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Magnetic field dependent transport through a Mn₄ single-molecule magnetF. Haque,^{1,a)} M. Langhirt,¹ E. del Barco,¹ T. Taguchi,² and G. Christou²¹*Department of Physics, University of Central Florida, 4000 Central Florida Blvd., Orlando, Florida 32816, USA*²*Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA*

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We present a preliminary study of the single-electron transport response of a Mn₄ single-molecule magnet in which pyridyl-alkoxide groups have been added to electrically protect the magnetic core and to increase the stability of the molecule during the experiments. Three-terminal single-electron transistors with nanogapped gold electrodes formed by electromigration and a naturally oxidized aluminum backgate were used to perform experiments at temperatures down to 240 mK in the presence of arbitrarily oriented magnetic fields. Coulomb blockade and electronic excitations that curve with the magnetic field and present zero-field splitting represent evidence of magnetic anisotropy. Level anticrossings and large excitation slopes are associated with the behavior of molecular states with high-spin values ($S \sim 9$), as expected from Mn₄. © 2011 American Institute of Physics. [doi:10.1063/1.3560891]

The use of single-molecule magnets (SMM) in nanoscale spintronic devices is expected to be transformative in that their unique magnetic behavior would lead to novel characterization and technological tools, such as high-sensitivity local magnetic field sensors and ultrafast writing/reading memory logic units.^{1–5} The quantum properties of SMMs have been typically studied in experiments with macroscopic single crystals containing a large number of nearly identical and decoupled SMMs. Thus the magnetic response of the crystal tends to reflect the quantum properties associated with each individual SMM within the sample. Perhaps the most striking property of SMMs is the presence of steps in the magnetic hysteresis loops that are attributed to resonant quantum tunneling of the magnetization (QTM).⁶ This unique feature of SMMs is a consequence of the quantum superposition of high-spin states of the molecule and has led to the observation of a variety of fundamental phenomena, such as quantum (Berry-phase) interference (BPI) between equivalent QTM trajectories.^{7–9} Quantum interference in SMMs would lead to extremely sensitive magnetic sensors at the molecular level,^{1–5} which could be integrated in nanoscale spintronic devices. Novel features of QTM are expected to manifest themselves in other observables as well. In particular, the effects of QTM on electronic transport remain to be explored in depth both theoretically and experimentally.

Notable advances have occurred in the last few years after several groups obtained strong evidence of the preservation of functionalized SMMs deposited on surfaces.^{10,11} Despite the fact that these are interesting attempts to obtain isolated molecules, it is still a challenge to access the properties of an individual SMM within a film or substrate. An alternative approach to address the magnetic properties of individual SMMs is based on the use of single-electron transistors (SETs) to measure the electronic transport through individual molecules placed between nanogapped electrodes.

Along these lines, several groups have reported observations of electrical transport through a SMM-based SET.^{12–15} Special mention is deserved for the work of Heersche and co-workers,¹² who first reported Coulomb blockade and conduction excitations characteristic of a molecular SET in an individual Mn₁₂ SMM functionalized with thiol groups. Although all these results are very encouraging, they have failed to provide unambiguous evidence that transport occurred through individual SMMs preserving the key quantum properties found in their solid-state form (i.e., QTM, BPI, etc.). On the contrary, the data seem to indicate that Mn₁₂ molecules tend to change and lose these properties when deposited on surfaces.

Within this context, we present preliminary single-electron transport measurements performed down to 240 mK in the SMM [Mn₄(hmp)₆(CH₃CN)₂(H₂O)₂](ClO₄)₄ (where hmp stands for 2-hydroxymethylpyridine). This molecule forms part of a family of Mn₄ SMMs identified as particularly attractive for the proposed studies for several reasons: (i) they contain low Mn oxidation states (2Mn²⁺, 2Mn³⁺) and thus no Mn⁴⁺ that may be the main reason for the fragility (due to redox reactions) of the Mn₁₂ SMMs initially employed by many groups for SET and other studies on surfaces; (ii) they contain pyridyl-alkoxide organic groups that both chelate (attach to Mn atoms at multiple positions) and bridge multiple Mn atoms with one or more alkoxide O atoms, thus making these Mn₄ molecules more structurally robust and resistant to degradation than Mn₁₂; and (iii) the organic groups can be easily varied, and additional derivatives can be targeted, providing a family of related Mn₄ SMMs for comparative subsequent studies.

