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## Terbocenium: completing a heavy lanthanide metallocenium cation family with an alternative anion abstraction strategy†

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**A series of heavy lanthanide metallocenium cations [Ln(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup> (Ln = Y, Gd, Dy, Ho, Er, Tm, Yb, Lu; Cp<sup>ttt</sup> = C<sub>5</sub>H<sub>2</sub><sup>t</sup>Bu<sub>3</sub>-1,2,4) were recently prepared by halide abstraction of [Ln(Cp<sup>ttt</sup>)<sub>2</sub>(Cl)], but curiously the Tb analogues remained elusive. Here we report an alternative anion abstraction strategy to access [Tb(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup>, completing the heavy [Ln(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup> family.**

Single-molecule magnets (SMMs) have potential for high-density data storage, but all examples to date only show magnetic hysteresis with expensive liquid helium cooling.<sup>1</sup> Significant research effort has concentrated on achieving SMMs that operate under cheaper liquid nitrogen temperature regimes (>77 K), and lanthanide (Ln) systems are widely considered to be the most promising candidates to realise this goal.<sup>2</sup> Since the first Ln SMM was reported in 2003,<sup>3</sup> systems containing Tb<sup>3+</sup> ions held record magnetic hysteresis temperatures up to 14 K.<sup>4</sup> However, these landmark examples were recently superseded by the dysprosocenium complex [Dy(Cp<sup>ttt</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Cp<sup>ttt</sup> = C<sub>5</sub>H<sub>2</sub><sup>t</sup>Bu<sub>3</sub>-1,2,4), which exhibits magnetic bistability up to 60 K.<sup>5</sup> Previous efforts to synthesise isolated Ln metallocenium cations were thwarted by the tendency for large Ln<sup>3+</sup> cations to exhibit equatorial interactions with counterions.<sup>6</sup> The combination of two bulky Cp<sup>ttt</sup> ligands and the weakly coordinating anion [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> was found to be sufficient to prevent such interactions in [Dy(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup>, providing it with enhanced magnetic properties over closely related [Dy(Cp<sup>\*</sup>)<sub>2</sub>{μ-(Ph)<sub>2</sub>BPh<sub>2</sub>}] (Cp<sup>\*</sup> = C<sub>5</sub>Me<sub>5</sub>).<sup>7</sup>

Prior to the report of [Dy(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup>, the synthetic community were guided by design criteria to develop improved Ln SMMs:<sup>8,9</sup> for Ln<sup>3+</sup> ions whose most magnetic *m<sub>J</sub>* projections have oblate-spheroidal electron densities (such as Tb<sup>3+</sup> and Dy<sup>3+</sup>), axial ligand fields were predicted to increase the effective barrier to magnetisation reversal (*U<sub>eff</sub>*). Following

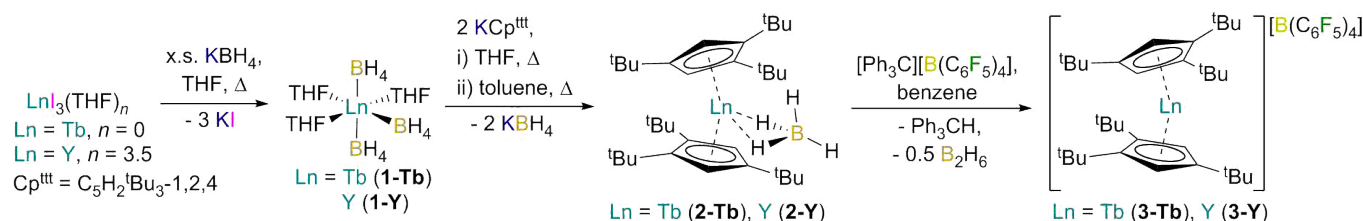
these strategies record *U<sub>eff</sub>* values were achieved for Dy<sup>3+</sup> SMMs, but these molecules did not exhibit magnetic hysteresis at higher values than Tb<sup>3+</sup> systems that preceded them.<sup>10-13</sup>

