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

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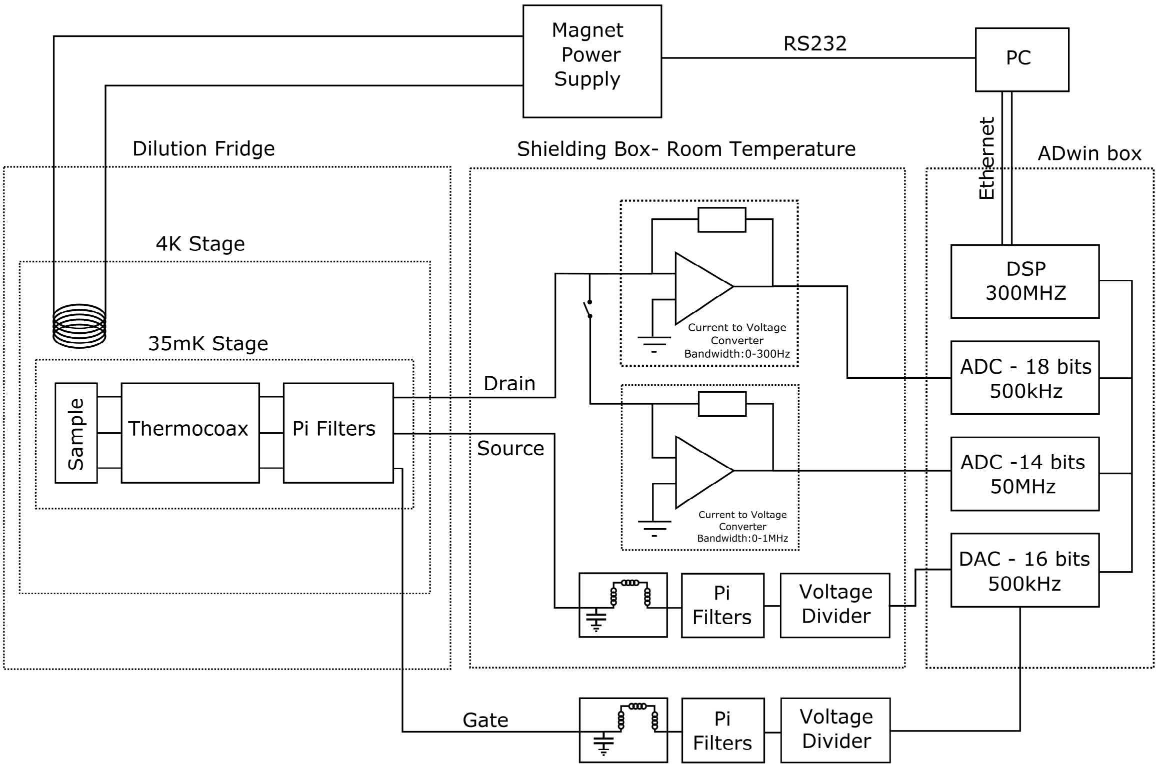

Fig. S. 1: **Simplified scheme of the experimental setup.**

I. EXPERIMENTAL SETUP

Sample preparation and details of the measurement procedure and system are described in the Methods section of the paper.

II. 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 [1, 2], carbon nanotube [3, 4], or single-molecule [5–7] quantum dots. In such strongly confined nanostructures, when the last electronic energy level is

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occupied by a single electron, the quantum dot behaves as a spin $S = 1/2$ magnetic impurity. In this case the conduction electrons in the leads are coupled antiferromagnetically to the magnetic impurity via second order tunnelling 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 [8, 9]. 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 $T \ll T_{\mathrm{K}}$. At $T = 260$ mK, we find $V_{\mathrm{b}}^{\mathrm{HWHM}} = 380$ μV, corresponding to $T_{\mathrm{K}} = 4.42$ 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 [10]. An empirical formula based on this calculation was found by Goldhaber-Gordon *et al.* [11] and is used to fit the experimental data, as shown in Fig. S. 2b, where we find $T_{\mathrm{K}} = 4.46$ K. An additional method is to use the magnetic field dependence of the conductance [12]. The Zeeman effect competes with the Kondo resonance so that a non-equilibrium Kondo peak appears roughly at $V_{\mathrm{b}} = g\mu_{\mathrm{B}}B$, as shown in Fig. S. 2c). This splitting is predicted to appear for $g\mu_{\mathrm{B}}B_{\mathrm{c}} = 0.5k_{\mathrm{B}}T_{\mathrm{K}}$ [10]. In Fig. S. 2d we linearly interpolate the position of these peaks and find $B_{\mathrm{c}} = 1.78$ T, which yields $T_{\mathrm{K}} = 4.78$ K. The value of T_{K} obtained with the three different methods are consistent and demonstrate a well defined T_{K}.

