Probing Transverse Magnetic Anisotropy by Electronic Transport through a Single-Molecule Magnet

M. Misiorny, 1, 2, * E. Burzurí, 3, † R. Gaudenzi, 3 K. Park, 4 M. Leijnse, 5 M. R. Wegewijs, 1, 6 J. Paaske, 7 A. Cornia, 8 and H. S. J. van der Zant 3

1 Peter Grünberg Institut & JARA, Forschungszentrum Jülich, 52425 Jülich, Germany
2 Faculty of Physics, Adam Mickiewicz University, 61-614 Poznań, Poland
3 Kavli Institute of Nanoscience, Delft University of Technology, 2600 GA, Delft, The Netherlands
4 Department of Physics, Virginia Tech, Blacksburg, Virginia 24061, USA
5 Solid State Physics and Nanometer Structure Consortium (mnC@Lu), Lund University, Box 118, S-22100, Sweden
6 Institute for Theory of Statistical Physics, RWTH Aachen, 52056 Aachen, Germany
7 Center for Quantum Devices, Niels Bohr Institute, University of Copenhagen, 2100 Copenhagen, Denmark
8 Department of Chemical and Geological Sciences and INSTM, University of Modena and Reggio Emilia, via G. Campi 183, I-41125 Modena, Italy

(Dated: July 22, 2014)

By means of electronic transport, we study the transverse magnetic anisotropy of an individual Fe4 single-molecule magnet (SMM) embedded in a three-terminal junction. In particular, we determine in situ the transverse anisotropy of the molecule from the pronounced intensity modulations of the linear conductance, which are observed as a function of applied magnetic field. The proposed technique works at temperatures exceeding the energy scale of the tunnel splittings of the SMM. We deduce that the transverse anisotropy for a single Fe4 molecule captured in a junction is substantially larger than the bulk value.

Single-molecule magnets (SMMs) [1] have been proposed as candidates for applications in molecular spintronics [2–7]. They owe this to their large molecular spin (S > 1/2) together with their strong magnetic anisotropy, which results in nontrivial spin-dynamics. Especially enticing is the prospect of using an individual SMM as a base component of a spintronic circuit which would be capable of storing [8] or processing [7, 9–11] classical and quantum information. In general, the essential prerequisite for this is a magnetic bistability which in nanomagnets stems from the dominant uniaxial magnetic anisotropy, given by a parameter D. This tends to fix the spin along an axis determined by the molecular structure, without favoring any specific direction along this axis. In consequence, an energy barrier DS2 protects the molecule’s spin against reversal between the two opposing, energetically degenerate orientations. From this point of view, detection of the additional transverse magnetic anisotropy, characterized by the parameter E in the Hamiltonian \( \hat{H} = -DS^2 + E(S_x^2 - S_y^2) \), is crucially important. Such transverse anisotropy can impair the bistability by opening under-barrier quantum tunneling channels for spin reversal [1, 12, 13]. These quantum tunneling processes are also of fundamental interest since the spin-dynamics displays pronounced geometric or Berry-phase effects [14–19].

Hitherto, most techniques aiming to extract the transverse anisotropy parameter E are based on the detection of the tunnel splittings it induces, which display a characteristic magnetic field dependence [1, 12]. The major challenge for all such approaches is that these splittings are complicated functions of E, and even more, the splitting for high-spin states and low magnetic fields are smaller than the parameter E itself by several orders of magnitude. Using Landau-Zener spectroscopy the tunnel splittings have been accurately determined in bulk Fe4 by measuring their pronounced Berry-phase oscillations [14]. Also in bulk crystals and solutions of SMMs the parameter E has been established by different methods, such as high-frequency electron paramagnetic resonance [20, 21] and inelastic neutron scattering [22]. These methods, however, probe large assemblies of molecules, and thus are not designed for investigating the magnetic properties of an individual SMM. As a result, little is known about the transverse anisotropy of individual SMMs in spintronic devices.

In this Letter we propose an approach for extracting the parameter E of a single molecule by employing electronic transport measurements. We study a Fe4 SMM [23] captured in a gateable junction—a geometry close to envisaged device structures—which is a unique tool for addressing the spin in different redox states of a molecule [5]. We show that, as a consequence of the mixing of the spin eigenstates of the SMM, the transverse anisotropy significantly manifests itself in transport. In particular, we predict and experimentally observe characteristic variations of the Coulomb peak amplitude with the magnetic field from which the parameter E can be estimated. Importantly, the method proposed here works at temperatures and electron tunnel broadenings \( \Gamma \) exceeding E by many orders of magnitude, while E in its turn much exceeds the tunnel splittings.

A scheme of a three-terminal SMM junction is shown in Fig. 1(a). An SMM bridges the source and drain gold
electrodes. An underlying aluminium electrode separated by a few nanometers of aluminium oxide allows for electrical gating of the molecule and, thus, accessing different redox states [23]. The chip containing the junctions is mounted on a piezo-driven rotator that enables us to change in situ the orientation between the external magnetic field $B$ and the magnetic anisotropy axes of the molecule, which is characterized by angles $\theta$ and $\phi$ as illustrated in Fig. 1(b). All the measurements are performed at $T = 1.8$ K.

The differential conductance plotted in Fig. 1(c) shows the standard signatures of sequential electron tunneling (SET) through a molecule with two competing charge states tuned by a gate voltage [24]. Strong high-conductance resonance lines separate adjacent charge-stable Coulomb blockade (CB) regions, labeled $N$ and $N + 1$, from the SET regions where transport is possible. Importantly, several fingerprint features of the stable Fe$_4$ SMM can be identified: (i) high charging energies expected for an individual molecule; (ii) a strong SET excitation at approximately 4.8 meV [5], specific to Fe$_4$ as it corresponds to the predicted transition energy between the ground ($S_N = 5$) and the first-excited ($S_N = 4$) spin multiplets for the neutral molecule [20]; (iii) split Kondo zero-bias anomalies in Coulomb blockade regimes of subsequent charge states, which show the zero-field splitting (ZFS) at the values expected for the Fe$_4$ SMM [5, 25]; (iv) a non-linear shift of the degeneracy peak in the presence of magnetic field as described by gate-voltage spectroscopy [23, 26]. These features also indicate that the molecule is in an intermediate coupling regime with the electrodes. An upper-limit for this electronic coupling is estimated to be $\Gamma = 1.5$ meV obtained from the full width at half maximum of the Coulomb peak [23].

In a magnetic field the position of the crossing (degeneracy) point of the Coulomb edges at zero bias, the Coulomb peak (CP), depends both on the magnitude and the orientation of an external magnetic field $B$ [26]. In short, the CP marks the transition between the ground states of two spin multiplets, with spin values $S_N$ and $S_{N+1}$, for the two neighboring charge states. The energy difference between these states is then a function of $B$, and in particular, it translates into a shift of the linear response degeneracy point in $V_g$, as shown in Fig. 1(d). From such a shift one can infer that the ground spin-multiplets of the two charge states evolve differently in the applied field; therefore, the shift provides information about the magnetic properties of the system. For example, in simple quantum dots the shift corresponds just to the linear Zeeman effect which is isotropic [27]. On the other hand, for magnetically anisotropic molecules, like the SMMs discussed here, not only does the CP shift depend on the relative sample-field orientation, allowing us to extract the value of the angle $\theta$, but it also provides information about the uniaxial magnetic anisotropy ($D$) [26]. However, the gate-voltage position of the peak, determined by the low-energy spectrum, is insensitive to the small tunnel splitting corrections induced by the transverse magnetic anisotropy. Below we show that information about the transverse magnetic anisotropy ($E$) can instead be inferred from a nonmonotonic dependence of the peak amplitude $G_{\text{max}}$, such as in Fig. 1(d), which relies on transition probabilities between different spin states.

