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An Organometallic Single-Ion Magnet

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S Supporting Information

ABSTRACT: An organometallic single-ion magnet is synthesized with only 19 non-hydrogen atoms featuring an erbium ion sandwiched by two different aromatic ligands. This molecule displays a butterfly-shaped hysteresis loop at 1.8 K up to even 5 K. Alternating-current (ac) susceptibility measurement reveals the existence of two thermally activated magnetic relaxation processes with the energy barriers as high as 197 and 323 K, respectively.

Magnets have been fascinating human beings since the time immemorial and played an important role in the transformation of our society into a well developed one in science and technology. The discovery of organic molecular magnets stimulated a renaissance of molecular magnetism.[1] Of particular interest are molecular nanomagnets that provide the possibility of maintain the magnetic moment in a low dimensional (zero or one-dimensional [1D]) structure rather than a magnetic domain composed of 3D connected lattices,[2] and their amazing behaviors in quantum effects make the crucial importance for the development of information storage, quantum computing, and molecular spintronics.[3−5] Since 2003, amazingly, a few single lanthanide or actinide ion-containing molecules behaving slow magnetic relaxation in the absence of dc field.[6−10] Due to the single ion features of them, these complexes are named single-ion magnets. These single ion magnets share some characters in common: all these magnets behave slow magnetic relaxation at zero dc field but seldom is found to behave hysteresis loop above 2 K; all these magnets can be found a quantum tunneling relaxation region range from 2 to 10 K; all the magnetic ions in the magnets enjoy a high order single axis coordination environment. We have shown recently that the ground states in the discovered single-ion magnets with a local symmetry of D_{4d} are Ising type; this result illustrated that the single-axial ligand-field symmetry is of great importance to control the single-axial anisotropy.[9] However, most of the metal ions of the former reported cases are coordinated by point-charge ligands other than a recent work on actinide with higher symmetry.[11] Herein we report a carbon ring coordinated single-ion magnet, featuring an Er(III) ion sandwiched by two aromatic ligands, pentamethylcyclopentadienide ($C_5Me_5^-$, Cp*) and cyclooctatetraenide ($C_8H_8^{2-}$, COT). The results suggest that by employing delocalized ligands it is possible to design single-molecule magnets (SMMs) with prominent uniaxial anisotropy.

The crystal structure of the molecule (Cp*)Er(COT) is shown in Figure 1. The Er(III) ion is sandwiched between the two aromatic rings, being closer to the COT center (1.66 Å) than to that of the Cp* ring (2.27 Å). The Er−C(COT) distances range from 2.500 to 2.523 Å (average 2.513 Å), while the Er−C(Cp*) distances are from 2.569 to 2.576 Å, with an average of 2.573 Å. The two aromatic rings are not parallel to each other, but with a tilt angle of 8.0°. Similar tilting is also found in the isomorphous Lu(III) complex, suggesting that the tilting is probably not due to any electronic effects.[12] The nearest Er···Er distance of 7.030 Å and adjacent molecules being perpendicular to each other suggest that intermolecular interactions, if any, are negligible. Because of the different rings and the tilting between them, the Er(III) is situated in an environment of low point group symmetry of C_s. The COT group is crystallographically disordered in the temperature range of 10−120 K. The disorder is assumed to be static by nature due to the coexistencxe of two stable conformers with different COT conformations in the crystal rather than dynamic position disorder.

The out-of-phase of ac susceptibility (χ'') of the title molecule shows a clear frequency-dependence in the temperature range of 2 to 25 K (Figure 2a). The increment on cooling below 10 K is a typical quantum tunneling relaxation due to the mixing of the Kramers ground states.[9] The relaxation time can be deduced by fitting the decay of magnetization from 1.8 to 3.5 K in the absence of dc field to the equation $M(t) = M_0 + M \exp[-(t - t_0)/\tau]$, where τ is the relaxation time, M_0 the residual slower relaxation due to a small fraction of the crystal (less than 5%), and t_0 the time error of the measurement using SQUID. The relaxation time in this temperature range is nearly temperature independent in the logarithmic scale, providing support to the quantum tunneling mechanism (see Supporting Information [SI], Figure S2). Generally, quantum tunneling between Kramers states is forbidden according to the selection rule (except for the ±1/2 states). However, in the present case, the dipole−dipole interaction as well as the deviation from the axial symmetry induced by the tilting of the two rings might give rise to the perturbation Hamiltonian which is responsible for the mixing of the Kramers states, allowing the quantum tunneling to occur. Dilution of the magnetic sites can reduce the dipole interaction, and the Zeeman splitting by applying dc field could break the degeneration between the Kramers states. As expected, low temperature quantum tunneling was quenched in such experiments, and the increment of out-of-phase susceptibility on cooling is suppressed (see SI, Figure S4). This kind of dc field breaking the degeneration may also be responsible for the observed field-induced slow magnetic relaxation in some other isolated lanthanide systems.[13]

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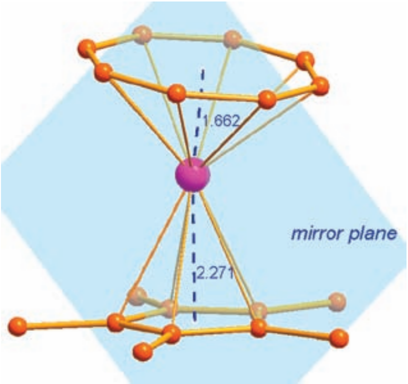

Figure 1. Schematic view of the title compound (Cp*)Er(COT). The purple sphere represents the Er(III) ion, while the two yellow rings are Cp* (bottom) and COT (upper), respectively. Hydrogen atoms are omitted for clarity.