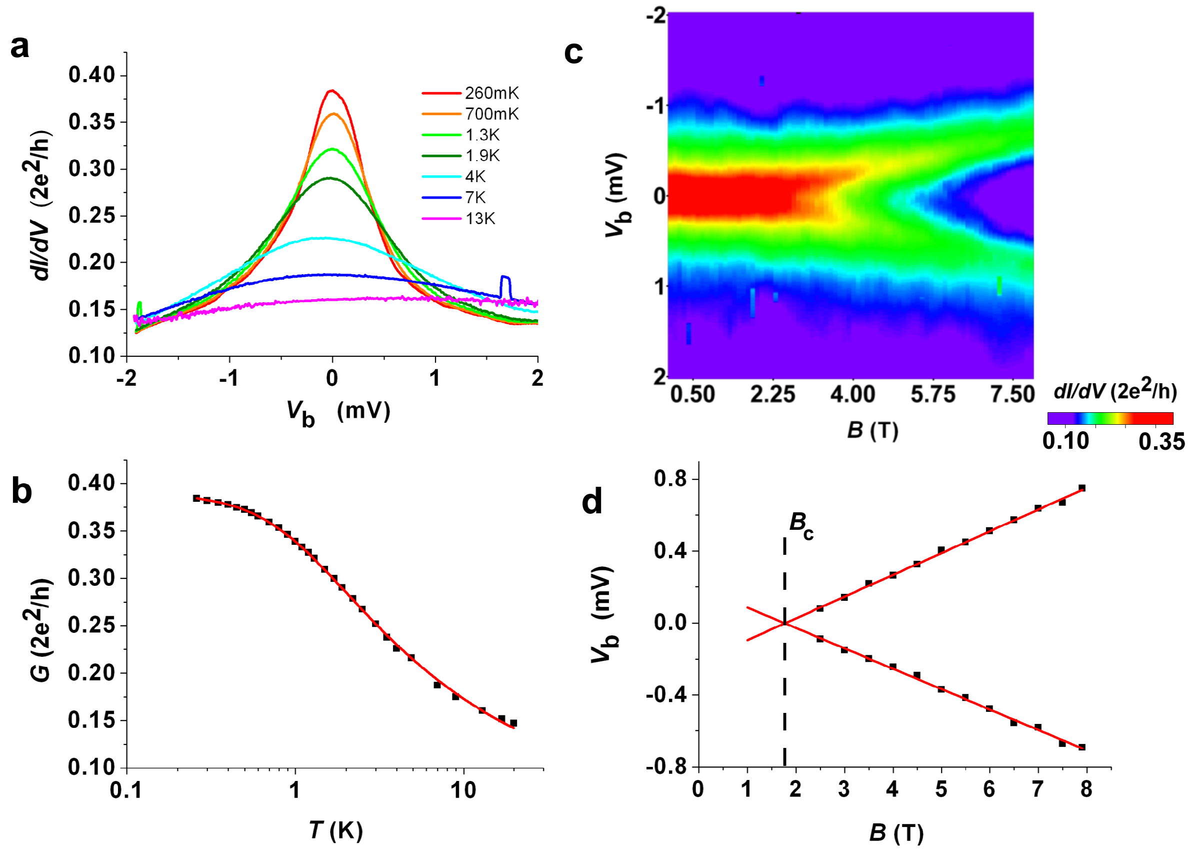

Fig. S. 2: **Temperature and magnetic study of fully-screened spin $S = 1/2$ Kondo effect.** **a,** Evolution of differential conductance versus bias voltage for several temperatures from 260 mK to 20 K. **b,** Temperature dependence of the conductance at V_b = 0 mV extracted from the **a** panel, with a fit to the empirical formula proposed by Goldhaber-Gordon *et al.* [11] which gives $T_\mathrm{K} = 4.46$ 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 $B_\mathrm{c} = 1.78$ T.

