Electrical manipulation of spin states in a single electrostatically gated transition-metal complex

Osorio, Edgar A; Moth-Poulsen, Kasper; van der Zant, Herre S J; Paaske, Jens; Hedegård, Per; Flensberg, Karsten; Bendix, Jesper; Bjørnholm, Thomas

Published in:
Nano Letters

DOI:
10.1021/nl9029785

Publication date:
2010

Document version
Early version, also known as pre-print

Citation for published version (APA):
Electrical manipulation of spin states in a single electrostatically gated transition-metal complex

Supplementary Information

Edgar A. Osorio,1 Kasper Moth-Poulsen,2 Herre S.J. van der Zant,1 Jens Paaske,2 Karsten Flensberg2, Per Hedegård,2 Jesper Bendix2 and Thomas Bjørnholm2

1 Kavli Institute of Nanoscience, Delft University of Technology, PO Box 5046, 2600 GA, The Netherlands
2 Nano-Science Center (Department of Chemistry and Niels Bohr Institute), University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen, Denmark.

Contents:

S1. Molecule synthesis and characterization.
S2. Assignment of the low-bias features: two molecules in parallel.
S3. Details on the assignment of spin states.
S4. Enhanced cotunneling near the singlet-triplet degeneracy.
S6. Model calculations.
S7. Spin blockade and cotunneling assisted sequential tunneling.

References

*Email addresses: TB (tb@nano.ku.dk) and HvdZ (h.s.j.vanderzant@tudelft.nl).
S1. Molecule synthesis and characterization.

Bis-4’-(6-acetylthiohexyloxy)-2,2’;6’,2’”-terpyridine manganese(II) hexafluorophosphate.

4’-(6-Acetylthiohexyloxy)-2,2’;6’,2’”-terpyridine [1] (204 mg, 0.5 mmol) was dissolved in acetone (20 mL) and heated to 50°C. A solution of Manganese(II)acetate tetrahydrate (61 mg, 0.025 mmol) in milliQ water (5 mL) was added, and the reaction mixture stirred for 1 hour. The solution was allowed to cool to room temperature and poured into 0.2 M aqueous potassiumhexafluorophosphate solution (100 mL). The resulting slurry was filtered through filter aid (Celite) and washed with water (200 mL) and ether (200 mL). Finally the celite was washed with acetone, to transfer the product. Evaporation of the acetone in vacuo afforded 160 mg of bis-4’-(6-acetylthiohexyloxy)-2,2’;6’,2’”-terpyridine manganese(II) hexafluorophosphate 12 as a white powder, corresponding to 55% yield.

Mp: 83.3-85.2°C. Anal. Calcd. for C_{46}H_{52}N_{6}O_{5}F_{12}P_{2}S_{2}Mn (M+H_2O): C, 46.87; H, 4.45; N, 7.13; Found: C, 46.98; H, 4.20; N, 6.99; MS (ESP\^+ (acetonitrile) shows a peak at m/z = 434.5 (100), 435.0 (80), 435.5 (50), 436.1 (60), 436.6 (20), 437.1 (20) corresponding to M^{2+} -2PF_{6}.

The NMR spectra showed strong line broadening due to manganese(II). $^1$H NMR (400 MHz, acetone-d6): $\delta$ 1.38 (12H), 1.74 (4H), 2.58 (6H), 2.82 (4H), 4.19 (4H), 7.45 (4H), 7.93 (8H), 8.67 (8H). It was not possible to obtain a C\(^{13}\) spectrum due to the presence of the magnetic Mn\(^{2+}\). Crystals for single crystal X-ray diffraction were obtained by slow diffusion of water into an acetonitrile solution of the complex [2].
Figure 1S. Magnetic susceptibility of the bulk sample.

Magnetic response was recorded on a powdered crystalline sample (6.28 mg) in a gelatine cup (see Fig. 1S). Data were corrected for diamagnetism of the container and for diamagnetism of the compound by use of tabulated values of Pascals constants. Measurements were performed on a Quantum Design MPMS5 system calibrated on a palladium sample and on CoHg(NCS)$_4$. The temperature independent magnetic moment with a value of close to 6 Bohr magnetons (theoretical spin-only value: 5.92 B.M.) is indicative of only weakly interacting high-spin manganese(II) centers.
S2. Assignment of the low-bias features: two molecules in parallel.

