Supplementary Information: Quantum phase transition in a single-molecule quantum dot

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Abstract

Quantum criticality is the intriguing possibility offered by the laws of quantum mechanics when the wave function of a many-particle physical system is forced to evolve continuously between two distinct, competing ground states. This phenomenon, often related to a zero-temperature magnetic phase transition, can be observed in several strongly correlated materials such as heavy fermion compounds or possibly high-temperature superconductors, and is believed to govern many of their fascinating, yet still unexplained properties. In contrast to these bulk materials with very complex electronic structure, artificial nanoscale devices could offer a new and simpler vista to the comprehension of quantum phase transitions. This long-sought possibility is demonstrated by our work in a fullerene molecular junction, where gate voltage induces a crossing of singlet and triplet spin states at zero magnetic field. Electronic tunneling from metallic contacts into the C\textsubscript{60} quantum dot provides here the necessary many-body correlations to observe a true quantum critical behavior.

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EXPERIMENTAL SETUP

The spin $S = 1/2$ Kondo effect in a C$_{60}$ molecular junction was observed for the first time by Yu and Natelson [1] (see also [2] in the case of ferromagnetic electrodes), and more recently by Parks et al. [3] using mechanically controllable break junctions. However, to our knowledge, no electromigration procedure has been carried out in a dilution refrigerator with a high degree of filtering. The creation of nanogaps with this technique requires minimizing the series resistance [4], which is generally incompatible with dilution fridge wiring and filtering. To overcome this problem, we developed a specific measurement setup described here. We emphasise that the possibility of accessing very low temperatures, as compared to relatively large Kondo scales, was central to the observation of quantum critical signatures associated to the singlet-triplet crossing in this system.

Our experimental setup (Fig. S.1) is divided into two parts. First, electromigration [5] is performed at 4 K with the fast part of the setup. As we wanted to perform such measurements in a dilution fridge, we developed an efficient electromigration technique since dilution wires and low-temperature filters are very resistive and add an important series resistance to the sample (few hundreds Ohms). Improvements of the original procedure [5] have already been reported recently [6, 7, 8, 9, 10, 11]. We ramp the voltage across the junction and measure its resistance using a very fast feedback-loop (1.5 $\mu$s) in order to set the voltage to zero when the resistance exceeds a defined threshold, typically 20 k$\Omega$. The fast feed-back loop was achieved with a real-time electronics (Adwin Pro II) and a home-built high-bandwidth current to voltage converter, as described in Fig S.1). With this technique, we obtained small gaps (1-2 nm) characterized by the tunnel current measured after electromigration, without molecules, in previous experiments.

The second step uses the low noise component of the setup to measure the single-molecule transistor. In addition to low-temperature filtering, we used $\Pi$ filters and ferrite bead filters developed at Harvard by J. MacArthur and B. D’Urso [12]. In order to minimise ground loops we integrated all the analogical electronics in a shielded box at room temperature. Because of its great versatility, Adwin Pro II can be programmed to perform DC or lock-in measurements, and apply gate or bias voltages, thus minimizing the possibility of ground loops. Depending on the measurements, we used an AC-excitation between 3 $\mu$V and 100 $\mu$V for the lock-in technique.
Fig. S. 1: Simplified scheme of the experimental setup. See text for details.

We note that previous studies of C$_{60}$ quantum dots did not require the use of a dilution refrigerator to investigate Kondo physics because the relevant energy scales are typically an order of magnitude larger than in carbon nanotubes or semiconducting devices, providing large Kondo temperatures of several kelvins. However, the study of single-molecule transistors using low-temperature techniques (previously reserved to 2DEG systems) was certainly crucial for unveiling the rich physics that takes place below the Kondo temperature at the singlet-triplet transition. Our low-temperature setup allowed a more precise investigation of the usual spin $S = 1/2$ Kondo effect in C$_{60}$ and is presented in the next section.