III. 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 [13], 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 cotunnelling via excited states. The main idea behind Kondo physics is the existence of a degeneracy, which is lifted by the conduction

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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 the energy difference between the two orbital levels δE and the strength of the ferromagnetic coupling J 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 [14]. 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 [3, 4, 15]. 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 [16], carbon nanotubes [3, 4, 17, 18] and even recently in an OPV5 molecule [19]. However, only the study reported by Paaske *et al.* [13] 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 cotunnelling. 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 cotunnelling 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 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,

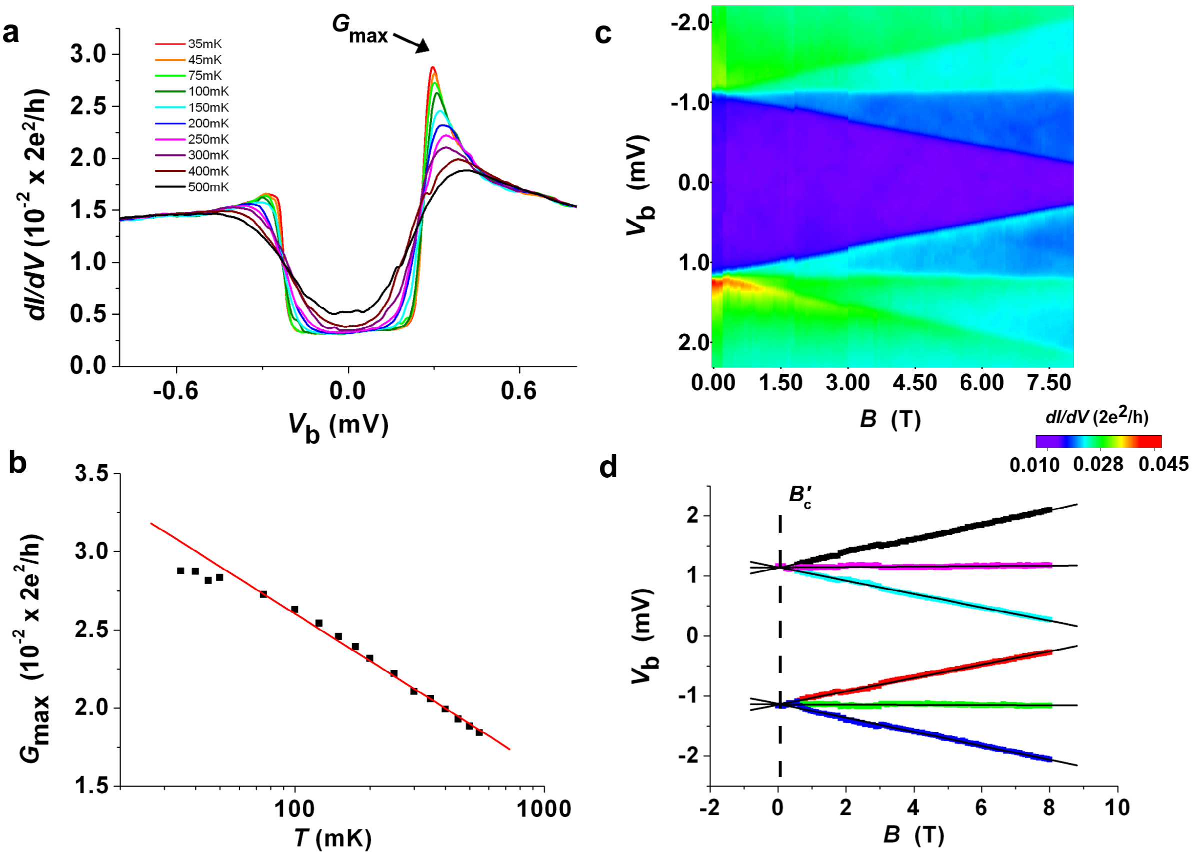

Fig. S. 3: **Non-equilibrium singlet-triplet Kondo effect on the singlet side. a,** Differential conductance versus bias voltage for temperature from 35 mK (black) to 500 mK (pink) at fixed $V_{\rm g} = 1.79$ V. **b,** Evolution of the "positive $V_{\rm b}$" peak height in a) with temperature on a logarithmic 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 $V_{\rm g} = 1.64$ 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 $B'_{\rm c} = 50$ mT.