We recently showed that the slow magnetic relaxation of [Dy(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup> is due to the constrained metal-ligand vibrational modes of the *bis*-Cp<sup>ttt</sup> framework;<sup>5a</sup> to further rationalise these remarkable magnetic properties we synthesised a series of structurally analogous heavy Ln metallocenium complexes, [Ln(Cp<sup>ttt</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Ln = Y, Gd, Ho, Er, Tm, Yb, Lu) by halide abstraction of the parent [Ln(Cp<sup>ttt</sup>)<sub>2</sub>(Cl)].<sup>5a,14</sup> Analysis of the magnetic relaxation mechanisms of these systems revealed that anomalously low Raman exponents are a defining feature of [Ln(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup> cations, and these return to 'normal' values when Cl<sup>-</sup> anions bind to the Ln<sup>3+</sup> ions.<sup>14</sup> Frustratingly, we were unable to access the homologous Tb<sup>3+</sup> cation [Tb(Cp<sup>ttt</sup>)<sub>2</sub>]<sup>+</sup>, as the attempted synthesis of the precursor [Tb(Cp<sup>ttt</sup>)<sub>2</sub>(Cl)] from TbCl<sub>3</sub> and two equivalents of KCp<sup>ttt</sup> consistently gave oily residues containing Cp<sup>ttt</sup>H.<sup>14</sup> The previous successes of Tb<sup>3+</sup> SMMs made this omission significant, as we wished to compare the effects of the *bis*-Cp<sup>ttt</sup> ligand environment on the magnetic properties of the Kramers ion Dy<sup>3+</sup> (<sup>6</sup>H<sub>15/2</sub>) with its neighbouring non-Kramers ion Tb<sup>3+</sup> (<sup>7</sup>F<sub>6</sub>).

To address this impasse we prepared [Ln(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub>] (**1-Ln**; Ln = Tb, Y) from the parent LnI<sub>3</sub> and a large excess of KBH<sub>4</sub> in THF by adapting literature procedures;<sup>15,16</sup> diamagnetic Y<sup>3+</sup> surrogates allow analogous complexes to be studied by NMR spectroscopy (Scheme 1). Treatment of **1-Ln** with two equivalents of KCp<sup>ttt</sup><sup>17</sup> gave [Ln(Cp<sup>ttt</sup>)<sub>2</sub>(BH<sub>4</sub>)] (**2-Ln**; Ln = Tb, Y) by salt metathesis, in common with the related syntheses of [Ln(Cp<sup>ttt</sup>)<sub>2</sub>(BH<sub>4</sub>)] (Ln = La,<sup>16</sup> Tm<sup>18</sup>). Gratifyingly, the separate reactions of **2-Ln** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>19</sup> in benzene gave the terbocenium complex [Tb(Cp<sup>ttt</sup>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**3-Tb**) and the previously reported Y analogue **3-Y**.<sup>5a</sup> The borohydride anion acts as a masked hydride to give Ph<sub>3</sub>CH, with an entropic driving force provided by the formation of half an equivalent of gaseous diborane. In agreement with previous studies,<sup>14</sup> we found that samples of **3-Ln** recrystallised from DCM layered with hexane decompose rapidly at room temperature, thus these were stored and manipulated at -25 °C.

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†Electronic Supplementary Information (ESI) available: Full synthetic details, crystallography, UV/Vis/NIR, NMR, FTIR, and EPR spectra, magnetism and *ab initio* calculations. CCDC 1844350–1844354. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of 1-3-Ln (Ln = Tb, Y).

The analytical data obtained for **3-Tb** are consistent with homologous complexes;<sup>5,14,16,18,20</sup> the data for **2-Ln** are similar to  $[\text{Ln}(\text{Cp}^*)_2(\text{BH}_4)]$  (Ln = La,<sup>16</sup> Dy<sup>20</sup>), and the characterisation data for **3-Y** has been reported previously.<sup>5a</sup> In common with the synthesis of  $[\text{La}(\text{BH}_4)_3(\text{THF})_4]$  from  $\text{LaI}_3$ ,<sup>16</sup> microanalysis and single crystal XRD data indicated that **1-Ln** contained iodide impurities (<15%), but these could not be detected in **2-Ln**. The paramagnetism of **3-Tb** precluded assignment of its <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, as previously reported for **3-Gd**.<sup>14</sup> However, paramagnetically shifted signals for  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  anions were seen in the <sup>11</sup>B (−27.49 ppm) and <sup>19</sup>F (*meta*: −182.42, *para*: −172.46, *ortho*: −144.60 ppm) NMR spectra of **3-Tb**; similar shifts were seen for the **3-Ln** series.<sup>14</sup> The <sup>11</sup>B NMR spectrum of **2-Tb** was featureless, but paramagnetically shifted <sup>1</sup>Bu group signals were seen in the <sup>1</sup>H NMR spectrum.