Figure 2S shows the same stability diagram as shown in Fig. 2a of the main text. Below, we shall argue why these data reflect electron transport carried by two molecules in parallel, and how the various low bias conductance features can be consistently assigned to these two different molecules.

As indicated in Fig. 2S by dashed black lines, the transport measurements exhibit two crossing points with equally sharp diamond boundaries having roughly the same slope. This is a strong indication that these two crossings separating regions (2-4) correspond to transport through the same molecule (Molecule B). Moreover the sharpness of these lines tell us that this a relatively weakly coupled dot, with a coupling $\Gamma$ to the leads of the order of a few meV, as compared to the charging energy which is of the order of 0.1 eV.

Between regions (1) and (2), we observe a much broader and lower ridge of high conductance which bears little resemblance to the two sharp crosses. Although it is difficult to draw diamond boundaries due to the large broadening, a slightly curved version of the sketched red dashed cross is clearly present. We interpret this as sequential tunneling through a different molecule (Molecule A) which is stronger.
coupled (broader ridge) and quite asymmetrically (lower peak-heights) coupled to source, and drain. In (4), we observe a similar region of high conductance and large broadening which is likely to be connected to transport through molecule A.

Zooming in on the low-bias features near the (2-3) cross (Fig. 3S), we observe that the gate dependent cotunneling lines in (3) continue through the single electron tunneling (SET) region into region (2) with hardly any change in their slopes. Figure 3b in the main text also shows that at high magnetic fields these lines display an identical splitting in three branches in regions (2) and (3). These observations again indicate that the two signals are merely superimposed, i.e. derive from two different molecules.

When crossing into region (2), these cotunneling lines are shifted a bit downwards (cf. Fig. 3a of the main text). The transition from (3) to (2) corresponds to the withdrawal of one electron from molecule B, and therefore this shift seems to indicate a capacitive coupling between the two molecules since this transition implies a change in the electrostatic environment of molecule A. From Fig. 3S, we also observe a zero-bias Kondo resonance in (2). The intensity of this Kondo resonance vanishes rapidly towards more negative voltages, indicating that it is connected to the charge degeneracy point of molecule B.

**Figure 3S.** Zoom-in of the low-bias region of the cross separating regions (2) and (3). Showing both first, and second derivatives of the current.
Following the cotunneling lines further left from region (2) into region (1), they change dramatically upon crossing the diamond boundaries (schematically shown by red dashed lines) of molecule A. The lines bend towards the zero-bias axis and a Kondo resonance appears at the far left (cf. supp. info. section 5). As described in the main text, this can be understood in terms of a transition from low, to high-spin giving rise to spin-blockade which suppresses the low-bias part of the SET cross. This entire spin-blockade scenario again makes it very natural to associate the two dominant gate-dependent cotunneling lines with molecule A.

Going (right) towards larger gate-voltages, the two gate dependent cotunneling lines in (3) extend into region (4) without any change in their slopes. Incidentally, the two lines cross zero practically at the point of transition from (3) to (4). As discussed already in the main text, the presence of a zero-bias Kondo resonance in region (4) at B=0T is consistent with a triplet ground state. From Fig. 4S we observe that the intensity of this Kondo resonance increases when going (right) further into region (4), indicating again that it is connected to the high conductance region on the far right, which we have attributed to molecule A.

Altogether, this interpretation of the whole set of transport data provides a consistent interpretation of regions (1-4) as the signal from two molecules in parallel. As we have argued, the two molecules are coupled very differently and we presume that this is the

Figure 4S. Zoom-in on the low-bias region of the crossing from region (3) to region (4). A zero-bias Kondo-peak with a gate-dependent Triplet-Singlet excitation grows stronger further inside region (4).
reason why only one of the two molecules shows the high-spin low-spin transition with the concomitant spin-blockade.