Three-terminal SET devices were used to measure the electrical transport through individual Mn₄ SMMs at low temperatures ($T = 235$ mK). In a molecular SET, the electric current flows between the source and drain electrodes through a sequential tunneling process whenever a molecular electronic level lies between the Fermi energies of the leads. For small bias voltages (V_{bias}) no current flows though the device

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because the excited molecular levels are not available to accept conduction electrons. This regime is known as Coulomb blockade (CB). As the bias voltage is further increased, excited states open new conduction channels through the device. The position of these current steps can be tuned by a gate electrode potential V_{gate} . This technique allows for the determination of the level structure of an individual molecule and thus constitutes a powerful spectroscopic technique to study the energy landscape of isolated SMMs. In our case, SET devices are obtained by low temperature electromigration breaking of gold nanowires, with a 1–2 nm wide gap separating the source and drain electrodes of the transistor. Naturally oxidized aluminum, to form a 1–2 nm Al_2O_3 insulation top layer, was used as a gate. The Mn_4 SMMs were deposited from solution onto chips with multiple three-terminal SET devices. The deposition process (i.e., solution molarity and deposition time) was previously optimized to attain a uniform coverage of the device with a monolayer of SMMs.

Figure 1(a) shows the dependence of the electrical current (I) through a single molecule as a function of the bias voltage (V_{bias}) for different gate voltages (V_{gate}). Steps in the I - V curves correspond to transitions between the transistor electrodes through an accessible charge state of the molecule. At $V_{\text{gate}} = 0$ (black line), a large bias voltage ($V_{\text{bias}} \sim 80$ meV) needs to be applied in order to allow current to flow through the molecule. This corresponds to the charging energy (i.e., redox potential) necessary to add/subtract one electron into/from the molecule. Below this energy, the current is sup-

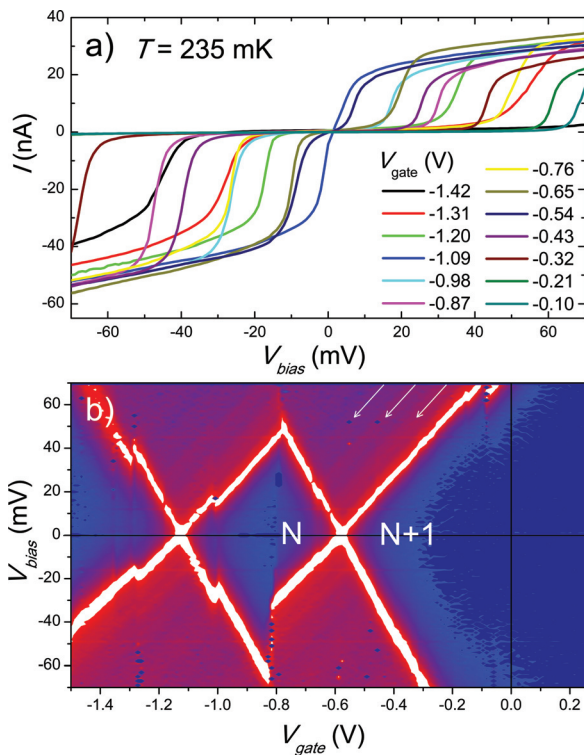


FIG. 1. (Color online) (a) Electrical current through a Mn_4 SMM as a function of the bias voltage, measured at different gate voltages at a temperature of 235 mK. (b) Differential conductance (logarithmic scale) of the Mn_4 -SET device as a function of the bias and gate voltages. The two observed charge states correspond to a conformational electrostatic change of the molecule relative to the gate. Transport excitations (white arrows) associated with excited spin states are observed outside the Coulomb-blockade areas (dark).