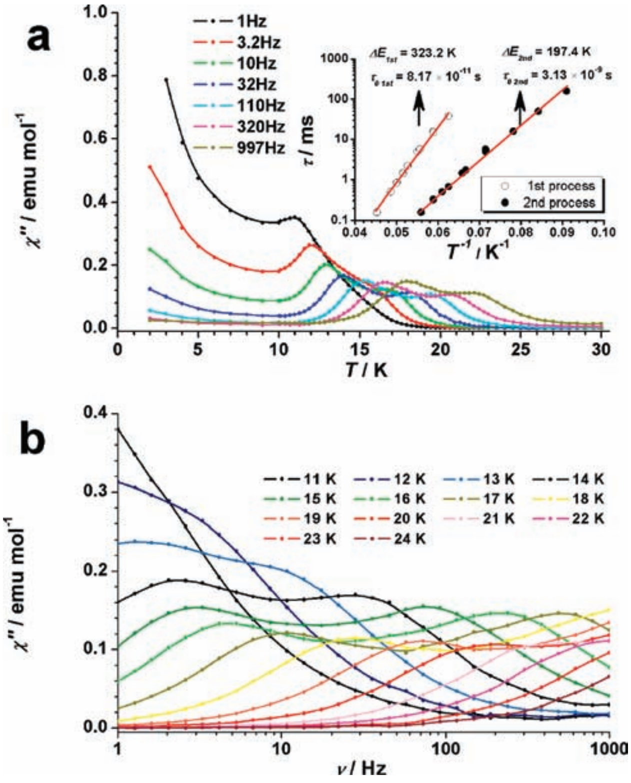

Figure 2. Out-of-phase of ac susceptibility at various temperatures and frequencies in the absent of dc field. (a) χ'' against temperature range from 2 to 30 K. (b) χ'' against frequency from 1 to 1000 Hz. Inset, Arrhenius analysis of the two relaxation processes.

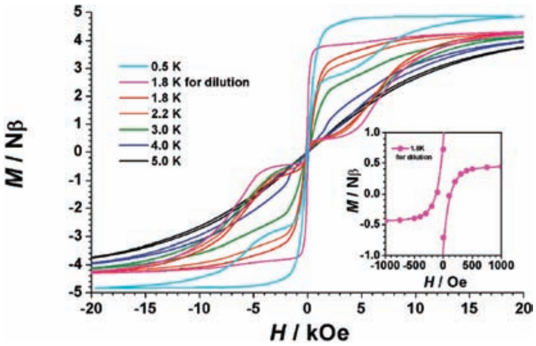

Figure 3. Hysteresis loops at different temperatures recorded on powder sample. The purple line and inset correspond to the hysteresis loop measured on the sample with 20 times magnetic site dilution at 1.8 K.

In the temperature range from 10 to 20 K two evident sets of peaks were observed, indicating the existence of two additional relaxation processes. The magnetic site-dilution measurement indicates the single-ion origin of such relaxation behavior. In the plots of χ'' vs frequencies at 14−18 K, two evident peaks at each temperature support the inference of two relaxation processes (Figure 2b). Arrhenius analysis shows that both are thermally activated (Figure 2 inset. $\tau = \tau_0 \exp(\Delta E/k_B T)$, where $\tau_0 = 8.17 \times 10^{-11}$ s, $\Delta E = 323$ K for one set, and $\tau_0 = 3.13 \times 10^{-9}$ s, $\Delta E = 197$ K for another). The energy barrier of 323 K is much higher than those of cluster-based SMMs[14] or single-chain magnets,[15] and is among the highest of the handful of single-ion magnets hitherto known.[6−10] Thermally activated relaxation in lanthanide compounds is generally attributed to the Orbach process between low-lying states generated from zero-field splitting, and the energy gap between the ground state and first excited state can be deduced from the barrier. However, it is intriguing that there are two thermally activated relaxation processes with different energy barriers. We believe that the aforementioned two stable conformers in the crystal are responsible for the two processes, consistent with magnetic susceptibility fitting results using ligand field theory as discussed in the following. The ac susceptibility data from 14 to 18 K can be fitted to a linear combination of two modified Debye models:[16]

$$\chi_{\text{total}}(\omega) = \chi_S + (\chi_T - \chi_S)\left[\frac{\beta}{1 + (i\omega\tau_1)^{1-\alpha_1}} + \frac{1-\beta}{1 + (i\omega\tau_2)^{1-\alpha_2}}\right]$$