Notice that a total of 206 samples incorporating the \([\text{Mn(terpy-O-(CH}_2}_6\text{-SAc)}_2]^{2+}\) molecule have been measured. For all samples, electromigration was carried out using a self-breaking method which has proven to significantly reduce the chances of creating small gold nano-particles during this process [3]. In nine of these 206 junctions transport could be attributed to transmolecular conduction; our reported yield is comparable with the work by other groups, i.e. a few percent [4]. In Fig. 5S, we show low-temperature measurements taken on a different sample in which only two charge states were accessible. The observed sharp spectroscopic lines in the SET region and the absence of cotunneling features indicate weak electronic coupling. Given the energy spacing of the excitations (a few meV) and their appearance at more or less the same energies for two subsequent charge states, we argue that the observed excitations originate from vibrational modes. Only the sample shown in the main paper had enough information in the stability plot for us to unambiguously indentify the charge and spin states.

**Figure 5S.** Stability diagram measured on a different three-terminal junction with \([\text{Mn(terpy-O-(CH}_2}_6\text{-SAc)}_2]^{2+}\), at \(T = 1.6\) K.
S3. Details on the assignment of spin states.

In this section we provide a few additional details to support the assignment of the different spin states as discussed in the main text. First, the transition $|S\rangle \rightarrow |T_0\rangle$ in regions (2) and (3), should be magnetic field independent as the difference in angular momentum between these states is zero. In Fig. 6S we present the same plots as in Fig. 3 of the main text (same bias and gate range is used). For the measurement at zero magnetic field (Fig. 6Sa) we have drawn the gate-dependent cotunneling lines in (2) and (3): orange and red dotted lines respectively. We have then copied these lines on the measurement at high magnetic fields at the same locations in Fig. 6Sb. We see that the red dotted lines match the $|S\rangle \rightarrow |T_0\rangle$ excitation (middle resonance on the left hand side of the S-T$_1$ crossing). A similar agreement is found for the orange dotted lines.

**Figure 6S.** a, b, Plots similar to Fig. 3a and 3b of the main text. In a, dotted lines are drawn along the gate dependent cotunneling lines in regions (2) and (3). In b, the lines drawn in a were copied to the same locations. Blue dotted line represents the zero-bias axis.
S4. Enhanced cotunneling near the singlet-triplet degeneracy.

We have measured exactly the same $dI/dV$ map inside charge state (3) for three different magnetic fields, 10T, 9.3T, and 7T (see Fig. 7S). We observe that the S-T$_{1}$ crossing, indicated by an orange dot, moves towards smaller gate voltages as we increase the magnetic field. One particular feature for all three measurements at high magnetic fields, but mainly clearly visible in Fig. 7Sa, is the appearance of a sharp, almost vertical, line going through the S-T$_{1}$ crossing. To our knowledge, this line has not been observed before and as we shall argue below, it appears to have a relatively simple explanation.

Basically, this line reflects a difference in elastic cotunneling on the two different sides of the S-T$_{1}$ crossing which is brought out when the molecule is coupled sufficiently asymmetrically to source, and drain electrodes. This can be seen from the plots in Fig. 8S produced within 2nd order perturbation theory in the effective cotunneling amplitudes. To be more specific, a unitary (Schrieffer-Wolff) transformation effectively projects out all real charge-fluctuations and one is left with an effective low-energy (Kondo, or cotunneling-) Hamiltonian. For the specific problem of a spin-singlet separated from a spin-triplet by an exchange-coupling, the effective Hamiltonian and the 2nd order current in the resulting amplitudes has been calculated in Ref.[5] and

![Figure 7S. a,b,c](image_url)

Figure 7S. a,b,c, Differential conductance map inside (3), at T = 1.7 K and for three different magnetic fields. The orange dot indicates the position of the S-T$_{1}$ crossing for each panel. Red
dashed line at $V_G = 0.7$ V is used as a guide to the eye. Arrows point at a resonance line that crosses the S-T, degeneracy point.

Fig. 8S is produced from those formulas simply by assuming the singlet-triplet splitting to depend on gate-voltage (and very weakly on the bias-voltage, in order to simulate the slope of this nearly vertical feature). For a sufficiently large asymmetry in couplings to source and drain, the impurity is practically kept in its ground state: Singlet on the left, and triplet (T,1) on the right side. In this case, the line arises from the fact that the elastic cotunneling matrix element for the triplet state is simply a factor of two larger than that for the singlet. With a slight bias-dependence on the singlet-triplet splitting a vertical step in the elastic cotunneling background finally turns into a peak ($V>0$) or a dip ($V<0$), respectively.

