**Discussion**

Most of exotic Kondo physics were previously studied using artificial quantum dots, where
multiple gates were applied to define the dots and fine tune the correlation parameters\textsuperscript{6,16,17}, yet the controlling of $T^*$ has been hard to achieve. In our single MnPc transistors, however, a clear tunability of $T^*$ with a single gate is realized (Fig. 3c, Fig. S4 in Supplemental Material). Extracted $T^*$ forms a straight line with gate voltages. The single-gate control of $T^*$ was unexpected, since $T^*$ represents the internal singlet binding energy of two electrons in the molecules and may not be tuned by gate voltage controlling chemical potential of the molecule, as in the case of spin 1/2 system\textsuperscript{6}.

The reason for this unexpected behavior could arise from a gate tunable singlet triplet level spacing in our devices. Fig.3a and 3b show that the energy difference between singlet and triplet ($\Delta \varepsilon = \varepsilon_T - \varepsilon_S$ the singlet triplet energy difference, $\varepsilon_S$ is spin singlet energy, $\varepsilon_T$ is spin triplet energy) become smaller at more negative gate voltages, while the opposite trend is observed in device 2 (Fig. S5 in Supplemental Material). This gate induced changes in singlet-triplet splitting, as has been observed in carbon nanotube\textsuperscript{24} and C$_{60}$ molecular device\textsuperscript{19}, could be due to different gate couplings of the two orbitals, or level renormalization effect induced by asymmetric tunneling couplings\textsuperscript{24}.

It was proposed that $T^*$ in two stage Kondo process decrease when approaching S-T transition point, as a function of effective exchange interaction $\Delta I$ between the two impurities ($\Delta I = \Delta \varepsilon + J/4$, $J$ is the exchange energy between the local electrons)\textsuperscript{13}. Fig.3c shows gate dependent $T^*$ and $\Delta \varepsilon$, in total agreement with theoretical prediction. $\Delta \varepsilon$ is acquired by taking the peak position of the split peaks at different gate potentials. In Fig.3d, the $T^*$ vs. $\Delta \varepsilon$ forms a linear relation. The early calculation\textsuperscript{13} indeed shows $T^* \sim \Delta I$, under the condition $\Delta I \sim T_K$. In our single molecule transistor, the obtained $\Delta \varepsilon$ is on the order of 0.5meV while $T_K$ is on the order of 10K, comparable to each other. Assuming $T^* = k \Delta I$, i.e. $T^* = k (\Delta \varepsilon + J/4)/k_B$, linear fit in Fig.3d shows $k = 0.30 \pm 0.02$ and $J = -(1.40 \pm 0.04)$ meV. The exchange energy of -1.4meV reveals a ferromagnetic interaction between the two electrons in our MnPc molecular devices. We note here, in our devices, both positive or negative $J$ can lead to singlet ground state as long as $\Delta I$ is positive, which is different from double quantum dot structure, whose S-T energy splitting is only determined by $J$\textsuperscript{25}. Similar analysis could be applied to device 2 (Fig. S5a in Supplemental Material). A similar value of $J$ = -1.6meV could be deduced, quantitatively in agreement with device1. The similarity of $J$ from two separate devices with different local environment suggests $J$ is an internal parameter of the molecule. Considering the ferromagnetic interaction and almost degenerate spin single and triplet, the two levels contributing to two-stage Kondo effect in our devices are mostly likely to be 3d$_{xz}$ and 3d$_{yz}$ of the Mn atom in MnPc molecule\textsuperscript{26}. 


Fig. 3 Gate voltage dependences of $T^*$ and singlet-triplet energy splitting. **a** Color plot of numerical derivative of $dI/dV$ as a function $V_{sd}$ and $V_g$ in region II for device 1. The black dash line indicates the peak position, which corresponds to the energy difference between spin singlet and triplet. **b** Line traces of $dI/dV$ against $V_{sd}$ in **a** at different gate voltages. The peak positions are marked by dash line. The curves are shifted vertically for clarification. **c** $T^*$ and $\Delta \epsilon$ of device 1 at different gate voltage. $\Delta \epsilon$ is acquired by taking the peak position of the split peaks at different gate potentials in **b**. **d** Plot of $T^*$ against $\Delta \epsilon$ for device 1. The dash line is a linear fitting.

The universality of Kondo effect, independent of physical systems and origin of the interactions, exhibits the importance of the theory and wide application of the experimental results. Most previous studies of universality were focused on single level Kondo effect and only involve temperature and voltage effect. We here address the universality of two-stage Kondo effect with temperature, voltage and magnetic field.

