

High-spin and magnetic anisotropy signatures in three-terminal transport through a single molecule

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ABSTRACT

We have studied three-terminal electron transport through an individual single-molecule magnet Fe₄. Several fingerprints of high spin and magnetic anisotropy have been observed: the Kondo effect in adjacent charge states in an intermediate coupling regime and zero-field splitting in the regime of a weaker coupling. We also observed spin transitions at energies close to the ones reported for bulk Fe₄ crystals. Finally, we have demonstrated electric-field control on the magnetic properties of a single molecule.

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1. Introduction

Magnetic materials are key components in today's information technology. Explosively growing amounts of data need to be stored in magnetic films on computer hard disks. This technological advancement is forcing researchers to direct their attention to the magnetic properties of nanoscale materials such as molecules, which may serve as single (quantum) bits [1]. Single-molecule magnets (SMMs) are a class of molecules characterized by a high spin and magnetic anisotropy that creates an energy barrier opposing spin reversal [2]. The magnetic properties of these compounds are extensively studied in bulk crystals and thin films: magnetic hysteresis and quantum tunneling of magnetization (QTM) have been observed [3,4], and the SMMs show long spin coherence and spin relaxation times [5]. The new field of molecular spintronics proposes the use of *individual* magnetic molecules incorporated into electric circuits [6]. Addressing individual molecules on a chip, however, remains extremely challenging and as a consequence only a few experiments have been described in the literature [7–11].

In this paper we report on electron transport measurements through an individual Fe₄ SMM wired between gold nanoelec-

trodes in a three-terminal geometry. The gate electrode allows to reversibly (dis)charge the molecule and study transport properties of oxidized and reduced charge states. Currently this is not possible with other techniques. Fe₄ molecules were chosen since it was shown that they retain their magnetic properties upon deposition on a gold surface [12]. The molecule consists of four iron(III) ions each having spin 5/2 coupled antiferromagnetically so that the total spin of the molecule $S=5$ (Fig. 1a). Two derivatives are studied: Fe₄Ph functionalized with phenyl rings [13] and Fe₄C₉SAC functionalized with 9-(acetylsulfanyl)nonyl chains [14].

The simplest model describing the magnetic properties of a SMM uses the spin Hamiltonian

$$\hat{H} = -D\hat{S}_z^2 + g\mu_B\vec{B} \cdot \hat{S}, \quad (1)$$

where the first term is the uniaxial magnetic anisotropy with the easy axis z . The second term is the Zeeman interaction of spin $\hat{S}$ with magnetic field $\vec{B}$, where g is the Landé factor and μ_B the Bohr magneton. The anisotropy breaks the rotational symmetry and the states forming each spin multiplet are split even at zero magnetic field (Fig. 1b). For Fe₄ in bulk crystals $D \cong 0.051$ – 0.056 meV, the anisotropy barrier $U = DS^2 \cong 1.3$ – 1.4 meV and the zero-field splitting (ZFS) between the lowest two-fold degenerate levels $|S_z = \pm 5\rangle$ and $|S_z = \pm 4\rangle$ is $\Delta = (2S-1)D \cong 0.46$ – 0.50 meV [13,14]. Importantly, model (1) predicts a non-linear dependence of excitation energies on the magnetic field if the angle between the easy axis

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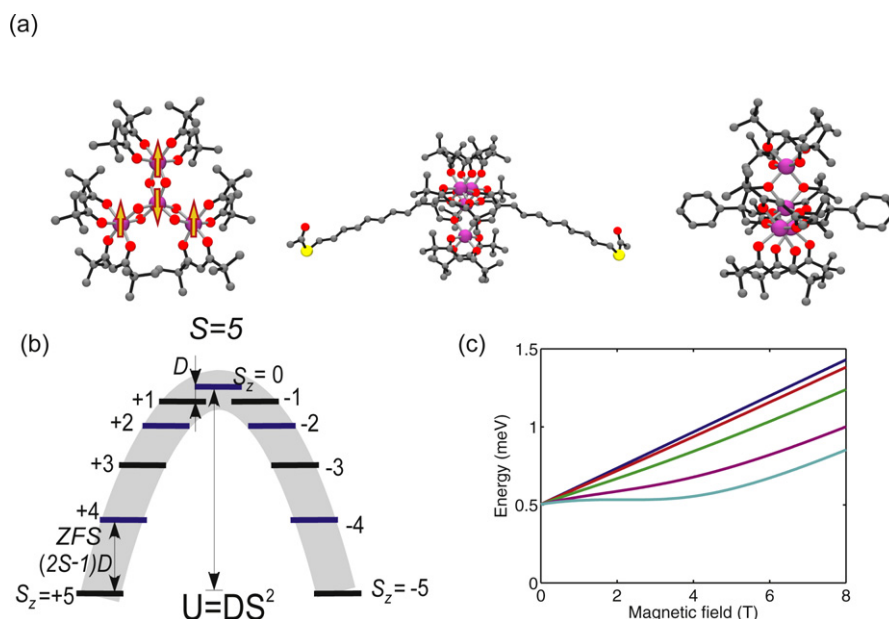