pressed (CB regime). As the gate voltage is increased, the current step moves to lower bias values. This can be clearly observed in Fig. 1(b), where the differential conductance (dI/dV) of the device is given as a function of V_{bias} and V_{gate} , showing the characteristic electrical excitation crossings separating CB areas (dark) with N and $N+1$ electrons in the molecule. The appearance of two charge crossings in the differential conductance, with a clear switch (excitations do not cross) between one and the other ($V_{\text{gate}} = -0.82$ V), is indicative of a conformational switching of the molecule between two different states, separated by an energy of ~ 49 meV. We think that these two states may be associated with different ground state electrostatic configurations of a single molecule which affect the coupling to the electrodes, making the crossing centers to be shifted along gate voltage. Note that all the excitations have the same slope (same coupling between molecule and electrode leads), which is indicative of transport through a single molecule, exclusively. In other words, the two zero-bias crossings belong to the same transition between the same two charge states (N and $N+1$) occurring at different gate voltages because the molecule “moves.”

Note that faint excitations, parallel to the main ones, are also observed (white arrows). Their faintness is indicative of short-lived states that the conduction electrons visit when transiting through the molecule. These weak excitations outside the CB areas move with an applied magnetic field, as can be seen in Fig. 2, which shows the magnetic field behavior of the data taken at a fixed gate voltage, $V_{\text{gate}} = -0.4$ V, for two arbitrary but orthogonal orientations of the field (i.e., along z and x axes). In this measurement it is clear how some of these excitations bend with the magnetic field. Solid lines highlight the electrical excitations to help identify their behavior with the applied magnetic field. The curvature of the excitations, and their distinct behavior for different orientations of the

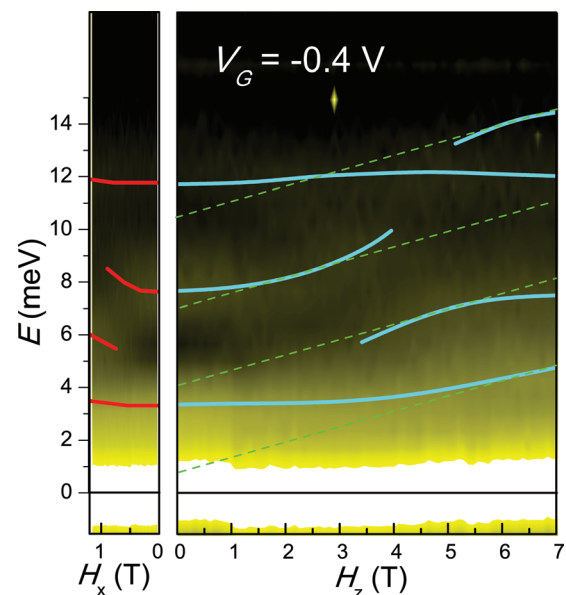


FIG. 2. (Color online) Behavior of the excited transport excitations ($V_{\text{gate}} = -0.4$ V) as a function of external magnetic fields applied at orthogonal directions, x and z axes (arbitrarily chosen). The continuous lines highlight the motion of the excitations with the field. The thin dashed lines represent slopes that would be generated by transitions involving a net change of spin equal to 9.

magnetic field, plus the fact of having them not going down to zero energy for zero magnetic field ($E_0 > 0$, measured from the main excitation), indicates the presence of magnetic anisotropy (zero-field splitting) in the molecule. In addition, the high magnetic field slope of the excitations (dashed lines) points toward transitions between states with very different spin values ($|\Delta S| \sim 9$). Also, anticrossings between different excitations may be indicative of quantum superpositions of the molecular spin states, which are observed in transport measurements through an individual SMM.

