Supplementary information : Cotunneling through a magnetic single-molecule transistor based on $N@C_{60}$

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SAMPLES PRESENTATION AND COMPARISON OF THE RESULTS

Single-molecule transistors (SMT's) based on N@C_{60} contacted by gold leads were prepared by blow drying a dilute toluene solution of the N@C_{60} molecule onto a gold nano-wire realized on an Al/Al_2O_3 back gate. Before blow drying the solution, the nano-wires were cleaned with acetone, ethanol, isopropanol and oxygen plasma. We then performed our electromigration procedure at 4 K. We tested 274 junctions and present in this section 3 samples having an addition energy greater than 200 meV (Fig.S.1)

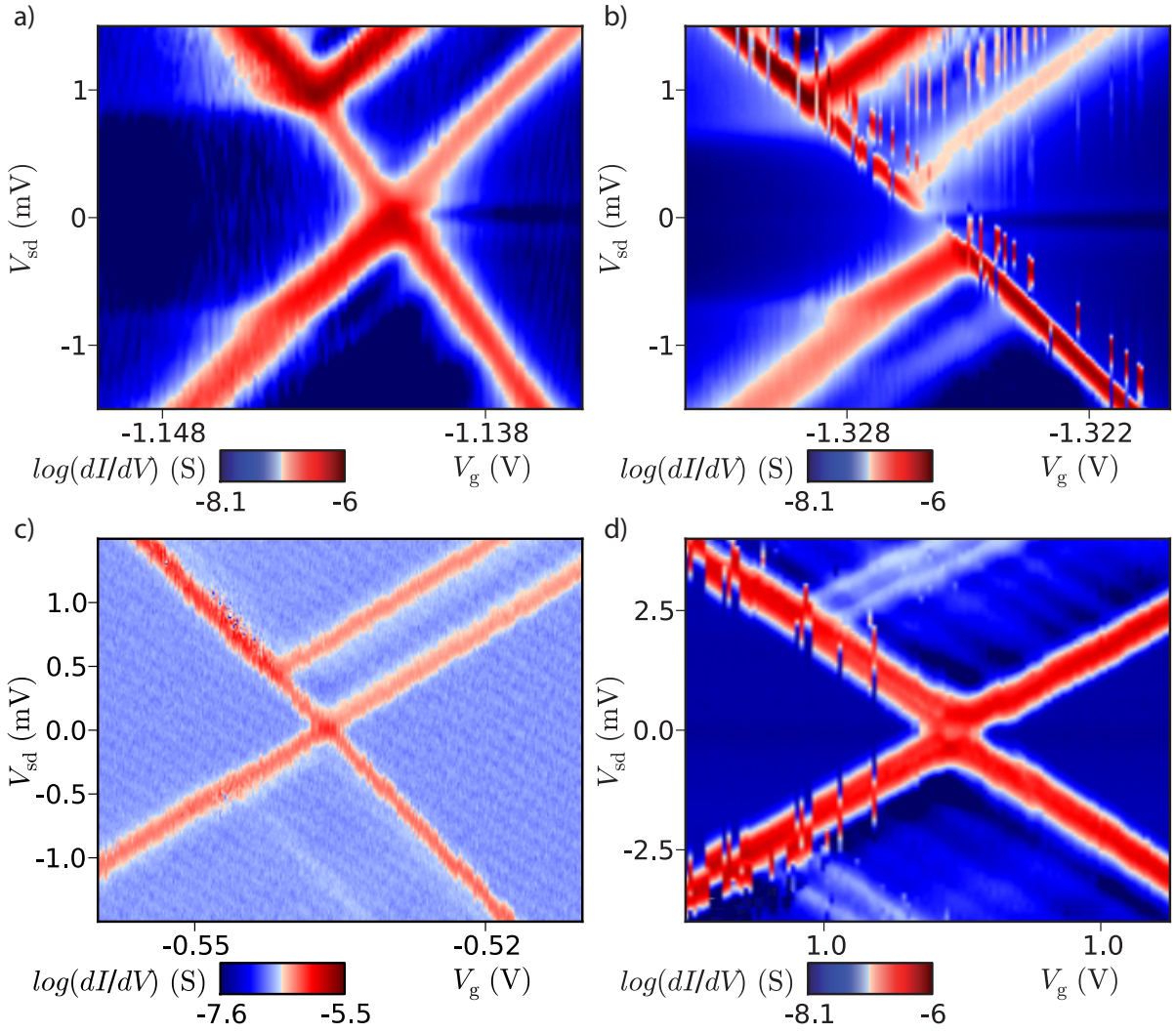

Fig.S. 1: Color scale plot of the differential conductance dI/dV as a function of bias voltage V_{sd} and gate voltage V_g : **a)** first run of measurements. **b)** second run of measurements. **c)** and **d)** other N@C_{60} SMT's in the weak coupling regime.

In Fig.S.1(a) and 1(b) we present first the stability diagram of the sample presented in the Letter, obtained at zero magnetic field during the first and the second run of measurements, respectively. The sample has been kept at cryogenic temperature ($T \leq 4$ K) during the two runs. However, changes in our electronic setup (different I-V converters, inversion of the ground connection) have probably generated a small electrical discharge inducing modifications of some measurement features, as exhibited by the modification of the capacitances and tunneling rates extracted from a fine analysis of the stability diagram. For the first run, we obtain $C_g : C_R : C_L = 1 : 3.09 : 2.96$, and $\Gamma_R/\Gamma_L \simeq 10$, while for the second run we get $C_g : C_R : C_L = 1 : 3.29 : 3.43$, and $\Gamma_R/\Gamma_L \simeq 6.7$. The SMT experienced then some unexpected changes inducing a different electrostatic environment leading to a modification of the anti-ferromagnetic exchange interaction J. The evolution of J will be addressed in the next section.