**Figure 8S.** Differential conductance maps calculated inside charge state (3). The three left panels show a series of calculations incorporating the full effects of nonequilibrium ($V$-dependent) occupation numbers for the molecule-spin states. Top to bottom panels illustrate the effects of increasing source-drain asymmetry in the tunnel-couplings between molecule and electrodes. Right panel shows a similar calculation leaving out the effects of nonequilibrium
occupation numbers but including an anisotropy term which mixes the \( T_{-1} \) and the \( T_{+1} \) components of the triplet. Parameters are chosen to match experimental conditions.

Notice that no such line was observed at the singlet-triplet crossing point investigated in Ref. [6]. According to the mechanism outlined above, this implies that the present device is much more asymmetrically coupled than the device studied in Ref. [6]. Since more than one orbital is involved in both of these systems it is not straightforward to deduce the asymmetry of the devices, but judging from the zero-bias Kondo peak heights in the neighboring odd charge-states, the device in Ref. [6] shows a saturation at 0.4 \((2e^2/h)\), whereas the peak observed in charge state \((1)\) of the present device reaches a mere 0.02 \((2e^2/h)\). This, admittedly crude, estimate would indeed suggest a more symmetrically coupled device in Ref. [6].

Comparing to the nearly vertical experimentally observed line, a few discrepancies still remain to be resolved. First of all, a closer investigation of the data shows that as bias voltage increases the line-shape as a function of gate-voltage has more structure to it than simply a peak or a dip. At this stage, we merely speculate that this is related to a cotunneling induced mixing of the various spin-states at higher bias-voltages. More importantly, perhaps, is the fact that the experimental line is observed to have a width of roughly 3 mV (estimated with a gate-coupling of 0.1), which is comparable to the maximum singlet-triplet splitting at zero-field. In our calculation, the extra line is only smeared by temperature, i.e. roughly 0.2 mV (1.7 K) and hence an order of magnitude too narrow.

In calculating the right panel of Fig. 8S we have also included a spin-anisotropy term, \( D S_z^2 + E(S_x^2 - S_y^2) \), for the spin-1 state. This term breaks the rotational invariance and angular momentum need no longer be conserved. In our calculation this shows up as an extra \( \Delta m=2 \) line reflecting a transition between \( T_{-1} \) and \( T_{+1} \). As pointed out earlier, this extra (nominally forbidden) line is also observed in the experiment. Such anisotropies could well arise from spin-orbit coupling on the Mn-atom in the presence of a nearly octahedral ligand-field.

In this section we present a detailed study of the zero-bias Kondo resonance observed in charge state (1). We also give clear evidence of the magnetic field splitting of the Kondo resonance in charge state (4). Figures 9Sa and 9Sb show the temperature dependence of the Kondo resonance observed at the far left of region (1). As expected for an underscreened spin $5/2$ [7,8], we find a logarithmic increase upon lowering the temperature. In a magnetic field, this Kondo resonance splits in two peaks, as shown in Fig. 9Sc. From the splitting of the Kondo resonance at $B=10T$ we estimated a $g$-factor of $g = 1.9 \pm 0.3$.

![Graphs showing dI/dV versus V, dI/dV versus T, and a grayscale plot of dI/dV versus V and B at V_G = -2.8 V.]

**Figure 9S.** a, $dI/dV$ versus $V$ at fixed gate voltage, inside charge state (1), for various temperatures with $V_G = -2.8V$. b, Zero-bias conductance as a function of temperature. c, Grey-scale plot of $dI/dV$ versus $V$ and $B$ at $V_G = -2.8 V$.

Due to the close proximity of the gate-dependent cotunneling lines at finite bias, similar plots could not be made to characterize the zero-bias Kondo-resonance in region (4).
Nevertheless, it is clear from Fig. 10Sa and 10Sb that at zero magnetic field we do observe a zero-bias resonance. The red dashed line in Fig. 10Sb is a fit to a $dI/dV$ trace taken inside charge state (4); it includes two lorentzians centered at finite bias and a third one which after convergence of the fitting procedure is found to be centered around zero bias. Figure 10Sc shows the same stability diagram as in Fig. 10Sa but at high magnetic fields (B = 10 T). Three $dI/dV$ traces taken from the former measurement at different gate voltages inside region (4) clearly demonstrates the splitting of the zero-bias Kondo resonance as shown in Fig. 10Sd.