In Fig. 2(a) the amplitude $G_{\text{max}}$ of the Coulomb peak, normalized to its value at $B = 0$, is plotted as function of $B$ for two different samples. For both samples, the gate-voltage analysis of the peak position allows us to conclude that the magnetic field lies in the hard plane ($\theta \approx 90^\circ$) [23]. Interestingly, $G_{\text{max}}(B)$ for the two samples exhibits a significantly different behavior. If only uniaxial magnetic anisotropy was present ($E = 0$), the transport properties of the molecule would be left unaffected upon rotation of the field in the hard plane. On the contrary, for $E \neq 0$ this rotational symmetry is broken. The dissimilar behavior of the amplitude $G_{\text{max}}$ as observed in Fig. 2(a) is therefore attributed to different values of the angle $\phi$ in the presence of a non-zero $E$. Although the values of $E$ for bulk samples/monolayers of SMMs are typically small (for Fe$_4$ $E/D \lesssim 0.07$ [21, 28]), the linear conductance through a molecule appears to
 Magnetic field lies in the hard plane ($\theta = 90^\circ$). (b) Analogous to (a) for a single sample, except that now $\theta$ is varied and $\phi$ is unknown. **Bottom panels:** Theoretical predictions for evolution of the Coulomb peak height with magnetic field $B$ kept in the hard plane: (c) for indicated values of $E/D$ and $\phi = 0^\circ$, whereas in (d) for several angles $\phi$ and the fixed value of $E/D$ estimated from (a). Bold dashed lines represent the case of $E/D = 0$ for $\phi = 0^\circ$ (c) and $\phi = 90^\circ$ (d). Noteworthy is the shape of $G_{\text{max}}$ for $E/D = 0$ is independent of $\phi$ due to the rotational symmetry around the molecule’s easy axis.

be measurably influenced by it. A similar change in the field-evolution of $G_{\text{max}}$ is also observed in a single sample C, shown in Fig. 2(b), by rotating the sample holder relative to the magnetic field.

In order to understand how the transverse magnetic anisotropy could qualitatively affect the linear conductance through an SMM (i.e., the CP amplitude), while hardly influencing its gate-voltage position, we use a minimal molecular quantum-dot model based on two giant-spin Hamiltonians [1], $\hat{H}_{\text{SMM}} = \sum_{n=N, N+1} [\hat{\mathcal{H}}_n + \hat{\mathcal{H}}_n^2]$, one for each charge state. Here, $\hat{\mathcal{H}}_n$ accounts for the magnetic anisotropy of the SMM in the $n$th charge state,

$$\hat{\mathcal{H}}_n = -D_n (\hat{S}_n^z)^2 + E_n \left[ (\hat{S}_n^x)^2 - (\hat{S}_n^y)^2 \right],$$

with the first/second term representing the uniaxial/transverse magnetic anisotropy, and $\hat{\mathcal{H}}_n^2 = g_{1B} B \cdot \hat{S}_n$ is the Zeeman term ($g \approx 2$). We combine this with a master equation description of the SET transport to nonmagnetic electrodes with tunnel coupling $\Gamma$ [16, 23, 29, 30]. The appearance of a clear CP in the experiment restricts $S_{N+1} = S_N \pm 1/2$ (otherwise spin-blockade would be seen) [5]. For the Fe$_4$ SMM we can estimate $S_N = 5$ and $D_N \equiv D \approx 56 \mu\text{eV}$ for the neutral state [23, 26], whereas from the CP position dependence for samples A and B we obtain $S_{N+1} = 9/2$ and $D_{N+1} \approx 1.2D = 68 \mu\text{eV}$ with approximately collinear easy axes for both charge states, all in agreement with previous measurements [23, 26]. We assume that upon charging only the overall energy scale of the magnetic anisotropy changes, i.e., $E_N/D_N \approx E_{N+1}/D_{N+1}$, leaving just a single parameter $E_N = E$ for the transverse anisotropy.

In Fig. 2(c) we plot the calculated CP amplitude $G_{\text{max}}$ for $\theta = 90^\circ$ and $\phi = 0^\circ$ as a function of the applied field $B$. Surprisingly, the calculations reveal that a non-zero value of $E$ significantly influences the current through the molecule in contrast to the CP voltage position that relies on spectroscopic information [23]. By adjusting the parameter $E/D$, qualitative agreement with the measured amplitude variation is obtained for sample A when $E/D \approx 0.15 - 0.2$. The dissimilar behavior of $G_{\text{max}}$ between samples A and B is then qualitatively reproduced when assuming strongly differing values of the angle $\phi$ as shown in Fig. 2(d). From the shape of the curves we estimate the value of $\phi$ to be $\phi A \approx 0^\circ$ for sample A and $\phi_B \approx 90^\circ$ for sample B. Note that the minimum of $G_{\text{max}}$ for $\phi = 90^\circ$ appears in Fig. 2(d) at a somewhat larger $B$ field value than for sample B which signifies larger $E/D$ [23]. Therefore, combining the information from Figs. 2(c)-(d), the CP amplitude could be used to estimate the values of $E$ and $\phi$. The obtained rough estimate $E/D \approx 0.17$ is larger than the values reported for bulk samples [28], as also suggested by XMCD experiments on Fe$_4$ monolayers deposited on gold [21].

To gain deeper insight into the mechanism leading to a modulation of $G_{\text{max}}$ we analyze in Fig. 3(a) how the calculated $B$-traces of the CP amplitude evolve with temperature. The appearance of a maximum at around $B = 3.25 \text{ T}$ (marked by the vertical dashed line) and its enhancement with increasing temperature suggests that this feature is build up from contributions of many excited states of the SMM. This is indeed confirmed by inspection of the evolution of the occupation probabilities shown in Fig. 3(b) for the experimental temperature $T = 1.8 \text{ K}$. To obtain this figure we first find the eigenstates of $\hat{\mathcal{H}}_n$, given by Eq. (1). For $n = N, N+1$ we obtain two sets of eigenspectra, $\{e_k^N\}$ and $\{e_k^{N+1}\}$. Here, $k$ and $k'$ index the states in order of increasing energy, starting from $k' = 0$ ($k = 0$) for the neutral (charged) ground state. Using these energies and states, we calculate the probabilities from the master equation. One should note that the energies (not shown) and occupation probabilities of corresponding states ($k = k'$) for different charge are very similar. From Fig. 3(b), however, it is not clear which of the maxima of the probabilities is responsible for the maximum of the $G_{\text{max}}(B)$ curves, indicated by the vertical dashed line.

Instead, to understand the $G_{\text{max}}(B)$ dependence in Fig. 3(a) one has to consider the transition energies
2.8

Transition energies (meV)
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
1
99.8
99.6
99.4
99.2
99
100
100.2
100.4
-0.6
-0.4
-0.2
0
0.2
0.4
0.6
T = 2.4 K
T = 1.8 K
\( \varepsilon_{N+1}^k - \varepsilon_N^k \) between levels of different charge states. This is demonstrated in Fig. 3(c), where the horizontal dashed lines represent the available thermal energy. The transition energies fall into three generic groups: (i) low-energy transitions \( (k = k' \text{- green lines}) \); (ii) transitions of low energy for small \( B \) but high energy for large \( B \) \( (k,k' = 0, 1 \text{ or } k,k' = 2, 3 \text{- orange lines}) \); (iii) high-energy transition (remaining \( k \) and \( k' \) pairs – blue lines). Importantly, the temperatures used in Fig. 3(a) lie just below the group of transition-energy curves exhibiting a minimum at finite magnetic fields roughly between 2-4 T (blue curves in Fig. 3(c)). As the magnetic field is augmented from zero, these curves thus initially approach the thermal energy (horizontal dashed lines) before moving away at higher fields towards their high-field asymptotes. This leads to an enhancement of \( G_{\text{max}} \) for \( B \gtrless 3.25 \) T, followed by a steady decrease, i.e., the characteristic non-monotonic behavior experimentally observed in Fig. 2(a). We emphasize that the above mechanism does not constitute a purely spectroscopic method: the current and probabilities depend on both the energies and quantum states, which determine the tunnel rates. The importance of including many excited states in the calculation is quantified in Fig. 3(d), where we show how the non-monotonic behavior can be strongly overestimated when including too few excited states [23].