The solid state structures of **1-3-Ln** were determined by single crystal XRD (see Figs. 1 and 2 for the structures of **2-Tb** and the cation of **3-Tb-CH<sub>2</sub>Cl<sub>2</sub>**, see ESI for other structures; **1-Y**<sup>21</sup> and **3-Y**<sup>5a</sup> have been reported previously but we obtained a new dataset for **1-Y**). Complex **1-Tb** is structurally analogous to **1-Y**, with a *pseudo*-distorted octahedral structure and a meridional arrangement of ligands. As expected, the larger Tb<sup>3+</sup> centre (six-coordinate ionic radii, pm: Tb<sup>3+</sup>, 0.923; Y<sup>3+</sup>, 0.900)<sup>22</sup> causes **1-Tb** to exhibit longer bond distances than **1-Y**. The same trends are seen for **2-Y** and **2-Tb**, which are disordered over two sites but are isostructural with the Dy<sup>3+</sup> congener: the mean Tb⋯Cp<sub>centroid</sub> distance (2.418(3) Å) and the Cp<sub>centroid</sub>⋯Tb⋯Cp<sub>centroid</sub> angle (148.13(5)°) in **2-Tb** are similar to the corresponding metrical parameters in  $[\text{Dy}(\text{Cp}^*)_2(\text{BH}_4)]$  (2.394(2) Å and 149.01(6)°).<sup>20</sup> Complex **3-Tb** has a shorter mean Tb⋯Cp<sub>centroid</sub> distance (2.332(6) Å) and a larger Cp<sub>centroid</sub>⋯Tb⋯Cp<sub>centroid</sub> angle (152.2(2)°) than for **2-Tb**. The  $[\text{Tb}(\text{Cp}^*)_2]^+$  cation of **3-Tb** is best compared with the Dy<sup>3+</sup> homologue **3-Dy**, which exhibits a Cp<sub>centroid</sub>⋯Dy⋯Cp<sub>centroid</sub> angle of 152.56(7)° and a mean Dy⋯Cp<sub>centroid</sub> distance of 2.316(3) Å.<sup>5</sup> Most importantly there are no equatorial interactions seen between the  $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  anion and the Tb<sup>3+</sup> centre of **3-Tb** in the solid state [closest Tb⋯F distance: 6.336(6) Å], hence the *bis*-Cp<sup>\*</sup> framework can be considered to be the sole contributor to crystal field (CF) splittings in **3-Tb**.

The magnetic susceptibility temperature products ( $\chi_{\text{MT}}$ ) of **2-Tb** (10.84 cm<sup>3</sup> K mol<sup>−1</sup> at 300 K) and **3-Tb** (11.60 cm<sup>3</sup> K mol<sup>−1</sup> at 260 K) were obtained for polycrystalline samples with SQUID magnetometry (Table S3). The high temperature values are lower than the free-ion Curie value for Tb<sup>3+</sup> (11.82 cm<sup>3</sup> K mol<sup>−1</sup>),<sup>6</sup> but are similar to that previously reported for  $[\text{Tb}(\text{Cp}^*)_2\{\mu\text{-(Ph)}_2\text{BPh}_2\}]$  (10.64 cm<sup>3</sup> K mol<sup>−1</sup>).<sup>7b</sup> The  $\chi_{\text{MT}}$  values for **2-Tb** and **3-Tb** (Fig. S25) show a gradual decrease with