![Figure 10S](image)

**Figure 10S.** a, Differential conductance map of the crossing between regions (3) and (4), at T = 1.7 K and B = 0T. b, $dI/dV$ trace taken at the position indicated in a by a thin dashed line. Red dashed line is a fit using three lorentzian peaks: one was found to be centered around zero bias after convergence of the fitting procedure. c, Same as in a but at B = 10 T. d, $dI/dV$ versus $V$ at three different gate voltages inside charge state (4). Arrows indicate the positions of the splitted zero-bias Kondo resonance for the trace at highest gate voltage.
S6. Model calculations.

The important orbitals of the molecule are the $d$-orbitals of Mn and the two ligand orbitals of the terpyridine. In solution, the molecule is known to be in a high-spin state, which suggests that the crystal field splitting of the $e_g$ and $t_{2g}$ orbitals is smaller than the Hund's rule coupling, $K$, and that the ligand orbitals lie higher in energy than the $e_g$ orbitals. As mentioned in the main text, some shifts of the ligand orbital energies are required to account for the observations, in particular the low-spin states. To clarify the situation, we present here more careful model calculations.

Our effective model operates with 7 orbitals: the three $t_{2g}$ Mn $d$-orbitals ($xy$, $yz$, $zx$), the two $e_g$ Mn orbitals ($x^2-y^2$, $3z^2$) and two ligand orbitals. The on-site energy of these orbitals are chosen, such that the $t_{2g}$-orbitals are degenerate with energy $\epsilon_d^0$, the two $e_g$ orbitals have energy $\epsilon_g^0 + \Delta$, while the ligand orbitals have energies, $\epsilon_1$ and $\epsilon_2$, which can vary relative to the $\epsilon_d^0$ as a function of the applied gate voltage. The largest energy in the problem is the Coulomb repulsion, $U$, among the Mn $d$-electrons. We include a ferromagnetic exchange coupling, with strength $K$, also among the $d$-electrons. The relevant ligand orbital of the terpyridines is shown in Fig. 11S.

Figure 11S. The relevant ligand orbital of the terpyridines included in our model. Colors denote the sign, and radius of the circles denote the amplitudes of the $p_z$ orbitals involved.
With an appropriate choice of axes, the dominant coupling (hopping matrix elements) is between the $xy$ orbital and one of the ligand orbitals and between the $zx$ orbital and the other ligand orbital. In our model these couplings will be denoted by $t$. There is a weaker coupling, $t'$, between one of the ligand orbitals, and the $3z^2-r^2$ orbital, and all other couplings are taken to be negligible in comparison. The model Hamiltonian is thus:

$$H = \varepsilon_{d}^{0}N_{t_{3g}} + (\varepsilon_{d}^{0} + \Delta)N_{e_{g}} + \varepsilon_{1}N_{1} + \varepsilon_{2}N_{2} + \frac{U}{2}N_{d}(N_{d} - 1) + KP_{ij} + t\sum_{\sigma}(c_{1\sigma}^{\dagger}c_{xy\sigma} + c_{2\sigma}^{\dagger}c_{1\sigma} + c_{3\sigma}^{\dagger}c_{xx\sigma} + c_{3\sigma}^{\dagger}c_{xx\sigma}) + t'\sum_{\sigma}(c_{1\sigma}^{\dagger}c_{3z^2-r^2\sigma} + c_{3z^2-r^2\sigma}^{\dagger}c_{1\sigma})$$

using second quantization notation. The exchange operator $P_{ij}$ exchanges two electrons in orbitals $i$ and $j$, thus implementing the ferromagnetic Hund's rule coupling.