Finally, worth of note is the larger-than-predicted modulation of the CP amplitude observed in the experiments. We briefly comment on the verifications to rule out some other contributions that could lead to such an amplification. First, the master equation analysis was constrained to a weak tunnel-coupling \( \Gamma \) as compared to temperature. We verified that higher-order tunnel processes that lead to broadening and inelastic tunneling do not increase the scale of the modulation of the CP height. For this we employed a perturbative approach including next-to-leading tunneling processes [31] and non-perturbative numerical renormalization group (NRG) method [32–34]. Second, we assumed symmetric tunnel-coupling of the SMM to both electrodes with the same energy \( \Gamma \). One can show that a junction asymmetry gives rise to an overall constant factor suppressing the conductance \( G_{\text{max}} \). Thus, this cannot change its field dependence. Third, taking into account higher-order magnetic anisotropy terms in the SMM model, Eq. (1), is also not likely to affect the magnitude of the modulation. We checked, for instance, the effect of the 4th order transverse anisotropy of the form \( C_n[\hat{S}_n]^4 - (\hat{S}_y)^4] \), for a range of values of the parameter \( C_{N/N+1} \) for which this term competes with the 2nd order transverse term. We thus conclude that the intensity of the modulation may rely on some intrinsic amplification mechanism not captured by our model, i.e., going beyond the giant-spin model [19, 35], when considering a single electron interacting with the molecule.

In conclusion, we have proposed a new method of probing the transverse magnetic anisotropy of an individual SMM embedded in a three-terminal device. It exploits the information contained in the spin states of the molecule through the analysis of the magnetic field evolution of the linear conductance amplitude \( G_{\text{max}} \). We found that the evolution of \( G_{\text{max}} \) in a magnetic field could only be reproduced when including a sufficient number of excited states. Estimates for the transverse anisotropy of the Fe4 SMM yield \( E \approx 0.17D = 9.5 \) µeV, a value of \( E \) significantly larger than the observed bulk/monolayer values. This is expected for a molecule put in the low symmetry environment of a transport junction. Importantly, the technique does not rely on the small induced tunneling effects and hence works well at temperatures by far exceeding the tunnel splittings and even \( E \) itself.
of in-situ mechanical tuning [3] or excitation [36, 37] of magnetic anisotropy of a single molecule.

This work was supported by NWO (VENI) and OCW, and by the EU FP7 project 618082 ACMOL and advanced ERC grant (Mols@Mols). M.M. acknowledges the financial support from the Alexander von Humboldt Foundation. K.P. was supported by U.S. National Science Foundations DMR-1206354.

* misiorny@amu.edu.pl
† E.BurzuríLinares@tudelft.nl

[1] D. Gatteschi, R. Sessoli, and J. Villain, *Molecular nanomagnets* (Oxford University Press, New York, 2006).
[2] L. Bogani and W. Wernsdorfer, Nature Mater. 7, 179 (2008).
[3] J. Grose, E. Tam, C. Timm, M. Scheloske, B. Ulgut, J. Parks, H. Abriuña, W. Harneit, and D. Ralph, Nature Mater. 7, 884 (2008).
[4] J. Parks, A. Champagne, T. Costi, W. Shum, A. Pasu-pathy, E. Neuscamman, S. Flores-Torres, P. Cornaglia, A. Aligia, C. Balseiro, G.-L. Chan, H. Abriuña, and D. Ralph, Science 328, 1370 (2010).
[5] A. Zyazin, J. van den Berg, E. Osorio, H. van der Zant, N. Konstantinidis, M. Leijnse, M. Wegewijs, F. May, W. Hofstetter, C. Danieli, and A. Cornia, Nano Lett. 10, 3307 (2010).
[6] M. Urdampilleta, S. Klyatskaya, J.-P. Cleuziou, M. Ruben, and W. Wernsdorfer, Nature Mater. 10, 502 (2011).
[7] R. Vincent, S. Klyatskaya, M. Ruben, W. Wernsdorfer, and F. Balestro, Nature 488, 357 (2012).
[8] M. Mannini, F. Pineider, P. Sainctavit, C. Danieli, E. Otero, C. Sciancalepore, A. Talarico, M. Arrio, A. Cornia, D. Gatteschi, and R. Sessoli, Nature Mater. 8, 194 (2009).
[9] M. N. Leuenberger and D. Loss, Nature 410, 789 (2001).
[10] D. Ferry, S. Goodnick, and J. Bird, *Transport in nanostructures* (Cambridge University Press, Cambridge, 2009).
[11] A. Zyazin, H. van der Zant, M. Wegewijs, and A. Cornia, Synt. Met. 161, 591 (2011).
[12] E. Burzurí, A. S. Zyazin, A. Cornia, and H. S. J. van der Zant, Phys. Rev. Lett. 109, 147203 (2012).
[13] R. Hanson, L. Kouwenhoven, J. Petta, S. Tarucha, and L. Vandersypen, Rev. Mod. Phys. 79, 1217 (2007).
[14] L. Gregoli, C. Danieli, A.-L. Barra, F. Neugebauer, G. Pellegrino, G. Poneti, R. Sessoli, and A. Cornia, Chem. Eur. J. 15, 6456 (2009).
[15] C. Timm and F. Elste, Phys. Rev. B 73, 235304 (2006).
[16] M. Misiorny, I. Weymann, and J. Barnaś, Phys. Rev. B 79, 224420 (2009).
[17] M. Leijnse and M. Wegewijs, Phys. Rev. B 78, 235424 (2008).
[18] R. Bulla, T. Costi, and T. Pruschke, Rev. Mod. Phys. 80, 395 (2008).
[19] A. Tóth, C. Moa, O. Legeza, and G. Zaránd, Phys. Rev. B 78, 245109 (2008).
[20] A. Tóth, C. Moa, O. Legeza, and G. Zaránd, “Manual for the flexible DM-NRG code,” arXiv:0809.3143v1 (2008), (the open access Budapest code is available at http://www.phy.bme.hu/~dmnrg/).
[21] A. Zyazin, H. van der Zant, M. Wegewijs, and A. Cornia, Phys. Rev. Lett. 98, 126601 (2006).
[22] G. González and M. N. Leuenberger, Phys. Rev. Lett. 99, 256804 (2007).
[23] E. Burzurí, F. Luis, O. Montero, B. Barbera, R. Ballou, and S. Maegawa, Phys. Rev. Lett. 111, 057201 (2013).
[24] S. Accorsi, A. L. Barra, A. Canesi, G. Chastanet, A. Cornia, A. C. Fábretti, D. Gatteschi, C. Mortalo, E. Olivieri, F. Parenti, P. Rosa, R. Sessoli, L. Sorace, W. Wernsdorfer, and L. Zobbi, J. Am. Chem. Soc. 128, 4742 (2006).
[25] M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, P. Sainctavit, M.-A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia, and R. Sessoli, Nature 468, 417 (2010).
[26] M. Leijnse and M. Wegewijs, Phys. Rev. B 78, 245109 (2008).
[27] R. Hanson, L. Kouwenhoven, J. Petta, S. Tarucha, and L. Vandersypen, Rev. Mod. Phys. 79, 1217 (2007).
[28] L. Gregoli, C. Danieli, A.-L. Barra, F. Neugebauer, G. Pellegrino, G. Poneti, R. Sessoli, and A. Cornia, Chem. Eur. J. 15, 6456 (2009).
[29] C. U. Timm and F. Elste, Phys. Rev. B 73, 235304 (2006).
[30] M. Misiorny, I. Weymann, and J. Barnaś, Phys. Rev. B 79, 224420 (2009).
[31] M. Leijnse and M. Wegewijs, Phys. Rev. B 78, 235424 (2008).
[32] R. Bulla, T. Costi, and T. Pruschke, Rev. Mod. Phys. 80, 395 (2008).
[33] A. Tóth, C. Moa, O. Legeza, and G. Zaránd, Phys. Rev. B 78, 245109 (2008).
[34] O. Legeza, C. Moa, A. Tóth, I. Weymann, and G. Zaránd, “Manual for the flexible DM-NRG code,” arXiv:0809.3143v1 (2008) (the open access Budapest code is available at http://www.phy.bme.hu/~dmnrg/).
[35] A. Wilson, J. Lawrence, E. Yang, M. Nakano, D. Hendrickson, and S. Hill, Phys. Rev. B 74, 140403 (2006).
[36] F. May, M. Wegewijs, and W. Hofstetter, Beilstein J. Nanotechnol. 2, 693 (2011).
[37] E. Burzurí, Y. Yamamoto, M. Warnock, X. Zhong, K. Park, A. Cornia, and H. van der Zant, Nano Lett. 14, 3191 (2014).
Supplemental Material for