The striking difference between the two runs is observed at the charge degeneracy point. In Fig.S.1(b), corresponding to the second run, we measure an opening of this latter. As it is not present in the first run as seen in Fig.S.1(a), we can rule out any correlation between this observation and the cotunneling step at low bias voltage observed for $n_{\mathrm{C_{60}}} = 2$ ($V_{\mathrm{g}} > V_{\mathrm{g}}^{\mathrm{D}}$). No further measurements were performed in order to explain this feature, but a similar behavior was observed in another SMT based on a single N@$\mathrm{C_{60}}$, as presented in Fig.S.1(d).

MAGNETIC FIELD SPECTROSCOPY IN THE COTUNNELING REGIME FOR $n_{\mathrm{C_{60}}} = 1$

In this section, we compare the magnetic field spectroscopy performed in the cotunneling regime, where $n_{\mathrm{C_{60}}} = 1$ ($V_{\mathrm{g}} < V_{\mathrm{g}}^{\mathrm{D}}$), for the two runs of measurements. As depicted in Figure 4 of the Letter, when the magnetic field increases, the different multiplet states are Zeeman split. For a magnetic field $B < B_{\mathrm{c}}$, the ground sate is $|1, +1\rangle$ and taking into account the selection rules, we observe four different transitions, until the magnetic field reaches the critical magnetic field B_{c} for which the ground state becomes $|2, +2\rangle$. Only two transitions are then allowed, obeying $|\Delta S^z| = 0$ or 1, as observed in Fig.S.2(a). Unfortunately, if the critical field B_{c} was experimentally accessible for the second run corresponding to $J = -0.3$ meV (Fig.S.2(a)), no spin transition could be observed for the first run (Fig.S.2(b)) as the value of $J = -0.4$ meV was too high. Indeed, as J depends exponentially on the distance