**FULLY-SCREENED SPIN $S = 1/2$ KONDO EFFECT IN A C$_{60}$ QUANTUM DOT**

In this section we present a detailed study of the standard spin $S = 1/2$ Kondo effect observed in the Coulomb diamond associated with an odd excess number of electrons into the C$_{60}$ molecule. In this particular region we clearly observe a zero bias anomaly in the
conductance, as shown in Fig.1c of the main paper. This signature has been widely observed in semiconducting devices [13, 14], carbon nanotube [15, 16], or single-molecule [11, 17, 18] quantum dots. In such strongly confined nanostructures, when the last electronic energy level is occupied by a single electron, the quantum dot behaves as a spin \(S = \frac{1}{2}\) magnetic impurity. In this case the conduction electrons in the leads are coupled antiferromagnetically to the magnetic impurity via second order tunneling processes. When the tunnel barriers between the dot and the electrodes are transparent enough, so that resonant Kondo scattering can occur at low temperature, quantum coherent transport establishes and allows the current to flow through the dot, thus beating the Coulomb blockade [19, 20]. When conduction electrons form a Kondo cloud around the dot to screen its magnetic moment, a sharp peak is created in the density of state at the Fermi level, giving rise to a narrow resonance in the differential conductance, which does not disperse with varying the gate voltage. Universality is a fundamental property of the Kondo effect and a single energy scale, associated with the Kondo temperature \(T_K\), fully describes the physical properties at low energy. When the typical energy of a perturbation, such as temperature, bias voltage, or magnetic field, is higher than \(T_K\), the coherence of the system is suppressed and the Kondo effect disappears.

We demonstrate in the following that all these features are very cleanly observed in our \(C_{60}\) quantum dot, thereby giving the basis of the study presented in the main paper of the singlet-triplet transition for the even charge valley (measured with the same device). In Fig. S.2a we plot the differential conductance versus bias voltage. When the temperature is lowered, the height of the peak increases due to the Kondo effect. We estimate the value of \(T_K\) by measuring the half width at half maximum (HWHM) of the peak for \(T \ll T_K\). At \(T = 260\) mK, we find \(V_{b}^{\text{HWHM}} = 380\) \(\mu\)V, corresponding to \(T_K = 4.42\) K. A second and more precise way to find \(T_K\) is to fit the temperature evolution of the conductance at zero bias. The precise shape of this curve is universal (up to the value of energy scale \(T_K\)), and can be calculated by Numerical Renormalization Group (NRG) theory [21]. An empirical formula based on this calculation was found by Goldhaber-Gordon et al. [22] and is used to fit the experimental data, as shown in Fig. S.2b, where we find \(T_K = 4.46\) K. An additional method is to use the magnetic field dependence of the conductance [23]. The Zeeman effect competes with the Kondo resonance so that a non-equilibrium Kondo peak appears roughly at \(V_b = g\mu_B B\), as shown in Fig. S.2c). This splitting is predicted to appear
Fig. S. 2: Temperature and magnetic study of fully-screened spin $S = 1/2$ Kondo effect. 

a, Evolution of differential conductance versus bias voltage for several temperatures from 260 mK to 20 K.
b, Temperature dependence of the conductance at $V_b = 0$ mV extracted from the a panel, with a fit to the empirical formula proposed by Goldhaber-Gordon et al. [22] which gives $T_K = 4.46$ K.
c, Differential conductance ($\partial I/\partial V$) map versus bias voltage ($V_b$) and magnetic field $B$.
d, Position of the Kondo peaks extracted from the c, plot. The linear extrapolation of the peak position gives a critical field $B_c = 1.78$ T.

for $g\mu_B B_c = 0.5k_B T_K$ [21]. In Fig. S. 2d we linearly interpolate the position of these peaks and find $B_c = 1.78$ T, which yields $T_K = 4.78$ K. The value of $T_K$ obtained with the three different methods are consistent and demonstrate a well defined $T_K$. 

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NON-EQUILIBRIUM SINGLET-TRIPLET KONDO EFFECT ON THE SINGLET SIDE

In this section, we demonstrate, in our $C_{60}$ molecular junction, an effect recently reported by Paaske et al. in a carbon nanotube quantum dot [24], namely the non-equilibrium singlet-triplet Kondo effect. These authors were the first to clearly identify sharp finite voltage bias features as a Kondo effect and not as simple cotunneling via excited states. The main idea behind Kondo physics is the existence of a degeneracy, which is lifted by the conduction electrons. This is clearly the case for a quantum dot with only one electron on the last orbital, leading to a doubly degenerate spin $S = 1/2$. For a quantum dot with two electrons and two nearly degenerate orbital levels, two different kinds of magnetic states occur: a singlet and a triplet. Depending on $\delta E$ the energy difference between the two orbital levels and $J$ the strength of the ferromagnetic coupling between the two electrons, the splitting between the triplet and the singlet can in principle be tuned, and eventually brought to zero, leading to the so-called singlet-triplet Kondo effect [25]. However the singlet is in most situations the ground state, leaving the triplet in an excited state, thus suppressing the Kondo effect. Kondo signatures can nevertheless be observed by tuning the degeneracy in a magnetic field [15, 16, 26]. Another way to retrieve the degeneracy is to apply a bias voltage, although it is of course more delicate to preserve the quantum coherence necessary to Kondo correlations. Indeed, finite-bias features clearly linked to magnetic excitations were observed in 2DEGs [27], carbon nanotubes [15, 16, 28, 29] and even recently in an OPV5 molecule [30]. However, only the study reported by Paaske et al. [24] was able to identify a clear non-equilibrium Kondo effect. Their first observation was the occurrence of sharp peaks in the differential conductance for both positive and negative bias voltage, very different from the cusps usually associated to cotunneling. Secondly the height of these peaks decreased logarithmically with temperature, which is another typical signature of Kondo correlations. Finally the shape of the peaks could be well accounted for in a non-equilibrium Kondo calculation, while a simple cotunneling model failed to reproduce the data.