Fig. 1. (a) Structure of the Fe₄ molecules (color code: iron = purple, oxygen = red, carbon = grey, sulfur = yellow). Left: Magnetic core with four $S = 5/2$ iron(III) ions antiferromagnetically coupled to give a molecular spin $S = 5$. Center: Fe₄C₉ SAc derivative. Right: Fe₄Ph derivative. (b) Energy diagram of the ground spin multiplet at zero field. The $S_z \neq 0$ levels corresponding to different orientations of the spin vector along the easy axis of the molecule are doubly degenerate. The $S_z = +5$ and $S_z = -5$ states are separated by a parabolic anisotropy barrier U . (c) Magnetic field evolution of the ZFS excitation for different angles θ with the easy axis and the magnetic field (blue: $\theta = 0^\circ$, red: $\theta = 20^\circ$, green: $\theta = 40^\circ$, purple: $\theta = 60^\circ$, cyan: $\theta = 70^\circ$), calculated by diagonalization of the Hamiltonian (1) using the parameters of the bulk neutral state. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of the molecule and the magnetic field is substantial (Fig. 1c). This non-linearity is caused by the mixing of $|S_z\rangle$ states due to the presence of a transverse component of the field.

2. Sample fabrication

For the nanoelectrodes fabrication we use standard electron-beam lithography followed by electromigration. Four lithography steps are needed. The first step defines contact pads and alignment markers by evaporation of 50 nm of gold with 3 nm of titanium sticking layer on an oxidized silicon substrate. Secondly, we fabricate the gate electrode by evaporating 75 nm of aluminium. Subsequent oxidation in an O₂ chamber at a pressure of 50 mTorr forms a thin (2–4 nm) aluminium oxide layer. During the next step we evaporate a thin (12 nm) and narrow (100 nm) gold wire on top of the oxidized gate electrode. We do not use a sticking layer at this stage. The final step connects the gold wire to the contact pads with thick (110 nm) AuPd electrodes. Each sample typically consists of 32 devices with two shared gates and four shared sources (see Fig. 2b); a zoom-in on a completed device prior to electromigration is shown in Fig. 2c.

Molecule deposition is done by placing the samples into a homemade liquid cell, filled with a dilute (0.1–1 mM) toluene solution of molecules, which is embedded inside a 4He probe. To create single-molecule junctions we use electromigration of gold wires with an active feedback. During this process the voltage is increased above the electromigration threshold (of order 100 mV) while measuring the current through the device. As soon as there is a significant change (typically around 10%) in the resistance, the voltage is reduced to a starting value and the process is repeated until the wire resistance reaches ~ 5 k Ω . This scheme protects the devices from a sudden breaking and junctions with a desired resistance are formed with a reproducibility close to 100%.

Due to a high mobility of gold atoms the process of breaking continues at room temperature even without applied voltage [15]. We use this self-breaking as a final step in the nanogap preparation. When the resistances reach 1–1000 M Ω the sam-

ple space is subsequently evacuated and the devices are cooled down to 1.6–1.7 K. The entire electromigration and self-breaking process is performed in a liquid environment at a room temperature, assuring that the molecules are exposed to nanogaps between the electrodes already at the stage of the creation of the gaps, minimizing the risk of contamination. Furthermore, in contrast to having a self-assembled monolayer of molecules prior to electromigration, the molecules in our scheme are not subject to excessive local heating due to the high currents needed for electromigration to occur. Another important issue is that self-breaking avoids the formation of gold nanoparticles; transport through these nanoparticles can mimic transport through molecules. Based on the characterization of thousands of samples we do not find any evidence of gold nanoparticles when self-breaking is used.

A drawback of the electromigration technique is that one cannot control the junction geometry on the atomic scale, while it is known that even the smallest changes in the atomic positions can result in significant variations in the transport characteristics. In particular, the electronic coupling of the molecule to the leads Γ cannot be controlled. This parameter is of crucial importance as it determines the width of spectroscopic features and hence the resolution of measurements. Moreover, when the device is in the intermediate coupling regime ($\Gamma \sim \Delta, E_C$) a broad zero-bias Kondo resonance can result, masking low-energy spectroscopic features. However, as we will show, even in this regime information on the spin state of the molecule can be extracted.

3. Experimental results and discussion

We probe differential conductance dI/dV using a lock-in detection of the tunnel current I by adding a 100- to 500- μ V AC modulation at ~ 100 –300 Hz to the DC bias voltage V . Measurements are typically performed at 1.6–1.9 K and all experimental plots in this paper are recorded at this temperature. The gate voltage V_g can be changed from -3 to 3 V; beyond these limits gate leakage starts to set in. The typical gate coupling β for our

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