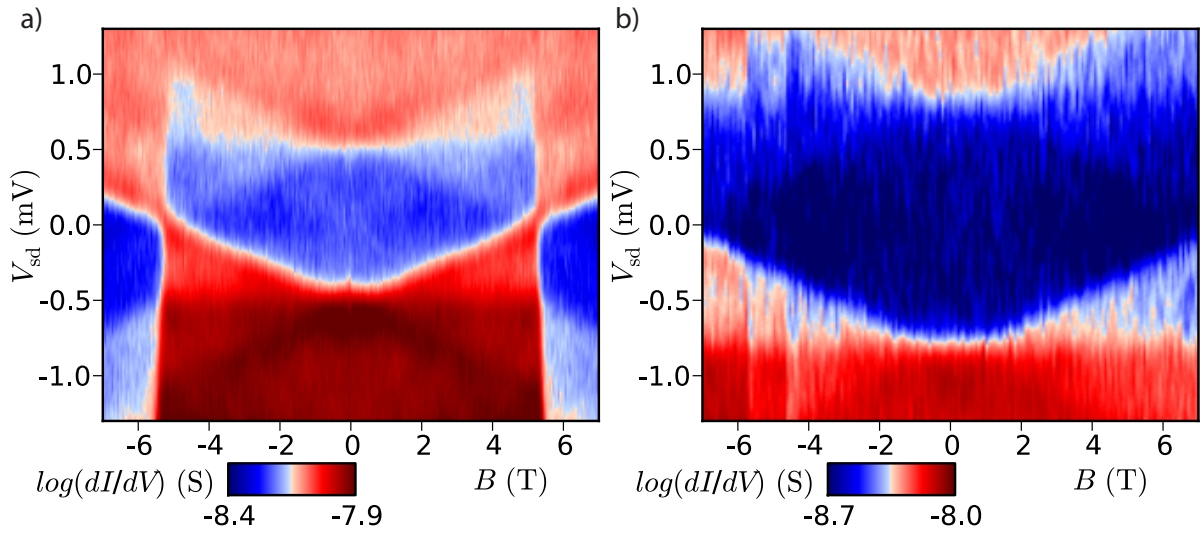

Fig.S. 2: Experimental differential conductance as a function of magnetic field for a fixed gate voltage $V_g < V_g^D$ ($n_{C_{60}} = 1$) for **(a)** $J = -0.3$ meV (second run) and **(b)** $J = -0.4$ meV (first run).

between the nitrogen and the C_{60} cage, a small deformation can modify J significantly. More precisely, J is given by an exchange integral, which depends strongly on the electronic wave function of the C_{60} LUMO. This wave function is not only changed by geometric deformation but also by electrostatics. For example, image charges in the metal electrodes draw it outwards towards the electrodes and away from the nitrogen. A modification of the environment can thus also lead to a variation of J.

MAGNETIC FIELD SPECTROSCOPY IN THE COTUNNELING REGIME FOR $n_{C_{60}} = 2$

In the Letter, we raised the question of the unexpected cotunneling steps at low voltage bias, obtained at zero magnetic field in the $n_{C_{60}} = 2$ region where the total spin of $N@C_{60}^{2-}$ is $S = 3/2$. In Eq. (1) of the Letter, we assume no anisotropy. In this case, performing a magnetic field spectroscopy, we should observe one cotunneling step increasing linearly with magnetic field (Fig.S.3(b)) corresponding to the transition from the $|3/2, +3/2\rangle$ state to the $|3/2, +1/2\rangle$ state as shown in Fig.S.3(a). In Fig.S.3(c), we present the dI/dV measurement as a function of magnetic field. We clearly observe that the cotunneling steps evolve linearly