‘Probing Transverse Magnetic Anisotropy by Electronic Transport through a Single-Molecule Magnet’

M. Misiorny,1,2,*, E. Burzuri,3,† R. Gaudenzi,3 K. Park,4 M. Leijnse,5 M. R. Wegewijs,1,6 J. Paaske,7 A. Cornia,8 and H. S. J. van der Zant3

1 Peter Grünberg Institut & JARA, Forschungszentrum Jülich, 52425 Jülich, Germany
2 Faculty of Physics, Adam Mickiewicz University, 61-614 Poznań, Poland
3 Kavli Institute of Nanoscience, Delft University of Technology, 2600 GA, The Netherlands
4 Department of Physics, Virginia Tech, Blacksburg, Virginia 24061, USA
5 Solid State Physics and Nanometer Structure Consortium (mnC@Lu), Lund University, Box 118, S-22100, Sweden
6 Institute for Theory of Statistical Physics, RWTH Aachen, 52056 Aachen, Germany
7 Center for Quantum Devices, Niels Bohr Institute, University of Copenhagen, 2100 Copenhagen, Denmark
8 Department of Chemical and Geological Sciences and INSTM, University of Modena and Reggio Emilia, via G. Campi 183, I-41125 Modena, Italy

CONTENTS

I. Materials and experimental method 2
   A. Details of the Fe4 single-molecule magnet (SMM) 2
   B. Details on the fabrication methods of the three-terminal junctions 2
   C. Details on the gate-voltage ‘position’ spectroscopy 3

II. Theoretical modelling 4
   A. Charge-dependent, giant-spin-based model of an SMM 4
   B. How does magnetic anisotropy affect the energy spectrum of a large spin? 5
   C. Transport in the SET regime 6
   D. Signatures of the transverse anisotropy parameter E without the Berry phase oscillations 8

III. Fitting procedure: how to find anisotropy parameters of a single molecule from its transport spectra 8

IV. Auxiliary figures 11

References 16

In this Supplemental Material we provide additional details that may help to understand the detection of the transverse anisotropy $E$ from the conductance of the Fe4 SMM transistors. First, in Sec. I we discuss some experimental issues, such as the configuration and magnetic properties of the Fe4 SMM (Sec. IA), as well as the fabrication details of the three-terminal transistors (Sec. IB), and we summarize how the Coulomb peak position in gate voltage is used to determine the values of $D$ and $\theta$ (Sec. IC). Next, in Sec. II we present a precise formulation of the model (Secs. II A-II B)
FIG. S-1. Details of the Fe₄ single-molecule magnet: (a) Sketch of the magnetic core of the Fe₄ SMM. (b) Ground-state spin multiplet ($S_N = 5$) of the Fe₄ SMM in a neutral charge state $N$ – for further explanation see Sec. II B. (c) Depiction of the Fe₄ SMM illustrating the orientation of the phenyl rings [omitted in (a)] that terminate the molecule. Note that both in (a) and (c) hydrogen atoms are disregarded for clarity.

and the method of deriving linear-transport characteristics used in the main text (Sec. II C). In Sec. III we outline the basic steps of the procedure leading to estimation of transverse magnetic anisotropy from transport measurements for a single SMM. Finally, in Sec. IV we enclose some auxiliary figures with proper comments providing some further insight into physical mechanism underlying the method under discussion.

Within the Supplemental Material references are numbered as, e.g., equation (S-1) and Figure S-1, whereas regular numbers, e.g., equation (1) and Figure 1, refer to the main article.

I. MATERIALS AND EXPERIMENTAL METHOD

A. Details of the Fe₄ single-molecule magnet (SMM)

We used an Fe₄ SMM with formula [Fe₄(L)₂(dpm)₆]·Et₂O where Hdpm is 2,2,6,6-tetramethylheptan-3,5-dione and H₃L is the tripodal ligand 2-hydroxymethyl-2-phenylpropane-1,3-diol, which carries a phenyl substituent.¹ In the bulk phase, the crystallographic symmetry is $C_2$.¹ The magnetic core of the Fe₄ SMM is made of 4 Fe³⁺ ions (each with spin $s = 5/2$) as illustrated in Fig. S-1(a). The antiferromagnetic exchange interaction between the central and peripheral ions yields a large molecular spin $S_N = 5$ in the ground state. Magnetic anisotropy due to the interaction with the crystal field lifts the degeneracy of the spin multiplet into five doublets and one singlet that are distributed over an energy barrier as shown in Fig. S-1(b) – for further discussion see Sec. II B. The height of the barrier, which hinders the spin reversal, is given by $U = D(S_N)^2$, where $D$ is the uniaxial magnetic anisotropy parameter. In the case of bulk Fe₄ the height is $U = 1.4$ meV.¹ The ‘zero-field splitting’ (ZFS), defined as the energy difference between the two lowest-lying doublets ($M_N = \pm 5$ and $M_N = \pm 4$) is 0.5 meV. The low symmetry of the molecule induces a transverse magnetic anisotropy $E$ that, in bulk, is $E = 2.85$ µeV from EPR measurements.¹ Finally, we note that the molecule contains two axial tripodal ligands $L^{3-}$ which hold the core together and six peripheral dpm⁻ ligands that create an hydrophobic envelope, see Fig. S-1(c).

B. Details on the fabrication methods of the three-terminal junctions

The three-terminal junctions are fabricated on a silicon substrate covered by 280 nm of SiO₂. The schematics of the fabrication process is described in Fig. S-2(a). The gate electrode is fab-
FIG. S-2. Three-terminal-junction fabrication: (a) Schematics of the three-terminal-device fabrication process. (b) Scanning electron microscope (SEM) image of a real three-terminal device before electromigration.

fabricated by e-beam lithography and subsequent e-beam deposition of Al. In the next step, the oxidation of the gate in a controlled oxygen atmosphere produces a dielectric coating layer of 2-3 nm of Al₂O₃. The source and drain electrodes are fabricated by self-breaking, controlled electromigration of a Au nanobridge deposited by e-beam lithography on top of the oxidized gate. The self-breaking technique prevents the formation of gold nano-grains in the junction that could mimic the behavior of a molecule. Figure S-2(b) shows a scanning electron microscope image of a device before electromigration.

The molecules are deposited onto the chip by drop casting a 10⁻⁴ M solution in toluene into a liquid cell containing the chip with the junctions. The electromigration of the bridge and subsequent self-breaking are carried out in solution to maximize the yield of junctions with a molecule.

C. Details on the gate-voltage ‘position’ spectroscopy

The molecule-electrode coupling Γ is estimated from the broadening of the Coulomb edge at low bias. In particular, the full-width at half-maximum (FWHM) of the Coulomb peak is used for this purpose. We find 1.6 meV, 2.0 meV and 1.4 meV for samples A, B and C respectively. Note, however, that these values are an upper limit for Γ since we can not resolve the presence of additional components for the broadening such as temperature or the contribution of other molecular levels very close in energy.