One possibility is that the conduction electron jumps into one of the manganese ions, most likely a Mn^{3+} (converting it into a Mn^{2+}), when entering the molecule, thus directly changing the molecular spin value. For the purpose of our discussion we can assume that the neutral state of the molecule (with N electrons) possesses spin $S = 9$ (as when the Mn_4 molecule is in the crystal), and the charged state corresponds to $S = 19/2$ ($9 + 1/2$), as depicted in Fig. 3. Assuming this, we can get a simple picture using a giant-spin description and the parameters given in Lecren *et al.*,¹⁶ where the magnetization behavior of Mn_4 in solid state form was first reported. The results according to this interpretation are pictured in Fig. 3. Here, 3 meV (the energy of the lowest transport excitation in Fig. 2) is similar to the separation between the ground projection state $m = 19/2$ and the highest projection state $m = 1/2$ of the spin multiplet $S = 19/2$ (double-headed arrow in Fig. 3), as obtained from diagonalization of the spin Hamiltonian with the parameters given in Ref. 16. Therefore, a possibility is that the main observed excitation corresponds to a transition from $m = 9$ (state N , with $S_N = 9$) to $m = 19/2$ (state $N+1$, with spin $S_{N+1} = 19/2$) (arrow 1 in Fig. 3), and then the first excited excitation (the one at 3 meV) would correspond to transitions from $m = 9$ (state N , with $S_N = 9$) to $m = 1/2$ (state $N+1$, with spin $S_{N+1} = 19/2$) (arrow 2 in Fig. 3). This would explain the observed separation and the slope with the magnetic field. However, things are more complicated in this molecule, which makes the data difficult to be explained quantitatively. Actually, according to Lecren *et al.*¹⁶ the weak exchange coupling constant between the Mn ions makes the excited state $S_N = 8$ to be only 5.2 K (0.44 meV) away from $S_N = 9$. This means that the ground projection state $m = 8$ (of $S_N = 8$) is about the

same distance from the ground projection state $m = 9$ (of $S_N = 9$) than the first excited state $m = 8$ (of $S_N = 9$), as pictured in Fig. 3. In addition, reduction of Mn^{3+} into Mn^{2+} may have important consequences for the molecular zero-field splitting (Mn^{2+} is known to be very isotropic), altering significantly the anisotropy barrier and consequently the separations between spin projections of the charged state ($N+1$) with respect to those of the uncharged molecule (N).

In addition, one needs to consider the excited spin states (not shown in the figure for clarity). Note that there are other observed excitations at zero field (~ 7.5 , ~ 12 meV, and an extra one at ~ 6 meV when a 0.6 T field is applied along the x axis). They also move with magnetic field and show anticrossings, and will likely correspond to crossings between spin levels of the molecule expected to occur within this field range. However, it is difficult to tell which ones would correspond to each transition, due to the uncertainty in the molecular orientation.

An alternative possibility is that the electron does not change directly the spin of the molecule but is accepted by a nonmagnetic center (i.e., one of the aromatic rings). Actually, this may be the most likely possibility in this compound since Mn_4 SMMs have not been established as capable of easily changing their Mn oxidation state, unlike other SMMs (i.e., Mn_{12}). It is then likely that the transport of the electron onto and off the molecule may involve a combination of Mn and the π orbitals of the aromatic ligands, since aromatic organics are known to be “good” conductors. Given this situation, the spin of the conduction electron is expected to couple antiferromagnetically to the molecular spin ($S = 9$). However, the coupling will be much weaker in this case (almost negligible splitting of each molecular spin projection level), making the conduction electron act basically as a proximity probe of the molecule’s magnetic behavior. This would naturally explain the high magnetic field slopes ($S \sim 9$) of the electrical excitations. In addition, the magnetic core will remain unaltered (no reduction of any manganese), maintaining the anisotropic characteristics of the uncharged molecule. However, the uncertainty in the molecular orientation and the presence of excited spin states in Mn_4 prevents a quantitative explanation of the observed phenomena also in this case.

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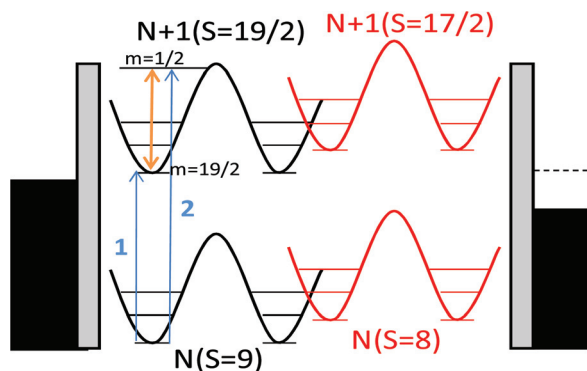


FIG. 3. (Color online) Representation of the possible two lowest lying spin states corresponding to the neutral (N) and charged ($N+1$) configurations of the Mn_4 SMM when placed in the SET device.

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