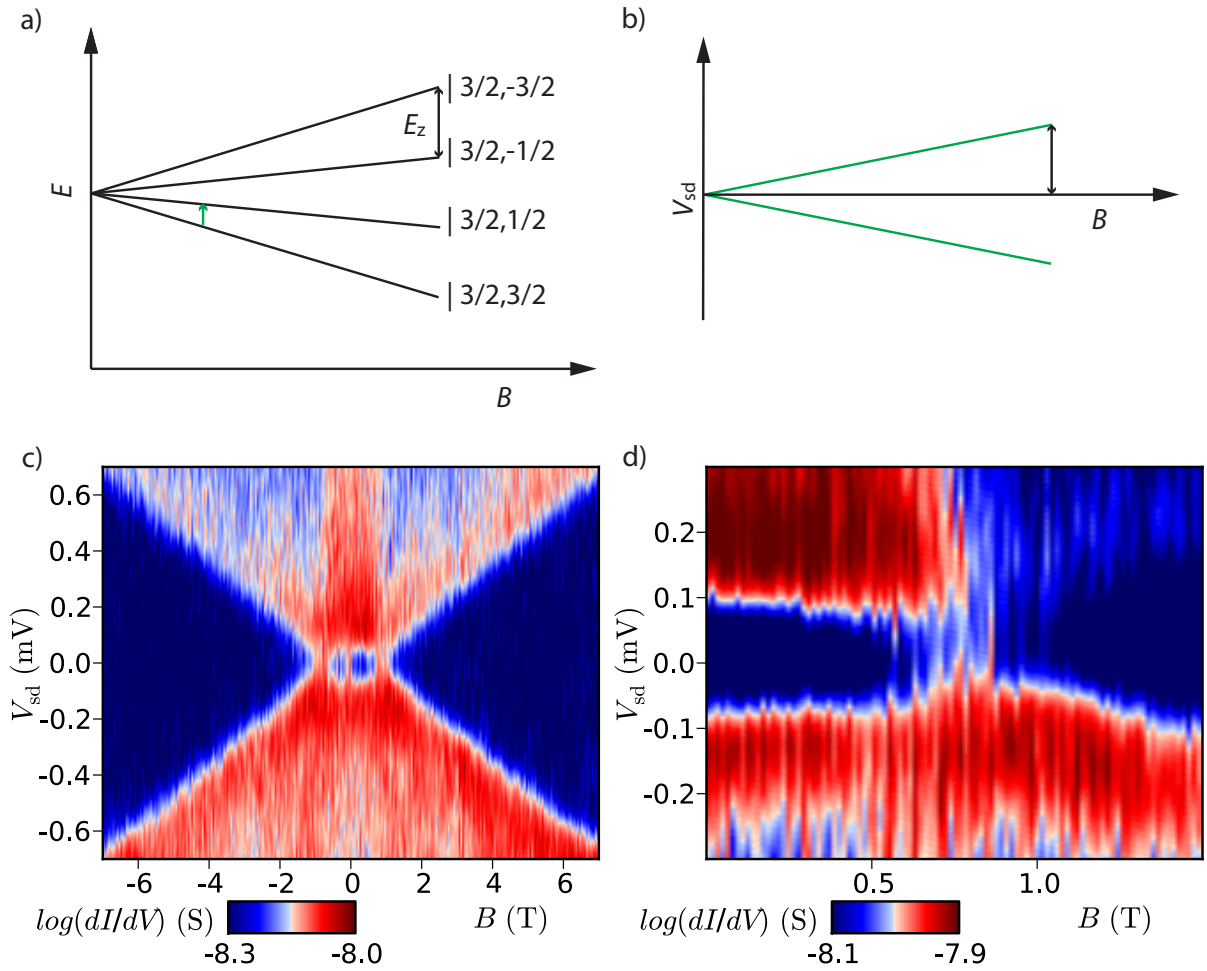

Fig.S. 3: **(a)** Zeeman diagram of the multiplet $S = 3/2$ for $N@C_{60}^{2-}$ ($n_{C_{60}} = 2$). **(b)** Schematic showing the expected cotunneling steps deduced from the Zeeman diagram. **(c)** and **(d)** dI/dV measurements as a function of magnetic field for a fixed gate voltage.

in the high magnetic field limit.

However, when we focus on the low magnetic field spectroscopy measurements (Fig.S.3(d)), we observe a non-linear decrease of the cotunneling step as a function of magnetic field. This cotunneling step and the non linear evolution could be interpreted as a signature of anisotropy [1–5] in $N@C_{60}^{2-}$. This interpretation relies on the assumption of significantly enhanced spin-orbit coupling on the nitrogen atom, which might be caused by the hybridization with the gold leads, as the anisotropy of $N@C_{60}$ should not exceed tens of mT [6–8].

The effect of anisotropy can be included in our model adding $E_{\text{ani}} = -K(S^z)^2$ in our Hamiltonian (Eq. 1 of the Letter), where E_{ani} is the anisotropic energy, K is the uniaxial

anisotropy constant, and S_z is the z component of the total spin. However, by including this term into the Hamiltonian, we should also observe extra cotunneling steps in the $n_{C_{60}} = 1$ region. We did not measured this signature, either because of a lack of sensitivity of our electronic, or because the finite anisotropy might be charge dependent, but up to now, we do not have a clear explanation of the possible charging-state dependence of K.

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