The unique nonmonotonic two stage Kondo effect shows two regimes at high temperature and low temperature. Close to zero temperature, the low energy excitation behavior is dominant by the smaller energy scale $T^*$. In Fig. 4a, the zero bias normalized conductance $(G-G_c)/G_0$ at different $V_g$ are plotted as a function of $T/T^*$. A clear universal scaling law could be seen for the two stage Kondo effect with $T/T^*$. The same universal scaling law could also be found in Fig. 4b,
where the normalized differential conductance vs. scaled biased voltage by T* plots fall into an identical dip profile. Comparing Fig 4a and b, the resonance profile tends to deviate from universal function at a lower energy(T/T* or V_{sd}/T*) when V_g become more close to the charge degenerate point between region I and II. This can be explained by the higher T_k near the charge degenerate point affecting the non-equilibrium Kondo effect more strongly, manifesting again the competition between itinerant correlation and impurity correlations.

Universality of two-stage Kondo effect could also manifest as a striking similar scaling form in seemingly unrelated physical phenomena if the based dynamics are similar. In our single molecular devices, upon excitation by temperature(T), electrical voltage(V_{sd}) and magnet field, the conductance suppression in the second stage is weaken, as shown in Fig. 4c, for they contribute to quench molecular internal binding correlation. The non-equilibrium low energy perturbation of our two stage Kondo resonance shows similar power law dependence\(^{14,27}\) with temperature(T), bias voltage(V_{sd}) and magnet field (Fig. 4c) scaled with T* when T<<T*. To determine the scaling relationship for T, V_{sd} and B, we fit the low-energy conductance to the form(Fig. 4c),

\[
G(V, T, B) = G_0 \left[ C_V \left( \frac{eV_{sd}}{k_BT} \right)^{P_V} + C_T \left( \frac{\pi T}{T} \right)^{P_T} + C_B \left( \frac{g\mu_BB}{k_BT} \right)^{P_B} \right] + G_c
\]

where P_v, P_T, P_B are scaling exponents and C_v, C_T, C_B are the scaling coefficients\(^{14,28}\). The best fit exponents are P_v=1.98±0.08 P_T=1.83±0.01 P_B=1.89±0.09, closing to 2 and revealing a Fermi liquid behavior\(^{28}\). Treating all the exponents to be 2, We replot the low-energy excitations against \(\left( \frac{eV_{sd}}{k_BT} \right)^2\), \(\left( \frac{g\mu_BB}{k_BT} \right)^2\) and \(\left( \frac{\pi T}{T} \right)^2\) (represented by a uniteless value X^2 ) in Fig.4d, in which the same quadratic behaviors are valid up to X^2=0.5. The valid quadratic dependence range is substantially large\(^{29}\). A full set of scaling coefficients, C_v, C_T and C_B of 0.42, 0.27 and 0.37 are extracted\(^{14}\). In two channel two stage Kondo effect, it was predicted the ratios between these values is not fixed. Our single channel two stage Kondo resonance is very close to strong asymmetric coupling limit in multilevel Anderson model\(^{29}\) with a Wilson ratio R = 2, where C_v/C_T=3/2 are expected. Our experimental value of C_v/C_T =1.55 at V_g=-2V. The C_B/C_T ratio is 1.4. Further understanding requires a yet to be constructed theoretical model of non-equilibrium properties of single channel two stage Kondo effect.
Fig. 4 Universal scaling of two stage Kondo resonance. a The normalized zero bias conductance, \((G - G_c)/G_0\) for device 1 in region II at various gate voltages, shows a universal function of \(T/T^*\). b The differential conductance vs. \(V_{sd}\) curves at different \(V_g\) are scaled to an identical line by \(T^*\). c The low-energy differential conductance (\(V_g=-2V\)) fitted to a power law with \(T\) (temperature), \(V\) (bias) and \(B\) (magnetic field). The solid lines are power-fits. d Plot of scaled low-energy differential conductance \((G - G_c)/C_i\) fitted to a power law with \(eV_{sd}/k_B T^*\), \((\pi T/T^*)^2\) and \((g \mu_B B/k_B T^*)^2\) (represented by \(X^2\)). The linear relation between conductance and \(X\) demonstrates a quadratic behavior for \(T\), \(V\) and \(B\).

We can also deduce local configuration of our molecular device based on above results. The resonance conductance is much less than conductance quanta, indicating the molecule is close only to one of the two gold electrodes. The observed single channel physics requires that electrons tunnels to the two d orbitals via a single conduction site, suggesting Mn ion couples to single gold atom. It would lead to a conclusion single channel two stage Kondo effect only happens when Mn is on top of single Au atom (top site), instead of in between several gold atoms (bridge site and hollow site, see Supplementary Material). Site dependent Kondo effect have been reported in STM studies where a dip was often seen when individual metal phthalocyanine...
molecule was on top of gold atom while disappear when it took other positions\textsuperscript{20,30}. We also perform the calculation of absorption energy of MnPc molecule on gold [111] surface and confirmed top site is the most stable site with 77meV more stable than the bridge site and 155meV than hollow site (see Supplementary Material). The linear magnetic field splitting of the two stage Kondo resonance also suggest the magnetic field is in the molecular plane\textsuperscript{20}. Above analysis suggest a plausible molecular device configuration in Fig.1a.