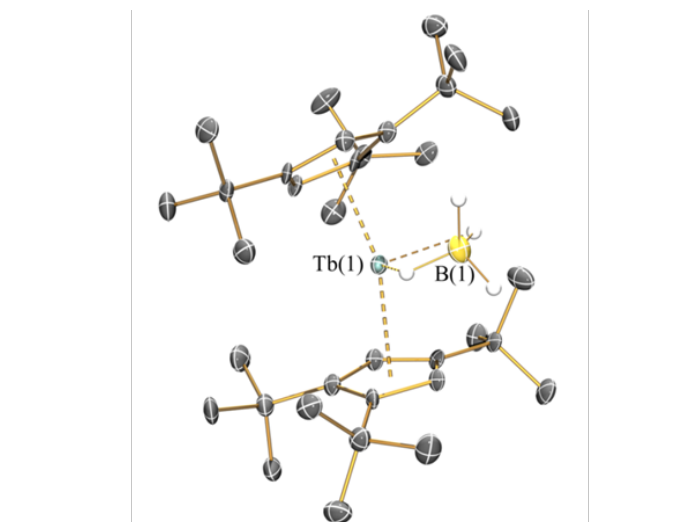


Fig. 1. Molecular structure of  $[\text{Tb}(\text{Cp}^*)_2(\text{BH}_4)]$  (**2-Tb**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms apart from those on B are omitted for clarity. Selected distances and angles: Tb1⋯Cpcentroid1, 2.420(2) Å; Tb1⋯Cpcentroid2, 2.415(2) Å; Tb1⋯B1, 2.714(5) Å; Cpcentroid1⋯Tb1⋯Cpcentroid2, 148.13(5)°.

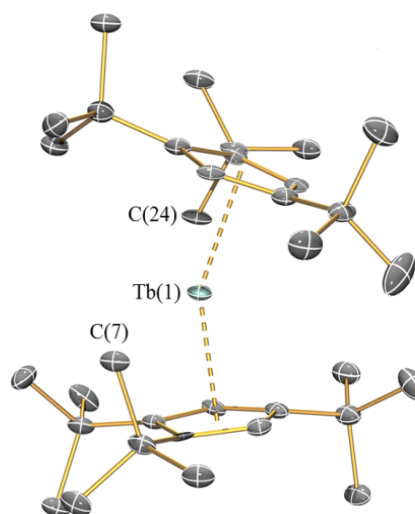
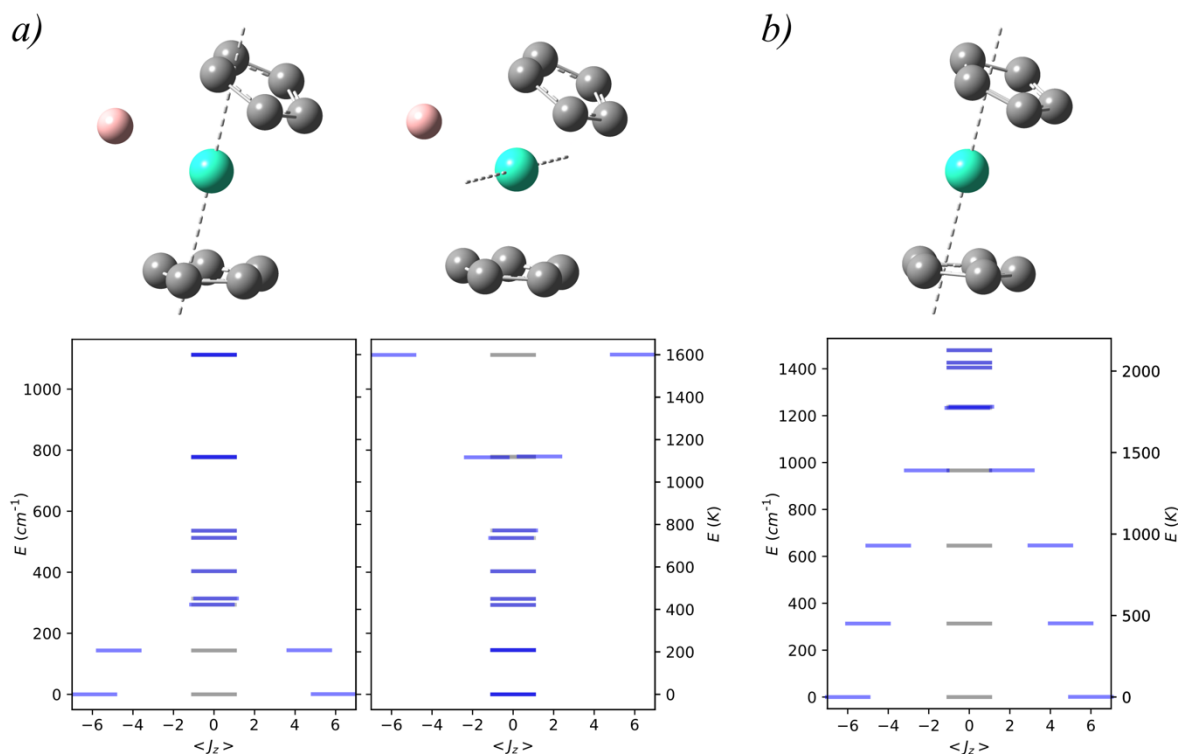