These striking features are also present in our experiment, for the case of an even charge state into the $C_{60}$ molecule. We focus here on the singlet side, but similar results are observed for the Kondo satellites on the triplet side (see main text). Indeed, while the conductance
Fig. S.3: **Non-equilibrium singlet-triplet Kondo effect on the singlet side.**

a, Differential conductance versus bias voltage for temperature from 35 mK (black) to 500 mK (pink) at fixed $V_g = 1.79$ V. 

b, Evolution of the "positive $V_b$" peak height in a) with temperature on a logarithmic scale, which can be linearly-fitted on nearly a decade.

c, Differential conductance map as a function of bias voltage and magnetic field at fixed $V_g = 1.64$ V.

d, Position of the excited triplet-peaks extracted from c. The linear fits demonstrate that the non-equilibrium singlet-triplet Kondo peaks split at a finite magnetic field $B'_c = 50$ mT.

At low bias is suppressed when the spin state of the system is a singlet, a clear finite-bias peak grows by decreasing temperature as shown in Fig. S.3a. In addition, the amplitude of the positive bias peak decreases logarithmically about a decade (Fig. S.3b), showing a clear signature of the non-equilibrium singlet-triplet Kondo effect. The magnetic field dependence of the differential conductance presented in Fig. S.3c is also very interesting. This plot, which was not numerically treated, shows the Zeeman splitting between the three triplet states at both positive and negative bias. The positions of those peaks are reported on
Fig. S. 3d and a linear fit is applied to each line, with a very good accuracy which enables us to determine, firstly, a critical field $B'_c$ of 50 mT before the splitting occurs, and secondly, a Lande factor $g = 2 \pm 0,1$. The existence of a critical field for the splitting of the zero-bias anomaly is well-documented in the case of the Kondo effect in equilibrium (see also our study for the spin 1/2 of section ). To our knowledge, these data are the first observation of this effect for the finite bias satellites associated to the non-equilibrium singlet-triplet Kondo effect. By applying the relation found by Costi [21] for the spin $S = 1/2$ case, we estimate the Kondo temperature $T_K = 130$ mK. This value must be taken as an approximation since the spin $S = 1/2$ model does certainly not apply quantitatively here, and also the base temperature $T = 35$ mK was not much smaller than $T_K$. Again, because the charging energy of a C$_{60}$ molecule is twenty times larger than that of a carbon nanotube quantum dot, we are able to access relatively high Kondo scale (the out-of-equilibrium Kondo temperature was estimated to be 2 mK by Paaske et al. in their device [24]).

**SINGLET-TRIPLET TRANSITION: LOW VERSUS VERY LOW TEMPERATURE**

In this section, we compare our C$_{60}$ quantum dot results on the singlet-triplet transition to previous studies on different quantum dot systems (2DEG or carbon nanotubes), and argue that the temperature required to observe a critical Kondo behavior was certainly too low in these previous experiments. The first important fact is that single molecules offer typically higher energy scales (charging energy, Kondo temperature...) due to their extremely small size. It is for example possible to study very well the spin $S = 1/2$ Kondo effect at liquid helium temperature in a C$_{60}$ molecular junction [1, 3]. The second crucial ingredient in our experiment was the development of the electromigration technique in a highly filtered dilution fridge, as discussed in section , which allowed us to reach temperatures well below the "high-energy" Kondo scale. Both points are well illustrated in Fig. S. 4, which shows the conductance maps at four different temperatures. Fig. S. 4a corresponds to measurements at $T = 1.25$ K. At this temperature, we observe a dip at the singlet side, but a single broad peak at the triplet side. This is reminiscent of the data reported by Kogan et al. [31] or Quay et al. [29], which showed a featureless change of behavior near the singlet-triplet crossing. On the contrary, our datas at the much lower base temperature $T = 35$ mK demonstrate more complex features (Fig. S. 4d), that we associated to a singlet-triplet quantum phase
Fig. S. 4: **Differential conductance maps versus bias voltage and gate voltage.** The maps at $T = 35$ mK (d), $T = 300$ mK (c) and $T = 600$ mK (b) were measured with the same parameters ($V_{AC} = 10 \, \mu V$) whereas the one at $T = 1.25$ K (a) was measured with an higher AC excitation amplitude ($V_{AC} = 30 \, \mu V$).

transition (see main text). In our point of view, the small Kondo temperatures obtained in other quantum dot systems prevented to observe those effects, even using a dilution refrigerator.