In conclusion, we studied single channel two stage Kondo effect using single molecule transistor platform. A clear linear gate dependence of the second stage Kondo temperature $T^*$ was achieved using only a single gate, revealing the linkage of $T^*$ to the effective exchange energy. The type and energy of exchange interaction of two electrons in the molecular devices are acquired accordingly. The universality showing here against all measurement suggest that the basic form of obtained two stage Kondo effect might apply widely in different system, regardless of impurity type or device structure. The construction and controlling of two stage Kondo effect, using single molecule transistor, open a new way for quantitatively study sophisticate strong correlation processes which is key for many unsolved physical problem today. Deliberate choosing kinds of molecules and correlations are expected to lead to fruitful studies and understandings in multiple fields.

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Supplemental Material

Gate tuning and universality of Two-stage Kondo effect in single molecule transistors

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1. Device fabrication

Single MnPc molecule transistors devices were fabricated by electromigration technique. A schematic diagram is shown in Fig. 1(a). A narrow gold nanowire was fabricated by electron-beam lithography on an aluminum pad with a ~3nm oxide layer serving as the gate electrode. Electrical current was applied to the gold nanowire to create two closely spaced electrodes with a gap about 1nm. To incorporate single molecules, dilute alcohol solution of MnPc was deposited on a chip containing the array of gold nanowires before the electromigration breaking. Immediately after breaking process, the chips are transferred to a cryostat and cooled down to base temperature to freeze electrodes and stabilize molecules.

2. Identification single MnPc molecule.

Excited states that arise from the internal vibration of measured molecules could be used to identify unique molecular devices. Devices 1 and 2 show pronounced excited states at 63meV and 16meV respectively (Fig.S1), matching infrared spectra of metal-phthalocyanine derivatives\textsuperscript{1-3} for out of plane vibration and in plane stretching modes. The additional energies, i.e. the energies required to add one more electron to a molecule, are typically hundreds of meV for the single molecule junctions. The addition energy of our devices cannot be measured directly due to the instability of molecular junction under a high bias voltage. But from the measurement range in both $V_{sd}$ and $V_g$, we estimate the lower bound of additional energy is 120meV for device1 and 160meV for device2, much larger than that of gold clusters occasionally formed during current breaking process. Observation of molecule specific vibration and large addition energy supports that measured signals come from electrons passing through individual MnPc molecule in the metal junction.

3. Characterization of spin 1/2 fully screened Kondo effect.
In blocking region I of both device 1 and 2, sharp zero-bias conductance peaks appear. The peak is strongly temperature dependent. Differential conductance (dI/dV) versus bias $V_{sd}$ for device 1 is shown in Fig. S2(a). As temperature is raised, the peak height decreases in a logarithmic fashion [Fig. S2 (b)]. The single peak also splits linearly under magnet field, as shown in Fig. S2(c), in which g factor is equal to 1.79. These phenomena indicate this is a Kondo resonance. The temperature dependence of spin $S=\frac{1}{2}$ Kondo peak height follows an approximate scaling form

$$G(T) = G_0/[1 + (2^{1/s} - 1)(T/T_{K,1/2})^{2s}] + G_c$$

where $G_0$ is the zero temperature conductance, $G_c$ is a background conductance and $T_{K,1/2}$ is the Kondo temperature. We use this formula to fit Kondo peak height at different temperature [Fig. S2(b)] and get $T_{K,1/2}=3.21 \pm 0.02$K. Fig. S2(b) also shows the data fitting to numerical renormalization group (NRG) result for $S=1$ and $3/2$ underscreened Kondo processes. The data fit best to spin $1/2$ model, excluding the underscreened Kondo effect for $S=1$ and $3/2$. The detailed temperature dependences analysis of Kondo resonance shows this is a fully screened single channel spin $1/2$ ground state instead of $3/2$ ground state. These evidence clearly proves that MnPc has $S=1/2$ ground state in region I and the Kondo resonance we observed in this region is fully screened spin $1/2$ Kondo process.