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 II). 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 [10] for the spin $S = 1/2$ case, we estimate the Kondo temperature $T_{\rm K} = 130$ 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

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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 [13]).

IV. 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 behaviour 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 [5, 20]. The second crucial ingredient in our experiment was the development of the electromigration technique in a highly filtered dilution fridge, as discussed in section I, 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.* [21] or Quay *et al.* [18], which showed a featureless change of behaviour near the singlet-triplet crossing. On the contrary, our data 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 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.

V. TEMPERATURE DEPENDENCE OF THE ZERO-BIAS CONDUCTANCE

The singlet-triplet transition in quantum dots was widely studied [3, 14, 15, 17, 18, 21]. In those cases, a clear maximum of conductance appeared when the singlet and the triplet

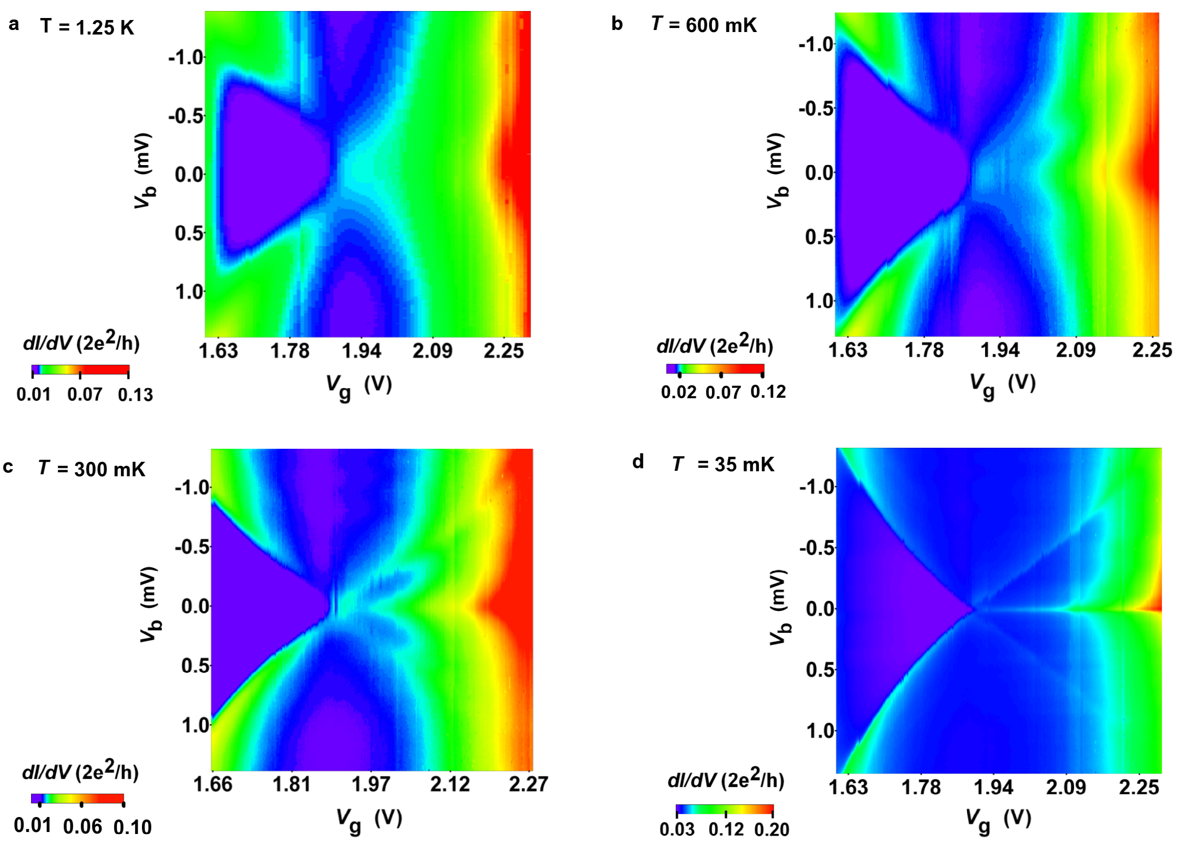