We shall consider many-body states with either 5 or 6 electrons in the system. If, for a moment, we neglect the hybridization, $t$, the eigenstates of the system have a fixed number of electrons in each orbital. The energy of the $d$-orbitals is low enough for the first 4 electrons to enter these orbitals. If electron number 5 is also in a $d$-orbital, the energy will increase by an amount $(\varepsilon_{d}^{0} + 4U)$, and the addition of a sixth $d$-electron will increase the energy by $(\varepsilon_{d}^{0} + 4U + U)$. In the following we shall chose the energy zero, such that $\varepsilon_{d}^{0} + 4U = 0$. In that case $d$-electron number 5 will have energy 0, and $d$-electron number 6 will have energy $U$. To these energies we must add the splitting $n\Delta$ depending on how many electrons are in the $e_{2g}$ orbital, and exchange energy $mK$, which will depend on the spin of the $d$-electrons. Electrons number 5 and 6 could also enter the two ligand orbitals. It is therefore of crucial importance where the ligand energies $\varepsilon_{1}$ and $\varepsilon_{2}$ are relative to 0 and $U$.

When hybridization is included (finite $t$), the problem becomes a true many-body problem. If the model molecule has 5 electrons, the Hilbert space will have dimension
**Figure 12S.** Density plot with $\varepsilon_1$ along the horizontal axis and $\varepsilon_2$ along the vertical axis. Green indicates that the ground state is a spin singlet, while purple indicates that it is a spin triplet. The other parameters are $U = 5.0 \, eV$, $K = 0.8 \, eV$ and $t=0.27 \, eV$, $t'=0.1 \, eV$.

1001. For 6 electrons the dimension becomes 2114. We shall therefore start with a numerically solution of the problem.

Let us first consider the 6 electron problem, seeking for a singlet-triplet transition. In the following figure a diagram is shown which indicates for which values of ligand energies, $\varepsilon_1$ and $\varepsilon_2$, the ground state is either singlet or triplet. The general layout of the diagram is quite robust with respect to reasonable variations of the parameters $U$, $K$ and $t$.

To get a better understanding of the physics, we can look at the actual states. The triplet state, $|6T\rangle$, for parameters at the phase boundary between singlet and triplet is shown in Fig. 13S. The exact eigenstate has many more terms, but the amplitudes shown are dominant. Their precise values depend rather weakly on the model parameters.
Figure 13S. The dominant part of the many-body triplet state. Parameters used are $U=5.0$, $\varepsilon_d^0+4U=0$, $\varepsilon_2=0.6$, $\varepsilon_1=-0.3$, $\Delta=2.0$, $t=0.26$, $t'=0.1$. All in units of $eV$.

Including only the two dominant terms, we can set up an analytical calculation based on the two coupled many-body states. The two basis states have energies

$$E_{T1} = 5\varepsilon_d^0 + \varepsilon_1 + 10U - 4K,$$
$$E_{T2} = 4\varepsilon_d^0 + 2\varepsilon_1 + 6U - 3K,$$

and the coupling between the two states is

$$\langle T2|H|T1 \rangle = -t.$$

The ground state energy of this simplified system is given by

$$E_T = E_{T0} - \sqrt{(\delta E_T/2)^2 + t^2},$$

where

$$E_{T0} = \frac{9}{2}\varepsilon_d^0 + 8U + \frac{3}{2}\varepsilon_1 - \frac{7}{2}K,$$

and

$$\delta E_T = \delta \varepsilon - K,$$

with $\delta \varepsilon = \varepsilon_d^0 + 4U - \varepsilon_1$. 

17
Turning to the singlet state with the same parameters, the dominant terms in the lowest energy state are shown in Fig. 14S. The first two terms are the singlet combinations of one electron in a d-orbital and another one in a ligand level. This state is coupled to a state with the two electrons in the ligand level. Again, setting up a simple two-state model, we can do an analytical calculation. The two states have energies

\[ E_{S1} = 5\varepsilon_d^0 + \varepsilon_1 + 10U - 4K, \quad E_{S2} = 4\varepsilon_d^0 + 2\varepsilon_1 + 6U - 2K. \]

The coupling matrix element of the two states is

\[ \langle S2|H|S1 \rangle = -\sqrt{2}t \]

and the ground state energy of the singlet sector is thus

\[ E_S = E_{S0} - \sqrt{(\delta E_S)^2 + 2t^2}, \]

where

\[ E_{S0} = \frac{9}{2}\varepsilon_d^0 + 8U + \frac{3}{2}\varepsilon_1 - 3K, \]

and
$$\delta E_S = \delta \varepsilon - 2K.$$  

From this, we can now determine the singlet-triplet splitting analytically, i.e.