The weight ratio of the two conformers is fitted to be 0.623:0.377 at 18 K, and the value is determined to be 0.624:0.376 by crystal refinement at 20 K (see SI, Figure S5 and Table S3). In comparison, the two thermally activated relaxation processes observed for the very first SMM Mn_{12} at about 2 and 5 K with energy barrier of 65 and 32 K, respectively, are attributed to the Jahn−Teller isomerism in the Mn_{12} cluster core.[17]

Magnetization hysteresis loops, the important phenomenon characteristic of magnetic bistability of magnets, were observed below 5 K on powder sample. Butterfly shaped hysteresis loops were recorded within ±2 T at an average scanning field speed of 550 Oe/min (Figure 3). On lowering the temperature to 0.5 K with the ^{3}He system, hysteresis was also observed at an average scanning speed of 320 Oe/min. On measuring the 20 times magnetic site dilution powder sample of the molecule at 1.8 K, loop could be recorded as well, indicating that it is the single-ion feature rather than the long-range ordering or magnetic interaction that responsible for the hysteresis. A remanence of 0.87 Nβ and a coercive field of 100 Oe was also observed at 1.8 K (Figure 3 inset). The emergence of the slight coercive field on the diluted sample may come from the suppressed quantum tunneling. The slow relaxation of the magnetization is also responsible for the large difference between the zero-field (ZFC) and field-cooled (FC) susceptibilities at 10 Oe to 10 kOe below 5 K consistent with the

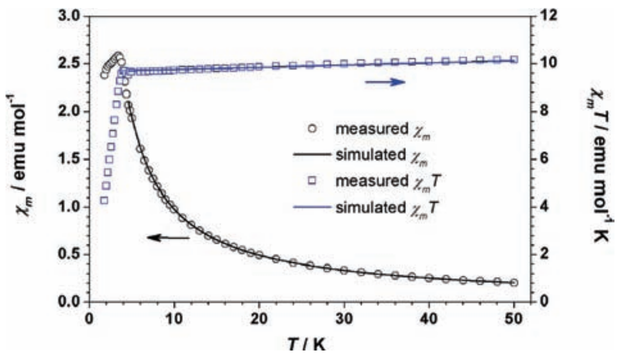

Figure 4. Plots of χ_m (black circle and line) and $\chi_m T$ (blue square and line) versus temperature, measured data and fitted data are plotted in circle/square and line respectively.

butterfly shaped loops. A much smaller coercive field of hysteresis may be typical for lanthanide containing single-ion magnet, and this may be attributed to the quantum tunneling between ground state as discussed previously. However, it is strange that the prominent quantum tunneling can be observed despite the enormous energy barrier as well as some previous well studied cases. It is an open question to overcome the quantum tunneling process and lack of coercive field to produce smaller magnets like this case with large coercivities intrinsically.

It is generally believed that the local symmetry of a metal ion's coordination environment is essential to its anisotropy and that an Ising-type magnetic anisotropy is usually generated by a ligand field with one high-order single axis C_n ($n > 2$). The Er(III) ion is situated in a low-symmetry coordination sphere environment with the overall symmetry of the molecule being C_s. Nevertheless, by approximation of the tilted carbon rings into parallel and considering the delocalized π type electron cloud on both ligands, the local symmetry of Er(III) may be approximated to be $C_{\infty v}$. Fitting the magnetic susceptibility measured at 1 kOe below 50 K to the ligand field symmetry of $C_{\infty v}$, the fine electronic structures are investigated with ligand field theory (Figure 4).[18] The analysis shows that the ground state is $|M_J = \pm 15/2\rangle$, which is indeed an Ising-type ground state, with the first excited state $|M_J = \pm 13/2\rangle$ lying 273 K above. This value lies precisely in the middle of the two values by the Arrhenius analysis (260 K). However, due to the approximation, the Ising nature of the molecule remains a hypothesis before a single crystal data is obtained.

Generally, permanent magnets possess 10^{20} atoms roughly, and multiple domains in micrometer meter scale have 10^{10} atoms; for the normal single-molecule magnets it is at the order of 10^2 atoms, and in our case it contains only 19 non-hydrogen atoms with a diameter of about 0.5 nm. Due to the high weight percentage of the magnetically active metal ions in the otherwise purely organic molecule, the crystals of the title compound could be easily lifted by a Nd−Fe−B magnet at room temperature (see SI, Figure S8 and movie).

In summary, an organometallic mixed sandwiched Er(III) molecule, was prepared and structurally characterized. Its single ion magnetic features have been also unambiguously demonstrated. The ring-shaped aromatic ligands are believed to generate higher local symmetry and responsible for the observed magnetic properties (magnetization hysteresis, two thermal relaxation processes with high energy barriers). The deviation from the axial symmetry induced by the tilting of the two rings may give rise to the quantum tunneling at zero static field and low temperature. Further research on this kind of molecule is under way.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedure, Figures S1−S8, Tables S1−S3, the cif files for the crystal at 120 K, 20, and 10 K, and the movie for the toy magnet moving the crystals. This material is available free of charge via the Internet at http://pubs.acs.org.

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