Fig. S. 4: **Differential conductance maps versus bias voltage and gate voltage.** The maps at $T = 35$ mK (**d**), $T = 300$ mK (**c**) and $T = 600$ mK (**b**) were measured with the same parameters ($V_{\rm AC} = 10\ \mu V$) whereas the one at $T = 1.25$ K (**a**) was measured with an higher AC excitation amplitude ($V_{\rm AC} = 30\ \mu$V).

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, 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.

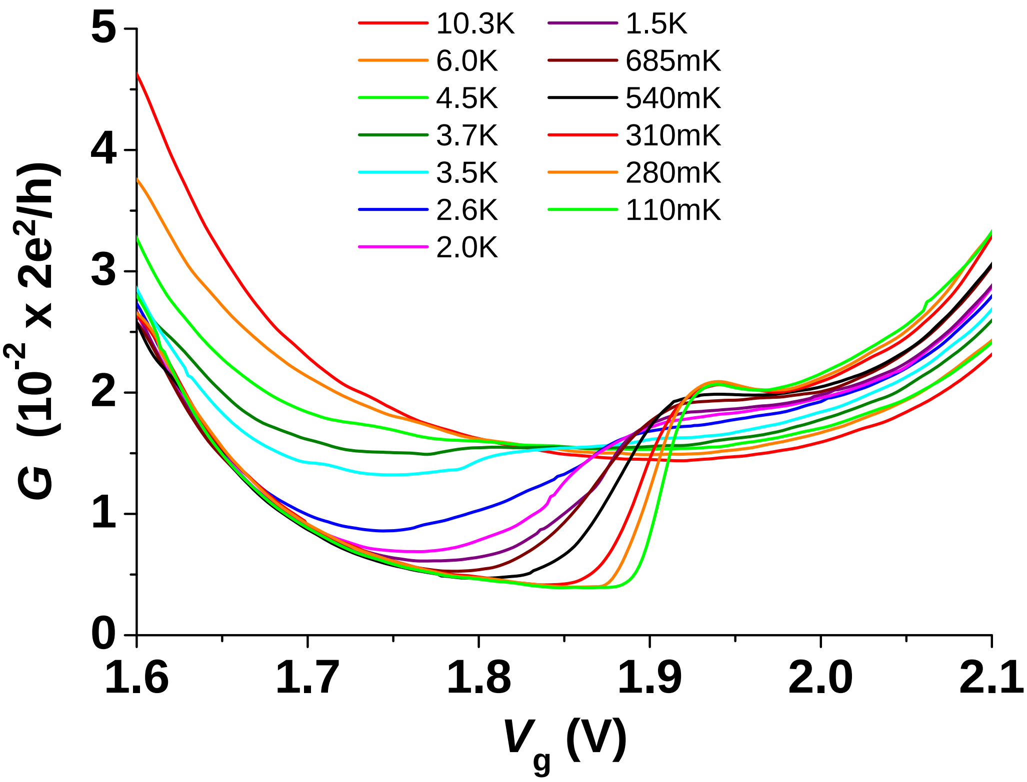

Fig. S. 5: **Conductance at zero-bias versus gate voltage for temperature from 110 mK to 10.3 K.**

VI. STATISTICS AND REPRODUCIBILITY OF THE RESULTS

Preparation of the single-molecule quantum dot presented in the letter was realized by blow drying a dilute toluene solution of the C_{60} molecule onto a gold nano-wire realized on an Al/Al_2O_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 if the electromigration procedure is well controlled, there is always a probability of realizing a few atoms gold aggregate transistor [22], 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: i) at least one order of magnitude change in the current characteristic as a function of the gate voltage for a 1 mV voltage bias; ii) 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