Fig. 2. Molecular structure of the cation of  $[\text{Tb}(\text{Cp}^*)_2][\text{B}(\text{C}_6\text{F}_5)_4] \cdot \text{CH}_2\text{Cl}_2$  (**3-Tb-CH<sub>2</sub>Cl<sub>2</sub>**) with selective atom labelling. Displacement ellipsoids set at 30 % probability level and hydrogen atoms, lattice solvent and anion are omitted for clarity. Selected distances and angles: Tb1⋯Cpcentroid1, 2.325(4) Å; Tb1⋯Cpcentroid2, 2.339(5) Å; Tb1⋯C7, 2.971(10) Å; Tb1⋯C24, 2.977(9) Å; Tb1⋯H, 2.5379(5) and 2.5097(5) Å; Cpcentroid1⋯Tb1⋯Cpcentroid2, 152.2(2)°.

temperature due to depopulation of excited CF states, reaching 9.30 and 9.06 cm<sup>3</sup> mol<sup>−1</sup> K for **2-Tb** (5 K) and **3-Tb** (2 K), respectively. All experimental  $\chi_{\text{MT}}$  values are close to those predicted by CASSCF-SO calculations, with minor discrepancies attributed to uncertainties in the diamagnetic corrections (Fig. S25). The low temperature magnetisation isotherms of **2-Tb** and **3-Tb** (Fig. S26) are in good agreement with calculated values, indicating that the calculations have captured the ground state wavefunctions accurately.



**Fig 3.** Electronic structure of (a) **2-Tb** and (b) **3-Tb**, calculated with CASSCF-SO. Grey and blue lines are electronic states under zero and an 0.1 T field applied along the quantization axis (dashed rod), respectively. (a, left) Quantisation axis is defined along  $g_3$  of the ground pseudo-doublet; (a, right); (b) quantisation axis is explained in the main text. <sup>t</sup>Bu groups and H atoms omitted for clarity.  $\langle J_z \rangle$  is the expectation value of  $J_z$  and is proportional to the magnetic moment.

Given the remarkable hysteretic properties of the  $[\text{Dy}(\text{Cp}^{\text{III}})_2]^+$  cation in **3-Dy**,<sup>5</sup> we studied the magnetisation dynamics of **2-Tb** and **3-Tb**. Complex **2-Tb** shows no out-of-phase signal in AC susceptibility measurements in zero field, however it shows signs of temperature dependent slow magnetic relaxation under an applied field of 0.1 T (Figs. S27 and S28). The relaxation rates are markedly temperature-dependent above *ca.* 6 K, however they approach a temperature-independent regime at lower temperatures, suggestive of quantum tunnelling of the magnetisation (QTM) with  $\tau_{\text{QTM}} \sim 0.9 \times 10^{-4}$  s (Fig. S29, Table S5). The data > 6 K can be modelled with either a power-law or an exponential temperature dependence (Table S5), however the exponential model suggests  $U_{\text{eff}} = 29$   $\text{cm}^{-1}$ , which our CASSCF-SO calculations rule out (see below). Therefore, we believe the thermally-activated relaxation to be a Raman-like process with  $C = 0.26$   $\text{s}^{-1} \text{K}^{-n}$  and  $n = 4.6$ . Compound **3-Tb** on the other hand shows slow magnetic relaxation in zero magnetic field (Figs. S30 and S31), where the temperature dependence of the relaxation rate displays power-law behaviour with coefficients  $C = 24$   $\text{s}^{-1} \text{K}^{-n}$  and  $n = 1.2$  (Fig. S32, Table S7). The  $n$  values for **2-Tb** and **3-Tb** are quite reduced from the value of  $n = 7$  traditionally expected for Raman relaxation in non-Kramers compounds,<sup>23</sup> however the values for **3-Tb** are similar to those for the related  $[\text{Ho}(\text{Cp}^{\text{III}})_2]^+$  cation in **3-Ho**, which has  $C = 3.4$   $\text{s}^{-1} \text{K}^{-n}$  and  $n = 2.9$ .<sup>14</sup> Indeed, we observe the same trend between **2-Tb/3-Tb** here as for the  $[\text{Ln}(\text{Cp}^{\text{III}})_2\text{Cl}]/[\text{Ln}(\text{Cp}^{\text{III}})_2]^+$  pairs, where the Raman exponent is much lower for the isolated metallocenium cation than for the neutral contact ion pair,<sup>14</sup> again suggesting that low Raman exponents are characteristic of the *bis*- $\text{Cp}^{\text{III}}$  framework. While a power-law temperature