**TEMPERATURE DEPENDENCE OF THE ZERO-BIAS CONDUCTANCE**

The singlet-triplet transition in quantum dots was widely studied [15, 25, 26, 28, 29, 31]. In those cases, a clear maximum of conductance appeared when the singlet and the triplet states were driven through degeneracy by magnetic field or gate voltage. On Fig. S. 5, the zero bias conductance is presented for different temperatures as a function of gate voltage. At $T = 10.3$ K we cannot discriminate the singlet from the triplet. Lowering the temperature,
Fig. S. 5: Conductance at zero-bias versus gate voltage for temperature from 110 mK to 10.3 K.

conductance decreases at the singlet side whereas it increases at the triplet side, no peak appearing at the singlet to triplet transition.

One remarkable aspect of this measurement is the absence of an enhancement of the zero bias conductance at the singlet to triplet transition. The lack of such gate-induced Kondo effect points towards a predominant coupling of the C$_{60}$ QD to a single screening channel, leading to a strong proof of the observation of a quantum phase transition.

STATISTICS AND REPRODUCIBILITY OF THE RESULTS

Preparation of the single-molecule quantum dot studied in the article was realized by blow drying a dilute toluene solution of the C$_{60}$ molecule onto a gold nano-wire realized on an Al/Al$_2$O$_3$ back gate. Before blow drying the solution, the electrodes were cleaned with acetone, ethanol, isopropanol solution and oxygen plasma. As it is known that even
Fig. S. 6: Colour-scale map of the differential conductance $\partial I/\partial V$ as a function of bias voltage $V_b$ and gate voltage $V_g$ at 40 mK and zero magnetic field. 

- **a**, This single-molecule quantum dot exhibits an excitation of the order of 30 meV and a fine gate-tuning of the singlet to triplet energy difference inside the Coulomb diamond (dotted rectangle).
- **b**, This device clearly exhibits a large charging energy and a spin $S = 1/2$ and $S = 1$ Kondo effects.

If the electromigration procedure is well controlled, there is always a possibility of realizing a gold aggregate containing few atoms, we studied several junctions prepared within the same procedure with a toluene solution only. In our opinion, it is relevant to state here that an "interesting" device to investigate must show at least one order of magnitude change in the current characteristics as a function of the gate voltage for a 1 mV voltage bias, and a charging energy greater than 20 meV. Within these drastic restrictions, we tested 38 bared junction with a toluene solution and 51 with a dilute C$_{60}$ toluene solution. If 3 bared junction showed one order of magnitude changes in the current as a function of the gate voltage after electromigration, only 2 had a charging energy higher than 20 meV, and only 1 of those 2 exhibited a zero bias anomaly. These transport structures were also not very well defined. For junctions prepared with a diluted C$_{60}$ toluene solution, we measured 7 junctions out of
51 with one order of magnitude changes in the current as a function of gate voltage, and 6 of those 7 had a charging energy higher than 20 meV and exhibited zero bias anomalies.

We present in this section measurements on two different samples, that we performed in the same conditions as the device presented in the article. The first one presented in Fig.6.b exhibits a large charging energy, spin $S = \frac{1}{2}$ and $S = 1$ Kondo effects, and multiple excited states. We did not investigate further this measurement because we could not discriminate, unlike the device presented in the main paper, the different triplet states by applying a magnetic field. However, on the right side of the degeneracy point, the zero bias anomaly splitted at a magnetic field of the order of 1.9 T, while the zero bias anomaly on the left side splitted for a magnetic field of the order of 100 mT. The second measurement we present in Fig.6.a exhibits the same Kondo behavior than the single-molecule quantum dot presented in the article, and an excitation that may be related to the vibrational excitation energy of a C$_{60}$ single molecule connected to gold electrodes. We also clearly observe the singlet to triplet out of equilibrium Kondo effect, and a gate-tuning of the energy difference between the singlet and the triplet, similar to the single-molecule quantum dot of the article. However, we do not measure an underscreened Kondo effect. We assume that the Kondo temperature is too low, because of a weaker coupling to the electrodes, to measure this effect, or, in contrast with the device exhibiting the quantum phase transition, that we are in the 2-screening channel limit. This device, currently under investigation, exhibits other kind of excitations in the Coulomb blockade diamond, which are not, so far, well understood. But it is important to state here that some of the physics that enabled us to observe the quantum phase transition in the single-molecule quantum dot presented in the paper is reproducible, and that we never measured such behaviors in junctions prepared without a dilute C$_{60}$ toluene solution.

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