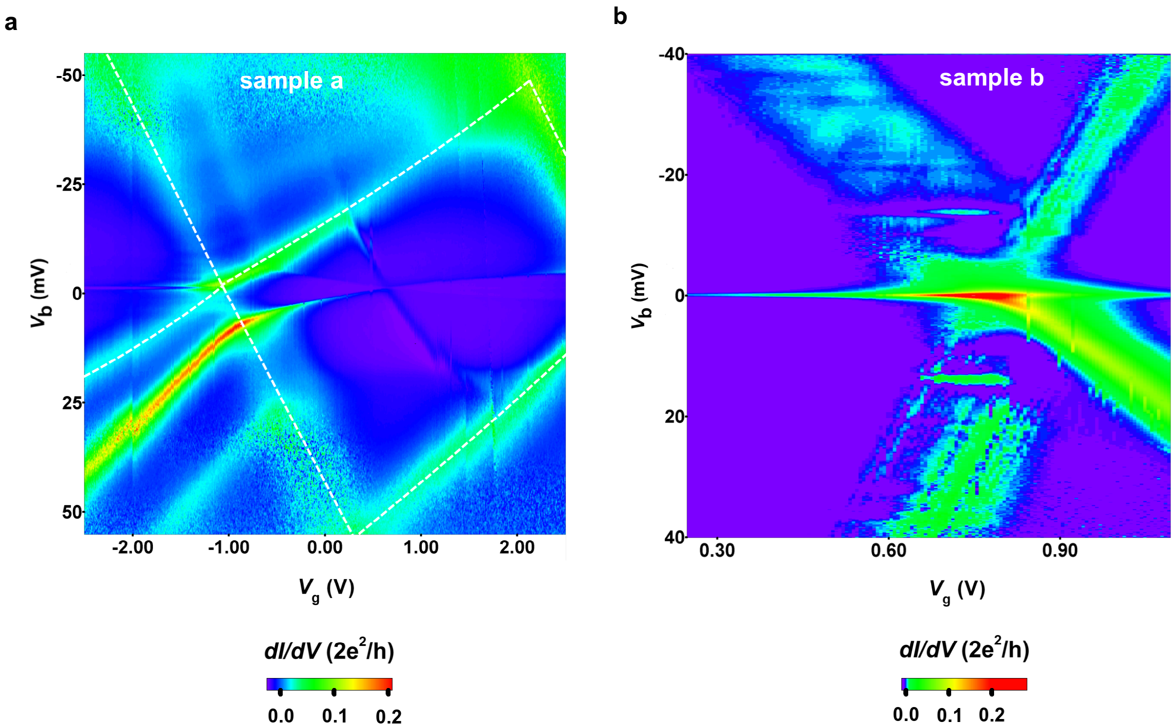

Fig. S. 6: **Colour-scale map of the differential conductance $\partial I/\partial V$ as a function of bias voltage V_b and gate voltage V_g at 40 mK and zero magnetic field. a,** This single-molecule quantum dot exhibits an excitation of the order of 30 meV and a fine gate-tuning of the singlet to triplet 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.

bared junction showed one order of magnitude changes in the current as a function of the gate voltage after the electromigration procedure, 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 dilute C_{60} toluene solution, we measured 7 junctions out of 51 with at least one order of magnitude change in the current as a function of gate voltage characteristic, and 6 of those 7 had a charging energy higher than 20 meV and exhibited zero bias anomaly.

In this section, we present measurements on two different samples, that we performed in the same conditions as the device presented in the letter. The first one presented in Fig.6.b exhibits a large charging energy, spin $S = 1/2$ 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 split at a magnetic field of the order of 1.9 T, while the zero bias anomaly on the left side split around 100 mT. The second measurement we present in Fig.6.a exhibits the same Kondo behaviour than the single-molecule quantum dot presented in the letter. An excitation that may be related to the vibrational excitation energy of a C_{60} single molecule connected to gold electrodes is clearly measured. We also observe the singlet to triplet out of equilibrium Kondo effect, and a gate-tuning of the energy difference between the singlet and the triplet, similarly to the single-molecule quantum dot studied in the letter. 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 to 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 behaviours in junctions prepared without a dilute C_{60} toluene solution.

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