$$J = E_T - E_S = -\frac{1}{2}K + \sqrt{(\delta \varepsilon - 2K)^2/4 + 2t^2} - \sqrt{(\delta \varepsilon - K)^2/4 + t^2}.$$  

This splitting is zero, when $\delta \varepsilon = t^2/K$. Since $t$ is somewhat smaller than $K$, the line where the singlet and triplet states are degenerate should therefore be close to $\varepsilon_1 = 0$ and independent of $\varepsilon_2$. This is in fact also what the 'exact' numerical calculation gives, at least for reasonably large values of $\varepsilon_2$ (cf. Fig. 12S).

In order to make contact between the model calculations and the measured stability diagrams, we need to understand how the model parameters are changed by changes in the gate voltage. A straightforward mechanism is pure electrostatics, which is to say that the different orbitals in the molecule are located at different regions and hence electrons occupying these orbitals can have their energies shifted differently by the gate. Orbitals in close proximity to one of the lead electrodes will therefore have a smaller shift since its electrical potential will be tied to that of the electrode. This is again consistent with our observation from Fig. 2S that molecule A must be asymmetrically coupled to source, and drain electrodes in order explain the relatively low and broad the conductance ridge due to sequential tunneling.
S7. Spin blockade and cotunneling assisted sequential tunneling.

From the previous section, we have learned that the two lowest lying five, and six-particle states are dominated basically by two states which differ by one electron being either on the $d$-orbitals or on the stronger coupled ligand orbital. From these we pick out the lowest (bonding) state, thus presuming that the tunnel coupling, $t$, between $d$, and ligand-orbitals is much stronger than the splitting between the two lowest 5, and 6-particle states (e.g. the Singlet-Triplet splitting for $N=6$). This gives the following energies of the relevant states near the $N=5,6$ charge degeneracy point:

\[
E_{6,0} \approx \frac{1}{2} \left( 3\varepsilon_1 - 6K - 20U - \sqrt{(\varepsilon_L + 2K)^2 + 2t^2} \right) - V_g
\]
\[
E_{6,1} \approx \frac{1}{2} \left( 3\varepsilon_1 - 7K - 20U - \sqrt{(\varepsilon_L + K)^2 + t^2} \right) - V_g
\]
\[
E_{5,5/2} \approx \frac{1}{2} \left( \varepsilon_1 - 16K + 4\Delta + 2\Delta' - 20U - \sqrt{(\varepsilon_L + 4K + 2\Delta')^2 + t^2} \right)
\]
\[
E_{5,1/2} \approx \frac{1}{2} \left( \varepsilon_1 - 7K - 20U - \sqrt{(\varepsilon_L + K + 2\Delta')^2 + t^2} \right).
\]

With these eigenenergies we can reproduce the basic features of the phase-diagram as calculated within the exact diagonalization. Notice the extra terms proportional to the parameter $\Delta'$, which we include to model the shift in the $e_g$ orbitals which is induced by charging of the ligand orbital.

With these eigenenergies we now proceed to calculate the sequential tunneling current near the $N=5,6$ charge degeneracy point. From the corresponding eigenstates we see that only the excited 6-particle triplet ($S=1$) and the excited 5-particle doublet ($S=1/2$) are coupled by tunneling in and out of the ligand orbital. Ground state ($S=0$) to ground state ($S=5/2$) transitions being (spin-)blocked[9], transport will therefore require an initial nonequilibrium (bias induced) population of the excited ($S=1$) 6-particle state to tunnel from there into the 5-particle state. This makes an interesting case in which transport takes place solely via the so called cotunneling assisted sequential tunneling (CAST) mechanism [10-12]. We note that parameters could in principle have made the
state | 5, $S=3/2$ \rangle lie lower than | 5, $S=1/2$ \rangle, but the former has negligible overlap with | 6, $S=0,1$ \rangle and hence would not lift the spin-blockade.