**Determination of spin ground state in Region II.** To determine the spin ground state, we perform a magnetic field dependent study by applying magnet field perpendicular to the device surface in Fig. 2(c). As the magnetic field increases, the splitting of the peak diminishes first but appears again and splits further at higher field. This crossing and linear dependence behavior of split peak is in consistent with spin singlet being ground state and the finite bias peak is associate with involving excitations into spin triplet with the position of when $V_{sd}$ meets with the energy difference between spin singlet and triplet. Spin states can be noted as $|S,m\rangle$, where $S$ is the total spin and $m$ is the spin projection of the total spin on $z$-axis. For two electron systems, the spin states include a spin singlet $|0,0\rangle$ and a spin triplet $|1,1\rangle,|1,0\rangle,|1,-1\rangle$. All the triplet states are degenerate at zero magnet field ($B=0$) but split into three levels in magnetic field $B$, with the energy shifting of each level equal to $mg\mu_B B$. If the singlet meets triplet $|1,-1\rangle$, a ground state transition happens. If the ground state is triplet, the line crossing would not happen. The corresponding energy level diagram is also shown in Fig.2(c).

**Calculation of configuration.**

To confirm the stable structure of an MnPc molecule on Au(111) surface, we resort to numerical simulations based on the density functional theory (DFT). The MnPc is put laying on an Au(111) surface. We choose three initial symmetric configurations (Fig. S6). The first one is called top site, where the central Mn atom of the MnPc is on the top of a surface Au atom. The second and the third ones are called bridge site and hollow site, respectively, where the Mn atom is above the bond center of two adjacent Au atoms or above the regular triangle center of three adjacent Au atoms in the outmost atomic layer. During the simulations, we take two Au(111) layers and fix the positions of the Au atoms to reduce computing workload. But all the atomic positions of the
MnPc molecule are flexible and waiting to be relaxed. The simulations are conducted by the software package of NANODCAL. The magnetization is treated as collinear-spin type. A double-zeta polarized atomic orbital set is utilized for each atom species, and the local density approximation (LDA_PZ81) is used for the exchange-correlation. The van der Waals interaction is considered. And the force convergence criterion for the relaxation is taken as 0.01eV/angstrom.

After structure relaxations, the top-site configuration has the lowest energy, which is about 0.106eV and 0.482eV lower than the bridge-site one and the hollow-site one, respectively (Fig. S6). The optimal top-site configuration of an MnPc molecule on Au(111) surface confirms our experiments, and agrees with that of an FePc molecule on Au(111) surface.
FIG. S1. Excited levels of MnPc molecule. Differential conductance plots showing a larger bias-voltage range than those in main text for device 1 (a), device 2 (b). Excited levels arising from internal vibrational modes of MnPc molecule are marked by black dash line and arrows.
FIG. S2. Spin 1/2 fully screened Kondo effect. a. Plot of differential conductance $dI/dV$ versus $V_{sd}$ at various temperatures (at $V_g=2V$ for device 1). b. Plot of the Kondo peak height $G(V_{sd}=0)$ in a as a function of temperature. The data is fitted to $S=1/2$, $S=1$ and $S=2/3$ model respectively. c. Differential conductance $dI/dV$ for device 1 at $V_g=1.6V$ as a function of $V_{sd}$ and magnet field $B$. 


FIG. S3 The differential conductance profiles at $B=0\text{T}$, $3.2\text{T}$ and $8\text{T}$ in Fig. 2c ($V_g=-2\text{V}$ for device 1). $B_0=3.2\text{T}$ is the critical point. The peak at $B=3.2\text{T}$ is not greater than the peaks at $B=0$, indicating only one channel participates.
FIG. S4 Plot scaled zero bias conductance \((G-G_c)/G_0\) at different gate voltage as a function of temperature. The temperature dependence of profiles at different gate voltage is different with each other, indicating \(T^*\) is gate dependent.
FIG. S5 Gate dependent singlet-triplet energy splitting in device 2. a, Color plot of numerical derivative of \( \frac{dI}{dV} \) as a function of \( V_{sd} \) and \( V_g \) in region II for device 2. The black dash line indicates the peak position. Far away from singlet-triplet transition point, the peak position varies almost linearly with gate voltage. When approaching transition point, the splitting deviate from linear relation, indicating a ferromagnetic coupling between two electrons (J<0). By extending the linear peak position to the gate voltage when transition should happens, we can estimate the value of \( J/4 \), about -0.4meV, which is quantitatively in agreement with device 1.  

b, Plot of \( \frac{dI}{dV} \) against \( V_{sd} \) in region II of device 2 at different gate voltage. The peak positions are marked by dash line. The curves are shifted vertically for clarification.
FIG. S6 Adsorption configurations of MnPc molecule on Au(111) surface and relative energy. Among all the six configurations, top1 has the lowest energy. The energies shown here of all the other configurations are relative to top1.
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