Figure S-3 shows the Coulomb peak (CP) position in gate voltage $V_g$ as a function of the magnetic field for the samples A, B and C described in the main text. The values of $V_g$ are multiplied by the gate coupling $\beta$ to obtain energy units ($\Delta \varepsilon$) and subsequently re-scaled to make $\Delta \varepsilon = 0$ for $B = 0$. The non-linearity of the field dependence is a clear signature of the magnetic anisotropy as described in the text (see also Ref. [2]). Moreover, the low-field ‘flatness’ of $\Delta \varepsilon$ observed in Figs. S-3(a)-(c) is an indicative of a high value of $\theta$ in contrast with Fig. S-3(d). The solid lines in Fig. S-3 are a fit of the data to $\Delta \varepsilon = \varepsilon_{N+1}^0 - \varepsilon_N^0$ as defined by the giant-spin
FIG. S-3. **Coulomb peak position gate-voltage spectroscopy:** The shift of the Coulomb peak position due to magnetic field for samples A, B and C. The solid lines are fits to \( \varepsilon_{N+1}^0 - \varepsilon_N^0 \), calculated from the giant-spin Hamiltonian described in the main text (see also Sec. II A). From the fit we get the following values – for sample A in (a): \( D_N = 68 \mu eV \), \( \theta_N = 90^\circ \) and \( \theta_{N+1} = 85^\circ \); for sample B in (b): \( D_N = 65 \mu eV \), \( \theta_N = 86^\circ \) and \( \theta_{N+1} = 84^\circ \); for sample C: in (c) \( \theta_N = 87^\circ \), \( \theta_{N+1} = 85^\circ \), and in (d) \( D_N = 68 \mu eV \) and \( \theta_N = 63^\circ \), \( \theta_{N+1} = 62^\circ \). We note that sample C was previously analyzed in Ref. [2].

Hamiltonian in the main text (and also discussed in detail in Sec. II A). We assume for simplicity that \( \theta_N \sim \theta_{N+1} \). In this scenario the CP position is mainly insensitive to \( E \), and therefore we can independently extract the parameters \( D \) and \( \theta \) related to the uniaxial anisotropy. Note that we fix the value of \( D_N \) (neutral state) to the bulk value \( D_N = 56 \mu eV \) and thus the free parameters are \( D_{N+1}, \theta_N \) and \( \theta_{N+1} \). See the caption of Fig. S-3 for the fitting values of these parameters.

II. THEORETICAL MODELLING

A. Charge-dependent, giant-spin-based model of an SMM

The central element of the theoretical description of the gate-spectroscopy technique is a proper choice of the model capturing essential features of an SMM. As introduced in the main article, the molecule is represented by a model based on two giant-spin Hamiltonians.\(^3\)–\(^5\) This allows us to take into account the fact that by tuning a gate voltage \( V_g \) the molecule can be switched between two different charge states,\(^6\) referred to as a *neutral* (N) and *charged* (N + 1) one. In general, each of these states can be characterized not only by different values of molecular ground-state spin (\( S_N \) and \( S_{N+1} \)), but also uniaxial (\( D_N \) and \( D_{N+1} \)) and transverse (\( E_N \) and \( E_{N+1} \)) magnetic anisotropy constants. Using the spin raising/lowering operators \( \hat{S}_n^+ \), the Hamiltonian of an SMM in the charge state \( n \) and subject to an arbitrarily oriented external magnetic field \( B \) takes the
FIG. S-4. Effect of magnetic anisotropy on the energy spectrum of SMM: Top/Bottom panel illustrates the case of a integer/half-integer value of a molecular spin. In particular, we use the values of spin known for a Fe₄ SMM, $S_N = 5$ for a neutral molecule and $S_{N+1} = 9/2$ for a charged one.⁶ (a)-(b) In the presence of exclusively uniaxial magnetic anisotropy $D > 0$ (and without magnetic field, $B = 0$) an energy barrier protecting the molecule’s spin against reversal between two opposing, energetically degenerate, orientations arises. The excitation between the ground state doublet and the first excited doublet is then commonly referred to as the ‘zero-field splitting’ (ZFS). (c)-(d) If additionally the transverse component of magnetic anisotropy occurs, it allows for mixing of pure $S_z$-states. Each new eigenstates is then formed from $S_z$-states belonging to one of two uncoupled, time-inversed sets, as schematically marked by two different colors. As follows from the Kramers theorem, for $S_N = 5$ the transverse magnetic anisotropy introduces tunnel-splittings $\Delta$, whereas for $S_{N+1} = 9/2$ all states remain doubly degenerate. (e)-(f) A characteristic feature of such anisotropic, large spins is that when an external magnetic field $B$ is applied along the system’s hard axis, one observes periodic changes of the tunnel-splittings.⁵,⁷ Other parameters assumed in the calculations: $D_N = 56 \, \mu$eV, $D_{N+1} = 68 \, \mu$eV, and $E_N/D_N = E_{N+1}/D_{N+1} = 0.3$.

B. How does magnetic anisotropy affect the energy spectrum of a large spin?

Before we analyze how electronic transport probes the transverse magnetic anisotropy of a molecule, it may be instructive first to discuss the consequences of the transverse magnetic anisotropy and external magnetic field for the SMM’s energy spectrum.

To begin with, as long as the transverse magnetic anisotropy is vanishingly small the system can be described simply by the first term of the Hamiltonian (S-1). As a result, the eigenvalues $M_n$
of the spin operator $\hat{S}_z^n$ become good quantum numbers for labelling the eigenstates of $\hat{H}_{\text{SMM},n} = -D_n (\hat{S}_z^n)^2$, that is $\hat{H}_{\text{SMM},n}|M_n\rangle = -D_n M_n^2 |M_n\rangle$. For $D_n > 0$ the energy spectrum of an SMM takes the form of an inverted parabola with an energy barrier of height $\sim D_n S_n^2$ for spin reversal, which basically corresponds to the indirect transition between the ground states $|-S_n\rangle$ and $|S_n\rangle$ by climbing the barrier via the intermediate states $|M_n\rangle$ for $M_n = -S_n + 1, \ldots, S_n - 1$, see Figs. S-4(a)-(b). Importantly, the excitation energy between the ground state $|\pm S_n\rangle$ and the first excited state $|\mp S_n\rangle$, the so-called ‘zero-field splitting’ ZFS $= (2S_n - 1)D_n$, sets the threshold energy scale for the reversal process to take place. Note that transition energies between neighboring excited states $|M_n\rangle$ and $|M'_n\rangle$ with $|M_n - M'_n| = 1$ are characterized by energies $(2M_n - 1)D_n$ (for $0 < M_n < S_n$) that are smaller than the ZFS, and these states remain generally unpopulated until the ground-to-first excited state transition becomes energetically permitted. This bottleneck behavior manifest then in electronic transport through an SMM, where it can be observed as a step-like feature in the conductance only at bias voltages $V_b = \pm ZFS/|e|$.$^{5,8}$

The relatively simple picture presented above is not valid, however, if the transverse magnetic anisotropy (or an external magnetic field perpendicular to the molecule’s easy axis) is significant. When $E \neq 0$, the second term of the Hamiltonian (S-1) breaks the system’s rotational symmetry around the easy axis $z$, so that $M_n$ is no longer a good quantum number. In fact, each of the $2S_n + 1$ eigenstates of $\hat{H}_{\text{SMM},n} = -D_n (\hat{S}_z^n)^2 + (E_n/2)[(\hat{S}_n^+)^2 + (\hat{S}_n^-)^2]$ is now a linear combination of the eigenstates $|M_n\rangle$, which, in turn, underlies the origin of the quantum tunneling of magnetization.$^9$ In particular, each of these eigenstates is formed from states $|M_n\rangle$ belonging to one of two uncoupled, time-inversed sets, as shown in Figs. S-4(c)-(d). For an integer spin $S_n$, the transverse magnetic anisotropy leads to splitting of energy levels, usually referred to as ‘tunnel-splittings’, Fig. S-4(c), whereas for a half-integer spin $S_n$ (in the absence of magnetic field) according to the Kramers theorem each energy level is doubly degenerate, Fig. S-4(d). Interestingly, if one applies an external magnetic field in the direction perpendicular to the system’s easy axis $z$, periodic changes of these tunnel-splittings can be observed if the field is oriented along or close the hard axis $x$, Figs. S-4(e)-(f), and they disappear as the field gets rotated towards the direction of the medium axis $y$.$^{5,7,9}$