To calculate the sequential tunneling current, we solve the following rate equations:

\[
0 = \sum_{i=1,2} \left[ (W_{5,i;6,1}^\alpha + W_{6,2;6,1}) P_{6,1} - W_{6,1;5,i}^\alpha P_{5,i} - W_{6,1;6,2} P_{6,2} \right]
\]

\[
0 = \sum_{i=1,2} \left[ (W_{5,i;6,2}^\alpha + W_{6,1;6,2}) P_{6,2} - W_{6,2;5,i}^\alpha P_{5,i} - W_{6,2;6,1} P_{6,1} \right]
\]

\[
0 = \sum_{i=1,2} \left[ (W_{6,i;5,1}^\alpha + W_{5,2;5,1}) P_{5,1} - W_{5,1;6,i}^\alpha P_{6,i} - W_{5,1;5,2} P_{5,2} \right]
\]

together with the constraint that $\sum_i (P_{5,i}+P_{6,i})=1$. The transition rates are given respectively by

\[
W_{6,j;5,i}^\alpha = \Gamma_{6,j;5,i}^\alpha n_F (\varepsilon_{6,j} - \varepsilon_{5,i} + \mu_\alpha) \\
W_{5,j;6,i}^\alpha = \Gamma_{6,j;5,i}^\alpha (1 - n_F (\varepsilon_{6,i} - \varepsilon_{5,j} + \mu_\alpha))
\]

for the sequential tunneling processes, and

\[
W_{N,j;i}^\alpha = \Gamma_{N,j;i}^\alpha \sum_{n=\pm 1} (\varepsilon_{6,j} - \varepsilon_{6,i} - nV) n_B (\varepsilon_{6,j} - \varepsilon_{6,i} - nV)
\]

for the cotunneling processes from an $N$-particle state. Here $n_{F/B}$ denote respectively the Fermi, and Bose functions, and subscripts $i,j \in \{1,2\}$ label ground state and first excited state for a given $N$. The energy-independent transition rates are given as

\[
\Gamma_{6,j;5,i}^\alpha = |\langle 6,j | H_T | 5,i \rangle|^2 \propto \pi \nu_F |t_\alpha|^2
\]

determined by the tunneling amplitudes from the stronger coupled ligand-orbital to the leads and by the overlap of the state | 6, $j$ \rangle with the state corresponding to | 5, $i$ \rangle with an extra electron on the ligand orbital.
Solving these rate equations for the occupation probabilities, we calculate the current as

\[ I = \sum_{i,j=1,2} (W_{5,j;6,i}^L P_{5,i} - W_{6,j;5,i}^L P_{6,i}) \]

thus neglecting for simplicity the contribution from the cotunneling current. Rather than trying to estimate the relevant matrix-elements, we shall derive a basic feature of the conductance near the \( N=5,6 \) charge-degeneracy point, which we propose as the underlying mechanism for the partially blocked cross observed in the experiment. In Fig. 15S, we show a density-plot of the nonlinear conductance as a function of gate, and bias voltage. Parameters are chosen such that the coupling between the two ground states, \( |5, S=5/2 \rangle \) and \( |6, S=0 \rangle \), is much smaller than any other coupling and this is why the “original” cross is extremely faint, i.e. spin-blocked. The horizontal black line is at \( V=0 \), and the vertical black line is at the gate-voltage corresponding to the charge-degeneracy point at which the two ground states, \( |5, S=5/2 \rangle \) and \( |6, S=0 \rangle \), become degenerate. As argued earlier, the rotational invariance is broken by the ligand-field and therefore the spin-blockade need not be complete, as also observed in the experiment. The stronger (broader white) feature corresponds to transport via sequential tunnelling between the better coupled excited states, \( |5, S=1/2 \rangle \) and \( |6, S=1 \rangle \). This transport mechanism requires a finite bias-voltage which is large enough to populate the excited states via an inelastic cotunneling process, i.e. the so-called \( CAST \) mechanism [10-12]. The conductance plot in Fig. 15S in fact bears a certain resemblance to the experimental results obtained in Ref. [10].
Figure 15S. Calculated density plot of $dI/dV$ as a function of $V_G$ and $V$. The blue background corresponds to nearly zero conductance and the white ridges of high conductance trace out the voltages for which sequential tunnelling can take place.

References:


