Million-fold Relaxation Time Enhancement across a Series of Phosphino-Supported Erbium Single-Molecule Magnets

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ABSTRACT: Maintaining strong magnetic anisotropy in the presence of collective spin interactions has become a defining challenge in the advancement of single-molecule magnet (SMM) research. Herein we demonstrate effective decoupling of these often competing design goals in a series of new phosphino-supported SMMs containing the anisotropic \([\text{Er(COT)}]^{±} (\text{COT}^{2−} = \text{cyclooctatetraene dianion})\) subunit. Across this series, a magnetic nuclearity increase from 1 to 2 and subsequent optimization of the relative local anisotropy axis orientation results in dramatic improvements to the long time scale behavior. Specifically, we observe a 6 orders of magnitude increase in relaxation time at 2 K and a consequent open magnetic hysteresis up to 6 K. This drastic scaling of the magnetic dynamics tracks monotonically with the introduction and approach to parallel of the angle between intramolecular anisotropy axes. These results illustrate the powerful implications of fully controlling direction and magnitude of anisotropy in the design of scalable SMMs.

The research field of single-molecule magnetism was founded upon the discovery that superparamagnetism could exist in discrete, molecular form. The molecular nature of a single-molecule magnet (SMM) means that the time scale on which it can maintain magnetic information is determined not by a classical energy barrier but by the energy spacing of its electronic states and the allowedness of transitions between them. This fact implies that targeted magnetic properties can be explicitly programmed into a molecule through rational synthesis as increasingly complex preparative methods and theoretical models are incorporated into the SMM design repertoire. Recently, an intensive focus on optimizing the electronic structure of single-ion lanthanide systems has developed since they offer simple and intuitive magnetostructural models for generating anisotropy via the combined spin−orbit and crystal field interactions. Continuing development of these models has led to an expanding array of remarkable SMMs which are quickly advancing the field toward quantum mechanical limits of anisotropy.

Progress, however, need not be limited to a single spin center; these complexes could be employed as building units to create larger collective-spin structures mimicking strong bulk magnetic materials with molecular precision, tunability, and the potential for incorporation into molecule-based devices. Although this general idea has been explored in various contexts, it has seen little success in achieving collective behavior while retaining the highly anisotropic nature of the individual units. The crux of this issue lies in the need to systematically introduce metal-bridging ligands without concomitant loss of single-ion anisotropy. Furthermore, the relative easy-axis orientations between anisotropy generators must be properly aligned in order to obtain a material which not only preserves but augments the magnetically axial nature of its components. This point is particularly crucial since low-temperature relaxation processes (viz. quantum tunneling of the magnetization, QTM), which often shortcut high-temperature effective magnetic barriers, are directly influenced by the axiability of exchange-coupled ground states.

Though a formidable challenge, it has been suggested that basic design criteria for strong and multifunctional molecule-based magnets can be met through a bottom-up or building-block strategy. Here, the goal is to develop anisotropic units which are amenable to incorporation into larger structures. One such approach is based on SMMs with anisotropy that can be enforced largely by a single metal−ligand interaction. For example, SMMs such as \([\text{Er(COT)}]^{2−} (\text{COT}^{2−} = \text{cyclooctatetraene dianion})\) take advantage of the interaction between the \(\text{Er}^{3+} J = 15/2\) ground state and the \(\text{COT}^{2−}\) crystal field. Here, two defining characteristics are observed: (1) the highest moment \(M_J = ±15/2\) states are stabilized compared to other projections of the total angular momentum, leading to SMM behavior, and (2) the orientation of the main magnetic axis has a well-defined real-space representation—namely, the vector normal to the \(\text{COT}^{2−}\) ring. Importantly, a single Er−COT interaction is capable of preserving both of these characteristics, despite replacement of the remainder of its coordination sphere with low-symmetry components. Systems with such magnetic robustness against coordinative perturbations form a solid basis for a rational SMM building-block approach. This inert anisotropy resulting from a judicious metal−ligand combination is a design principle we have referred to as metal−ligand pair anisotropy.

Herein we present an initial investigation on the efficacy of the Er−COT unit as a magnetic building block. By utilizing the robust nature of local Er−COT anisotropy axes, we demonstrate how control over nucleus and intramolecular anisotropy axes angles in coupled systems has far-reaching effects on static and dynamic magnetic properties. We have synthesized four new phosphino-supported SMMs containing the anisotropic \([\text{Er(COT)}]^{2−}\) fragment (Scheme 1): mononuclear \(\text{Er(COT)}(\text{DMPE}) (\text{DMPE} = 1,2\text{-bis(dimethyl-..."}
phosphino)ethane) \(1\), and dinuclear \([\text{Er}^3\text{COT}]_2\) \(2\), \([\text{Er}^3\text{COT}]_3\) \(3\), and \([\text{Er}^3\text{COT}]_4\) \(4\). The relative angle of Er–COT axes has been varied from 113.6° to 180.0° in 2–4 by changing the bulk on the supporting phosphine, resulting in a 100-fold increase in relaxation time \(T_1\) at 2 K. Furthermore, the importance of nuclearity is drastically highlighted by the 6 orders of magnitude improvement of \(T_1\) in 4 over 1.

Since our previous work with asymmetric mononuclear systems had shown strong evidence that the Er–COT vector is a good proxy for the ground-state anisotropy axis, we set out to design a series of dinuclear complexes with two additional components: a simple magnetic coupling bridge and a weakly coordinating, non-coupling bridge solely designed to alter the angle between Er–COT axes. To achieve these goals, a relatively rare synthetic target was employed — molecules with lanthanide–phosphine coordination bonds. Er–P adducts 1–4 were prepared via a two-step inert atmosphere synthetic route (Scheme 1). Initially, a Lewis acid–base competition reaction between \(\text{Er}^{3+}\) and \([\text{Er}^{3}\text{COT}]_2\) THF was employed to displace THF from the lanthanide and produce a coordinatively reactive, solvent-free intermediate. Volatile AlMe\(_3\) THF was removed in vacuo, and a non-crystalline, insoluble material conforming to the molecular formula \([\text{Er}^{3}\text{COT}]I\) was isolated. Crystals of 1–4 were obtained from reaction of \([\text{Er}^{3}\text{COT}]_2\) with DMPE, DPPE, DPPM, and MDPP, respectively, followed by vapor diffusion of pentane into the reaction mixtures. In the solid state, 1–4 are stable at room temperature for several weeks, yet, consistent with the weak nature of the Ln–P bonding, exposure to ppm levels of coordinating solvent results in their degradation.

Solid-state structures of 1–4 were determined by single-crystal X-ray crystallography using a Mo K\(\alpha\) source (Figure 1 and Table 1, Figures S1–S4). These structural determinations clearly reveal that the steric demand imposed by a coordinating phosphine plays an important role in determining the nuclearity of the resulting complexes. The least demanding ligand utilized, DMPE (Tolman cone angle\(^{10}\) \(\theta_{\text{Tol}} = 107°\)), is able to chelate the Er\(^{3+}\) center in an \([\text{Er}^{3}\text{COT}]_2\) fragment and thus stabilizes mononuclear 1. Ligand cone angles of DPPE, DPPM, and MDPP are larger (\(\theta_{\text{Tol}} = 125, 121,\) and 136°, respectively), and evidently only a single Er–P interaction is possible. In the absence of coordinating solvent, the vacant coordination site forms a \(\mu_2\)-interaction with a second \([\text{Er}^{3}\text{COT}]_2\) fragment, and consequently 2, 3, and 4 are dinuclear. Of these three, only complex 4 exhibits crystallographically enforced inversion symmetry at its center. Complexes 2 and 3, on the other hand, have been determined to be pseudo-symmetric\(^{11}\) above a threshold error value (eq S1, \(E = 0.37\)). Given their range of steric demands, these phosphines are effective directors of the local Er–COT axes whose relative angles, \(\theta_{\text{Er}-\text{COT}}\), increase from 113.6° to 134.0° in 2, 3, and 4, respectively.

Using input geometries determined from crystallographic data, electronic structures of 1–4 were modeled with MOLCAS 8.2\(^{12}\) via complete active space self-consistent field (CASSCF) techniques (Table 2). Understanding single-ion anisotropy was the primary focus of this \(ab\) \textit{initio} study, and consequently one Er\(^{3+}\) ion in the symmetry-related pairs (vide

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**Scheme 1. Synthesis of Phosphine-Supported [Er(COT)I] Derivatives**

![Scheme 1](image)

**Table 1. Selected X-ray Crystallographic Structural Parameters**

<table>
<thead>
<tr>
<th></th>
<th>(d_{\text{COT}}) (Å)</th>
<th>(d_{\text{Er-P}}) (Å)</th>
<th>(\theta_{\text{COT}}) (deg)</th>
<th>symm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7598(17)</td>
<td>2.9260(14)</td>
<td>113.64(2)</td>
<td>C(_2)</td>
</tr>
<tr>
<td>2</td>
<td>1.7321(3)</td>
<td>2.9923(14)</td>
<td>132.53(12)</td>
<td>(\sigma)</td>
</tr>
<tr>
<td>3</td>
<td>1.713(3)</td>
<td>2.9922(14)</td>
<td>135.40(12)</td>
<td>(\epsilon)</td>
</tr>
<tr>
<td>4</td>
<td>1.745(3)</td>
<td>2.9573(14)</td>
<td>180.00(2)</td>
<td>(i)</td>
</tr>
</tbody>
</table>

*Entries with two lines represent lower and upper limits, respectively.*

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**Figure 1.** Solid-state structures of 1–4 with spheres representing Er (pink), I (purple), P (orange), and C (gray). Hydrogen atoms and outer-sphere solvent molecules have been omitted for clarity. Colored lines depict the direction of the Er–COT\(_{\text{entral}}\) vectors in each molecule.

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The dinuclear complexes display similar declines in (centroid) axes (−decline as higher-energy MJ matrix elements connecting states within the which is close to the value expected for an ensemble of Er3+ S14, S18, and S22). At 300 K, between 2 and 300 K under DC magnetic fields ranging (simultaneously components (|H|f = 1000 Oe) were collected between 2 and 300 K, and measured data were plotted as the thermal susceptibility product χM versus temperature (Figures S11, S14, S18, and S22). At 300 K, χM(T = 11.8 cm3 K mol−1 for 1, which is close to the value expected for an ensemble of Er3+ ions in the free-ion approximation (χM(Tcalc) = 11.48 cm3 K mol−1, J = 15/2, g = 6/5). Upon cooling, χM(T displays a steady decline as higher-energy M1 states become depopulated, and below 3 K an abrupt drop to χM(T = 6.2 cm3 K mol−1 is evident. The dinuclear complexes display similar declines in χM(T with temperature from their 300 K values: χM(Texp = 24.6 (2), 21.7 (3), and 22.8 (4) cm3 K mol−1 (χM(Tcalc = 22.96 cm3 K mol−1). Below 15 K, 2, 4 show a rise in χM(T versus T which is indicative of a net ferromagnetic intramolecular interaction between Er3+ centers. Although ferromagnetic interactions are far less common in molecular magnetism than antiferromagnetic interactions, this qualitative result is reminiscent of the coupling observed in a structurally similar chloride-bridged compound, [Er(μ-Cl)(COT)(THF)2]24 Further experimental and computational studies expanding on the prevalence and nature of this coupling are ongoing. Isothermal magnetization measurements were collected between 2 and 300 K under DC magnetic fields ranging from −7 to 7 T (Figure 2, Table 3, and Figures S11, S14, S18, and S22, 10.1 Oe s−1 sweep rate). At 2 K, each complex displays typical saturation behavior in the high-field limit (Msat = 5.0, 9.6, 8.9, and 9.9 μB mol−1 for 1−4, respectively), and magnetic hysteresis is observed when the field is swept from 171 to 0 T. Typical of unoptimized SMMS, the hysteresis of 1 and 2 is waist-restricted, and neither compound exhibits appreciable remanent magnetization, Mreman on this time scale. This type of hysteresis is commonly attributed to QTM, which is observed when transition rates between ground-state doublets (or pseudo-doublets in non-Kramers systems) are high with respect to the measurement rate. In stark contrast to 1 and 2, compounds 3 and 4 display open hysteresis with similar coercive fields. These results demonstrate an extreme alteration in the magnetic dynamics generated by a simple synthetic variation. Taking into account their comparable ab initio single-ion electronic structures, the lack of hysteresis in 2 and presence of it in 3 and 4 highlight the importance of intramolecular anisotropy axis alignment in long time scale magnetic performance. Open hysteresis at any temperature is rarely displayed by Er-based magnets, and its observation here implies that single-ion anisotropy generated by the Er−COT metal−ligand pair can be augmented significantly via linking with a single metal center but only if the synthetic design accounts for alignment of the anisotropy axes.

Because of the marked differences in their low-temperature magnetization data, the relaxation dynamics of 1−4 were studied using AC susceptibility and DC relaxation measurement techniques. Short time scale relaxation times τ for all compounds were extracted from AC susceptibilities by simultaneously fitting the in-phase (S) and out-of-phase (S) components (HDC = 0 Oe, f = 0.1−1000 Hz) to a generalized Debye equation14 (Figures S12, S15, S19, and S23). Cole−Cole plots (S vs S) of these data form semicircles with low eccentricities which indicate that only a single relaxation time is associated with each measurement temperature. Long time scale relaxation times were extracted from DC magnetic relaxation data collected at 2−3 K for 2 and 2−4 K for 3 and 4. An idealized exponential analysis of the

**Table 2. Selected Theoretical Magnetic Parameters**

<table>
<thead>
<tr>
<th>gJ</th>
<th>gJ′</th>
<th>gJ′′</th>
<th>θDW (deg)</th>
<th>KD1 (cm−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0027</td>
<td>0.0048</td>
<td>17.7215</td>
<td>6.07</td>
</tr>
<tr>
<td>2</td>
<td>0.0004</td>
<td>0.0006</td>
<td>17.8816</td>
<td>1.29</td>
</tr>
<tr>
<td>3</td>
<td>0.0000</td>
<td>0.0000</td>
<td>17.8808</td>
<td>0.70</td>
</tr>
<tr>
<td>4</td>
<td>0.0006</td>
<td>0.0009</td>
<td>17.9051</td>
<td>1.48</td>
</tr>
</tbody>
</table>

**Table 3. Selected Experimental Magnetic Parameters**

<table>
<thead>
<tr>
<th>Hc (T)</th>
<th>Ueff (cm−1)</th>
<th>τa (ns)</th>
<th>τs (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75.6 (15.2)</td>
<td>69 (43)</td>
<td>1.43 (3) \times 10−3</td>
</tr>
<tr>
<td>2</td>
<td>183.6 (3.5)</td>
<td>0.19 (4)</td>
<td>35.3 (7)</td>
</tr>
<tr>
<td>3</td>
<td>0.293</td>
<td>201.5 (1.3)</td>
<td>0.098 (7)</td>
</tr>
<tr>
<td>4</td>
<td>0.288</td>
<td>175.9 (5.0)</td>
<td>0.18 (4)</td>
</tr>
</tbody>
</table>

*Values in parentheses represent 95% confidence intervals.*
long time scale behavior indicated that multiple relaxation processes were operant at low temperature, and therefore characteristic relaxation times were extracted using a stretched exponential of the form

\[ M(t) = M_f + (M_0 - M_f) \exp \left( -\frac{t}{\tau} \right)^\beta \]

where \( M_0 \) and \( M_f \) are the initial and final measured moments, respectively (Figures S16, S20, and S24). Analysis of the combined Arrhenius plot of all extracted relaxation times (Figure 3, Table 3) clearly reveals several key points about the superparamagnetic behavior. In the high-temperature limit for 1–4, \( \ln(\tau) \) varies linearly with \( 1/T \), and here a thermally activated overbarrier Orbach relaxation mechanism is active. Arrhenius fits to data in this region show an approximate 100 cm\(^{-1}\) increase in effective barrier \( U_{\text{eff}} \) between 1 and 2–4. The similarity in barrier heights for 2–4 indicates that they share comparable low-energy crystal field manifolds irrespective of their small structural differences—this result, in conjunction with our \textit{ab initio} study, indicates that the second excited Kramers doublet, KD\(_2\), is a part of the overbarrier relaxation pathway. We note that the effects of magnetic coupling and intramolecular axis orientation are presumably negligible in this high-temperature regime. Below 10 K, \( \tau \) values for 1 display little dependence on \( T \), and fast QTM processes explain these data and the lack of open hysteresis. Relaxation times gathered from DC relaxation measurements for 2–4 show a weak but non-zero dependence on temperature. Importantly, at 2 K, \( \tau \) values span a 6 orders of magnitude range going from mononuclear 1 to anisotropy-axis-aligned dinuclear 4 and a 2 orders of magnitude range from 2 to 4. This result agrees well with behavior observed in field-dependent magnetization studies, and it further highlights the crucial roles that nuclearity and intramolecular axis orientation play toward stabilizing robust magnetic ground states.

In summary, we have synthesized one mononuclear (1) and three dinuclear (2–4) phosphine-supported SMMs containing the anisotropic Er–COT fragment. Nuclearity and Er–COT axis orientations in these complexes were rationally controlled by varying steric bulk on the weakly coordinated phosphine ligands. An \textit{ab initio} analysis of 1–4 revealed that COT\(^{2-}\) is effective at generating spatially well-defined anisotropy along the Er–COT vector, and, consequently, simple magnetostructural correlations could be drawn from the experimental and magnetic data. Highlighting the validity of Er–COT as a robust magnetic building unit, a million-fold increase in maximum relaxation time was measured between 1 and 4. This enhancement offers a stark demonstration of how magnetic coupling of aligned anisotropy axes can prevent the breakdown of Orbach-type dynamics and augment long time scale SMM performance. Furthermore, the magnitude of this effect in coupled systems was shown to be strongly dependent upon the relative local anisotropy, leading to a 100-fold difference in the maximum relaxation time as this vector was synthetically tuned from 113.6° to 180.0° in 2–4. We envision that isolation and tuning of important design parameters based on the Er–COT framework will continue to provide magnetostructural insights toward the goal of encoding magnetic properties into molecular materials through rational synthetic design.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b13514.

Experimental procedures and physical and computational data for all new compounds, including eq S1, Figures S1–S30, and Tables S1–S12 (PDF)

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**Notes**

The authors declare no competing financial interest.

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