C. Transport in the SET regime

For a weak tunnel-coupling between an SMM and electrodes, transport in the single electron tunneling (SET) regime can be considered in the leading-order perturbative approach (Fermi golden rule combined with a master equation).$^{10-12}$

We describe metallic, nonmagnetic electrodes $\{q \equiv (L)eft, (R)ight\}$ as reservoirs of noninteracting electrons, whose tunneling processes to/from a molecule are modelled by the following Hamiltonian

$$\hat{H}_{\text{tun}} = \sum_{qkl\sigma} t_{kl}^q \hat{d}_{l\sigma}^q \hat{a}_{k\sigma}^q + \text{H.c.} = \sum_{qk\sigma} \sum_{a_N b_{N+1}} T_{a_N b_{N+1}}^{q} |a_{N+1}\rangle \langle b_N| \hat{a}_{k\sigma}^q + \text{H.c.} \quad \text{(S-2)}$$

with

$$T_{a_N b_N}^{q} = \sum_{l} t_{l}^{q} \langle a_{N+1}| \hat{d}_{l\sigma}^{q}|b_N\rangle, \quad \text{(S-3)}$$

where $t_{l}^{q}$ is the tunneling matrix element, $\hat{d}_{l\sigma}^{q}$ represents creation of an electron with spin $\sigma$ in the molecular orbital $l$, and $\hat{a}_{k\sigma}^{q}$ denotes the annihilation operator for the $q$th electrode with $k$ standing for an orbital quantum number. Note that the molecular state has been expanded in the basis of eigenvectors $|a_{N+1}\rangle$ and $|b_N\rangle$ of $\hat{H}_{\text{SMM}} = \sum_{n=N,N+1} \hat{H}_{\text{SMM},n}$. Next, we express the molecular
eigenstates $|a_N\rangle$ and $|b_{N+1}\rangle$ with respect to the basis of angular momentum (spin) eigenstates. In principle, an arbitrary molecular state can be decomposed as $|\chi_n\rangle = \sum_{S_nM_n} \chi_{S_nM_n} |S_nM_n\rangle$. As a result, one obtains

$$T_{a_{N+1}b_N}^{\sigma q} = \sum_{l} \sum_{S_{N+1}M_{N+1}} \sum_{S_NM_N} t_{\sigma}^{q} a_{S_{N+1}M_{N+1}}^{\ast} b_{S_NM_N} \langle S_{N+1}M_{N+1}||d_{\sigma}^{l}\rangle |S_NM_N\rangle. \quad (S-4)$$

The key problem one encounters when analyzing the above equation is that the operator $d_{\sigma}^{l}$ involves two degrees of freedom, namely, the orbital one ($l$) and the spin one ($\sigma$). Consequently, it may seem that in the next step we need to calculate $\langle S_{N+1}M_{N+1}||d_{\sigma}^{l}\rangle |S_NM_N\rangle$ explicitly. This complication, however, can be avoided by making use of the the Wigner-Eckart theorem,\textsuperscript{13} which basically allows for finding matrix elements of an operator with respect to angular momentum eigenstates,

$$\langle S_{N+1}M_{N+1}||d_{\sigma}^{l}\rangle |S_NM_N\rangle = \langle S_NM_N; \frac{1}{2}; \sigma||S_{N+1}M_{N+1}||d_{\sigma}^{l}||S_NM_N\rangle. \quad (S-5)$$

The first factor of the RHS is a Clebsch-Gordan coefficient for adding spins $S_N$ and $1/2$ to get $S_{N+1}$. This depends only on how the system is oriented with respect to the $z$ axis. On the other hand, the second factor, the so-called reduced matrix element, remains independent of the spatial orientation, as it does not contain the magnetic quantum numbers $M_N, M_{N+1}$ or $\sigma$. Thus, we get

$$T_{a_{N+1}b_N}^{\sigma q} = \sum_{S_NS_{N+1}} T_{a_{N+1}b_N}^{\sigma q} T_{S_{N+1}S_N}^{q} \quad (S-6)$$

with

$$T_{a_{N+1}b_N}^{\sigma q} = \sum_{M_NM_{N+1}} a_{S_{N+1}M_{N+1}}^{\ast} b_{S_NM_N} \langle S_{N+1}M_{N+1}; \frac{1}{2}; \sigma||S_NM_N\rangle \quad (S-7)$$

and the term $T_{S_{N+1}S_N}^{q} = \sum_{l} t_{\sigma}^{q} \langle S_{N+1}||d_{\sigma}^{l}||S_N\rangle$ regarded in calculations as a single free parameter to be adjusted for each electrode. Specifically, assuming a symmetric coupling between the molecule and two identical electrodes ($t_{\sigma}^{l} = t_{\sigma}^{R}$), the tunnel coupling takes the from $\Gamma = \Gamma_L = \Gamma_R = \Gamma/2$, where $\Gamma = 2\pi \rho |T_{S_{N+1}S_N}|^2$ and $\rho$ denotes the constant, spin-independent density of states in electrodes.

The stationary current flowing through a molecule is calculated as $I = (I_L - I_R)/2$, where $I_q$ (for $q = L, R$) stands for the current flowing from the $q$th electrode to the molecule,

$$I_q = \frac{e \Gamma}{2\hbar} \sum_{n'\sigma} \sum_{a,b,a',b'} (n' - n) f_q(\Delta \varepsilon_{b,a}) \sum_{\sigma \in q} |T_{b,a}^{\sigma q}|^2 \mathcal{P}_{a}. \quad (S-8)$$

where $\Delta \varepsilon_{b,a} = \varepsilon_b - \varepsilon_a$, and $f_q(\omega) = (1 + \exp[(\omega - \mu_q)/(k_B T)])^{-1}$ is the Fermi-Dirac function of the $q$th electrode, with $T$ and $\mu_L(R) = \mu_0 \pm eV_{0}/2$ standing for temperature and the relevant electrochemical potential, respectively. The probabilities $\mathcal{P}_{a}$ of finding an SMM in a specific state $|a\rangle$ are then derived from a stationary master equation.\textsuperscript{10} Finally, since SMMs are typically characterized by long spin coherence and spin relaxation times as a result of a weak spin-orbit and hyperfine coupling to the environment,\textsuperscript{14-16} we neglect relaxation of the spin states other than due to the electron tunneling.

In Fig. 3(d) of the main article (and also in Figs. S-7–S-10), we present the current $I_r = (I_L - I_R)/2$ which includes first $r$ lowest-in-energy states in the spin multiplet of each charge state. We use this to show that many excited states in both charge state have to be taken into account in order to describe current correctly. We define $I_r^q$ in the following way

$$I_r^q = \frac{e \Gamma}{2\hbar} \sum_{n'\sigma} \sum_{b,a} \sum_{a'} (n' - n) f_q(\Delta \varepsilon_{b,a}) \sum_{\sigma \in q} |T_{b,a}^{\sigma q}|^2 \mathcal{P}_{a}. \quad (S-9)$$
with $\sum_{n}^{r'}$ denoting summation over states $|a_n\rangle$ in the charge state $n$ that is limited only to first $r$ states of lowest energy.

**D. Signatures of the transverse anisotropy parameter $E$ without the Berry phase oscillations**

In the main article we discuss the initial increase of the current with magnetic field followed by a decrease. The key insight of our calculations using the method described in the previous section is that the mechanism for this effect is significantly enhanced and modified for $E \neq 0$ giving rise to the characteristic $G_{\text{max}}$ curves shown in Fig. 2 of the main paper. Since this is at the basis of our scheme of detection, it deserves a further comment. In particular, the relation to the Berry phase oscillations which underlay most of the previously used techniques for determining the parameter $E$.

(i) Upon increase of $E$ the minima of the transition-energy curves are shifted to higher field values and the value achieved at the minimum is lowered, cf. Fig. 3(c) of the main paper with Fig. S-7(e)-(h). For a fixed temperature, this leads to a more pronounced maximum conductance attained at a higher field value.

(ii) Generally, the transition energies in Fig. 3(c) of the main paper show sharp features (i.e. oscillations below $B = 2$ T) due to Berry-phase interference on which several techniques for extracting $E$ rely – by analyzing the field dependence of the tunnel splitting between two selected states.\textsuperscript{5,7,9,17} However, the detection of such behavior in the conductance requires very specific low temperature conditions. This is in contrast to the present experimental conditions where these Berry-phase features are averaged out when taking into account multiple accessible states. This leaves only the large scale, collective variations of the transition energy spectrum caused by $E$ which as we have shown suffice for estimation of $E$. In Fig. 3(d) of the main article we illustrate the importance of taking into account many excited states for both charge states to describe current correctly.

(iii) Finally, Fig. 2(c) of the main article shows the relative CP amplitude for increasing $E/D$. A qualitative distinction from the $E \ll D$ limit is the appearance of an additional shoulder close to $B = 6$ T. It is tempting to see such a shoulder in the sample A curve of Fig. 2(a) of the main article, although the sample B curve exhibits features of similar size where it should theoretically be smooth. In summary, the calculations certainly show that a sizeable $E$ term leads to fingerprints in the linear conductance as clear as those for the $D$ term, even for relatively high temperatures.

**III. FITTING PROCEDURE: HOW TO FIND ANISOTROPY PARAMETERS OF A SINGLE MOLECULE FROM ITS TRANSPORT SPECTRA**

We summarize here in a few steps how to determine magnetic anisotropy of an individual SMM (see Eq. (1) of the main article and Sec. II A) by exploiting the information contained both in the Coulomb peak position as well as in the magnetic field evolution of its amplitude. In particular, the gate-voltage spectroscopy method under discussion allows for finding both the magnetic anisotropy constants $D_n$ and $E_n$ in two charge states (i.e. for $n = N, N + 1$) of an SMM, and the orientation of an external magnetic field relative to the molecule’s principle axes, given by the angles $\theta$ and $\phi$. 
FIG. S-5. How to determine the transverse magnetic anisotropy constant $E$ of an individual SMM from its transport characteristics: The position (a)-(b) and amplitude (c)-(f) of the Coulomb peak are shown for different values of the parameters $D$ and $E$ of the SMM model with $S_N = 5$ and $S_{N+1} = 9/2$ for $T = 1.8$ K. Note that we employ the assumption for the Fe$_4$ molecule from the main text, that is $D = D_N = D_{N+1}/1.2$ and $E = E_N$ with $E_N/E_{N+1} = D_N/D_{N+1}$, and a relatively large value of $E/D$ (red lines) is used for clear illustration of the effects under discussion. In panels (a,c,e) the external magnetic field $B$ is oriented along the SMM’s hard axis $x$ [see inset in (c)], whereas in panels (b,d,f) the field is parallel to the medium axis $y$ [see inset in (d)]. In panel (g) we present how temperature affects the occurrence of characteristic peaks associated with the presence of transverse magnetic anisotropy for $B$ along the hard axis $x$ – for further details see Fig. S-10. To make the discussion complete, in panel (h) we show analogous dependencies but in the case when the field lies along the medium axis $y$. Finally, the frame at the bottom contains a schematic summary of the procedure leading to estimation of $E$: (i) Using the analysis of the Coulomb peak position, find $D_n$ and adjust the magnetic field $B$ so that it is contained in the hard plane, i.e., the plane perpendicular to the easy axis $z$. (ii) Rotating systematically the magnetic field $B$ in the hard plane, analyze the Coulomb peak amplitude to find the direction of the molecule’s hard axis. This will be characterized by occurrence of additional peaks in the amplitude, whose field-position allows for estimating $E_n$. (iii) If no local maxima in the amplitude can be seen, adjust (try increasing) the temperature.
(i) Let us first consider only the Coulomb peak position, shown in the left panel of Fig. S-5. As explained in Ref. [2], by analyzing the position of the Coulomb peak one can immediately conclude whether a molecule captured in the junction exhibits magnetic anisotropy at all. If the molecule is spin-isotropic, one observes a linear dependence on the magnetic field [see dashed line in Figs. S-5(a)-(b)] that reflects the linear Zeeman effect. On the other hand, if the molecule is spin-anisotropic, this dependence becomes nonlinear, and the uniaxial magnetic anisotropy parameter $D_n$ together with the angle $\theta$ can be estimated from it. This, in turn, permits for systematic adjustment of the magnetic field’s orientation so that the field is kept perpendicular to the molecule’s easy axis $z$, which corresponds to $\theta = 90^\circ$.

(ii) As discussed in Sec. II B, the transverse magnetic anisotropy breaks the molecule’s rotational symmetry around the easy axis $z$. In consequence, one expects that such a symmetry breaking should manifest itself in different transport characteristics of the system occurring for various orientations of the magnetic field in the hard plane (i.e. the plane perpendicular to the easy axis). From Figs. S-5(a)-(b) it is clear that the sole position dependence in practice does not allow one to derive reliably either the transverse magnetic anisotropy constant $E_n$ or the angle $\phi$. For this purpose, also the amplitude of the Coulomb peak has to be taken into consideration.

(iii) The presence of transverse magnetic anisotropy can be confirmed by observation of how the field dependence of the Coulomb peak amplitude changes when rotating the field orderly in the hard plane, or in other words by varying the angle $\phi$. Specifically, one should notice then two significantly different shapes of the amplitude showing up every $90^\circ$, cf. red lines with others in the right panel of Fig. S-5. These two limiting cases represent the situation when the magnetic field lies either along the molecule’s hard axis $x$ ($\phi = 0^\circ$ or $\phi = 180^\circ$), Fig. S-5(c,e), or along the molecule’s medium axis $y$ ($\phi = 90^\circ$ or $\phi = 270^\circ$), Fig. S-5(d,f). Consequently, this enables one to determine the approximate value of the angle $\phi$.

(iv) The effect of transverse magnetic anisotropy on the Coulomb peak amplitude should be most pronounced for the magnetic field aligned along the molecule’s hard axis $x$, see Sec. II B and Figs. 2(c)-(d) of the main article. For a sufficiently high temperature $T$ [see Fig. S-5(f)-(g) and Fig. S-10] one observes then formation of local maxima, marked by red arrows in Figs. S-5(c,e), from whose position the value of the transverse magnetic anisotropy constant $E_n$ can be numerically estimated.

Importantly, the method under discussion relies on a simultaneous fitting of position (sensitive to $D_n$) and the amplitude (sensitive both to $D_n$ and $E_n$) of the Coulomb peak. This strictly limits the freedom of the parameters’ choice, basically leaving $E_n$ to be determined from the field value at which the maximum amplitude is acquired. For instance, making the parameters $D_n$ smaller by 25% than the one used above (given the fixed experimental temperature $T = 1.8$ K), while assuming $E_n = 0$, may also produce a maximum, see green lines in Figs. S-5(c)-(f). However, not only does it result in peak positions at completely wrong magnetic fields [cf. position of green and red arrows in Fig. S-5(e)], but also the amplitude shape remain unaltered upon changing the orientation of the field in the hard plane [cf. red and green lines between Figs. S-5(e) and (f)]. This restriction, combined with the sensitivity of the qualitative curve shape of the conductance to the parameters is advantageous for extracting the anisotropy parameters of SMMs \textit{in situ}. 
FIG. S-6. Transition energies relevant for the SET processes at the Coulomb resonance: Panel (a) is identical to Fig. 3(c) of the main article but now for each transition-energy line we specify the initial $|\chi_N^k\rangle$ and final $|\chi_{N+1}^{k'}\rangle$ states between which the transition occurs. Recall that $k$ is an index which numbers states in a given spin multiplet with respect to energy, with $k = 0$ denoting the ground state. Moreover, by labelling the lines with $(k, k')$ we mean that $k$ refers to the final state of a charged SMM $(N + 1)$ whereas $k'$ represents the initial state of a neutral SMM $(N)$. We note that information shown in (a) cannot be readily seen from energies $\varepsilon_n^k$ $(n = N, N + 1)$ of the individual levels, which for the completeness of the present discussion are plotted in (b). Observe that since energies in (b) are calculated at the Coulomb resonance, the curves for $k = 0$ overlap.
FIG. S-7. Signatures of the transverse magnetic anisotropy in electronic transport (magnetic field along the hard axis, $\theta = 90^\circ$ and $\phi = 0^\circ$): Analogous to Figs. 3(b)-(d) of the main article with each column corresponding now to a different value of $E/D$: (a)-(d) Occupation probabilities for several lowest-in-energy states in the spin multiplets for $N$ and $N + 1$ at $T = 1.8$ K; (e)-(h) Transition energies $\varepsilon_{N+1}^k - \varepsilon_N^{k'}$ relevant for the SET processes at the Coulomb resonance (i.e. $\varepsilon_{N+1}^0 = \varepsilon_N^0$ is restored for each $B$ by tuning $V_g$) for $k, k' \leq 4$. Different colors of lines are used to distinguish groups of transitions with respect to possible combinations of indices $k$ and $k'$ (see the text of the main article as well as Fig. S-6); (i)-(l) energies $\varepsilon_n^k$ for $n = N, N + 1$ at the Coulomb resonance – observe that the curves for $k = 0$ overlap; (m)-(p) Dependence of the current on the number of spin-multiplet states $r$ included from each charge state. The left/right most column represents the case of absent/significant transverse magnetic anisotropy. Importantly, each column shows a detailed analysis of selected conductance curves from Fig. 2(c) of the main article. We note that transition-energy lines in (e)-(h) can be easily identified with the use of Fig. S-6. It can be seen that increasing $E/D$ results in shifting the minima of the transition-energy curves in (e)-(h) towards higher values of the field. Such a behavior, in turn, affects the occupation probabilities (a)-(d), so that the probability of finding an SMM either in the ground ($k = 0$) or first excited ($k = 1$) state for both charge states $N$ and $N + 1$ remain equal for a larger magnetic-field range (compare the outermost columns). Recall that the position of the Coulomb peak is fixed mostly by $D$, see Fig. S-3.
FIG. S-8. Signatures of the transverse magnetic anisotropy in electronic transport (magnetic field along the medium axis, \( \theta = 90^\circ \) and \( \phi = 90^\circ \)): Generally, this figure is analogous to Fig. S-7 except that now the external magnetic field is rotated to align with the molecule’s medium (y) axis. To begin with, we note that the results shown in the leftmost column (i.e. for \( E/D = 0 \)) are identical to those in the leftmost column of Fig. S-7, which is the manifestation of the molecule’s rotational symmetry about the easy (z) axis in the absence of transverse component of magnetic anisotropy. Unlike for the case of \( \phi = 0^\circ \), the consequence of the increase of \( E/D \) is the displacement of the transition-energy curves minima (e)-(h) towards smaller values of the field. Interestingly enough, in the situation under discussion one thus observes a more abrupt decrease of the current [see dashed lines in (m)-(p)] for larger \( E/D \) occurring at smaller values of \( B \).
FIG. S-9. Dependence of transport signatures of the transverse anisotropy on the orientation of magnetic field in the hard plane \( \theta = 90^\circ \) for \( E/D = 0.17 \). Analogous to Figs. 3(b)-(e) of the main article with each column corresponding now to a different value of \( \phi \). Note that the case of \( \phi = 0^\circ \) is presented in Figs. 3(b)-(e) of the main article. Furthermore, here each column shows a detailed analysis of selected conductance curves from Fig. 2(d) of the main article.
FIG. S-10. Evolution of the Coulomb peak amplitude in the absence of transverse magnetic anisotropy ($E = 0$): This figure serves to illustrate the fact that even if the transverse magnetic anisotropy is absent, by making the uniaxial magnetic anisotropy parameter $D$ smaller (keeping a fixed temperature) one can eventually also produce a maximum as for $E \neq 0$. However, this maximum occurs at a completely different (smaller) value of magnetic field. Moreover, the shape of $G_{\text{max}}(B)$ remains invariant under rotation of the field in the hard plane, this is when the angle $\phi$ is varied. None of these are the case in the experiment under discussion. (a)-(b) Dependence of $G_{\text{max}}(B)$ on the value of the uniaxial magnetic anisotropy parameter $D \equiv D_N$ (and $D_{N+1} = 1.2D$) for an external magnetic field applied along the molecule’s hard axis ($\theta = 90^\circ$ and $\phi = 0^\circ$). A detailed analysis of selected curves from (a)-(b) is carried out in (c)-(s), with each column corresponding to the indicated value of $D$. 
Tuning anisotropy barriers in a family of tetrairon(III) single-molecule magnets with an $S = 5$ ground state. *J. Am. Chem. Soc.* **128**, 4742 (2006).

Burzurí, E., Zyazin, A. S., Cornia, A. & van der Zant, H. S. J. Direct observation of magnetic anisotropy in an individual Fe$_4$ single-molecule magnet. *Phys. Rev. Lett.* **109**, 147203 (2012).

Kahn, O. *Molecular Magnetism* (VCH Publishers Inc., New York, 1993).

Boća, R. *Theoretical foundations of molecular magnetism*, vol. 1 of *Current Methods in Inorganic Chemistry* (Elsevier, Louanne, 1999).

Gatteschi, D., Sessoli, R. & Villain, J. *Molecular nanomagnets* (Oxford University Press, New York, 2006).

Zyazin, A. et al. Electric field controlled magnetic anisotropy in a single molecule. *Nano Lett.* **10**, 3307–3311 (2010).

Wernsdorfer, W. & Sessoli, R. Quantum phase interference and parity effects in magnetic molecular clusters. *Science* **284**, 133–135 (1999).

Misiorny, M. & Barnaš, J. Effects of transverse magnetic anisotropy on current-induced spin switching. *Phys. Rev. Lett.* **111**, 046603 (2013).

Gatteschi, D. & Sessoli, R. Quantum tunneling of magnetization and related phenomena in molecular materials. *Angew. Chem. Int. Ed.* **42**, 268–297 (2003).

Romeike, C., Wegewijs, M. R. & Schoeller, H. Spin quantum tunneling in single molecular magnets: Fingerprints in transport spectroscopy of current and noise. *Phys. Rev. Lett.* **96**, 196805 (2006).

Timm, C. & Elste, F. Spin amplification, reading, and writing in transport through anisotropic magnetic molecules. *Phys. Rev. B* **73**, 235304 (2006).

Misiorny, M., Weymann, I. & Barnaš, J. Spin effects in transport through single-molecule magnets in the sequentail and cotunneling regimes. *Phys. Rev. B* **79**, 224420 (2009).

Messiah, A. *Quantum mechanics* (Dover Publications, New York, 1999).

Ardavan, A. et al. Will spin-relaxation times in molecular magnets permit quantum information processing? *Phys. Rev. Lett.* **98**, 57201 (2007).

Bertaina, S. et al. Quantum oscillations in a molecular magnet. *Nature* **453**, 203–206 (2008).

Bogani, L. & Wernsdorfer, W. Molecular spintronics using single-molecule magnets. *Nature Mater.* **7**, 179–186 (2008).

Burzurí, E. et al. Quantum interference oscillations of the superparamagnetic blocking in an Fe$_8$ molecular nanomagnet. *Phys. Rev. Lett.* **111**, 057201 (2013).