dependence with  $n = 1$  is expected for the Direct relaxation process,<sup>23</sup> CASSCF-SO calculations (see below) suggest that **3-Tb** has a near-degenerate *pseudo*-doublet ground state, rendering Direct relaxation ineffective at zero magnetic field. However, despite the observation of slow magnetic relaxation in zero field, there is no significant opening of the magnetic hysteresis even at 2 K for **3-Tb** (Fig. S33). Field-cooled/zero-field-cooled susceptibility experiments show that while there is bifurcation below 20 K, and thus some slow relaxation, there is no clear maximum > 2 K, suggesting the absence of magnetic blocking (Fig. S34). We note that the SMM properties for **3-Tb** appear to be markedly worse than the related complex  $[\text{Tb}(\text{Cp}^*)_2\{\mu\text{-(Ph)}_2\text{BPh}_2\}]$  which shows Orbach-type relaxation with an effective barrier to magnetisation reversal of  $U_{\text{eff}} = 221$   $\text{cm}^{-1}$ .<sup>7b</sup> However, those data were collected under a 0.24 T applied field and the magnetic relaxation of  $[\text{Tb}(\text{Cp}^*)_2\{\mu\text{-(Ph)}_2\text{BPh}_2\}]$  in zero field is actually 20 – 60 times faster than **3-Tb** under the same conditions; notably,  $[\text{Tb}(\text{Cp}^*)_2\{\mu\text{-(Ph)}_2\text{BPh}_2\}]$  also does not show open magnetic hysteresis.<sup>7b</sup>

The lack of a barrier to magnetisation reversal and hysteresis for **3-Tb** compared to **3-Dy** was unexpected, thus we determined the electronic structures of **2-Tb** and **3-Tb** with complete active space self-consistent field spin-orbit (CASSCF-SO) calculations using MOLCAS 8.0<sup>24</sup> (Fig. 3, see ESI for full details). For **2-Tb** we find a highly axial ground pseudo-doublet with the main  $g$ -value approaching that for the  $m_j = \pm 6$  state (Tables S8 and S9). Along with the first excited state (dominated by  $m_j = \pm 5$ ), the ground *pseudo*-doublet is quantised along the  $\text{Cp}^{\text{III}}\text{-Tb-Cp}^{\text{III}}$  direction (Fig. 3a left) suggesting that the CF imposed by the  $\text{BH}_4^-$  anion is much weaker than that of the  $\text{Cp}^{\text{III}}$  ligands. However, the most

excited states of the multiplet correspond to a *pseudo*-doublet that resembles the  $m_j = \pm 6$  state quantised along the vector normal to the plane of Cp<sup>ttt</sup>-B-Cp<sup>ttt</sup> (Fig. 3a right, Tables S10 and S11): a similar situation was observed for [Ln(Cp<sup>ttt</sup>)<sub>2</sub>(Cl)],<sup>14</sup> which is the hallmark of anisotropic ions in low-symmetry environments.<sup>25</sup> In common with **2-Tb**, **3-Tb** has a highly axial ground *pseudo*-doublet, however in this case the five lowest lying *pseudo*-doublets are well described as  $m_j = \pm 6, \pm 5, \pm 4, \pm 3$  and  $\pm 2$  quantised along the Cp<sup>ttt</sup>-Tb-Cp<sup>ttt</sup> direction (Fig. 3b, Tables S12 and S13). In this case, we clearly observe a singlet most-excited state which corresponds to  $m_j = 0$ : this indicates a higher degree of uniaxiality in the electronic structure of **3-Tb** compared to **2-Tb**.

For **2-Tb** and **3-Tb** under zero applied magnetic field, the ground state *pseudo*-doublet is mixed between the  $m_j = +6$  and the  $m_j = -6$  states. For **2-Tb** this causes a tunnelling gap of ca. 0.03 cm<sup>-1</sup>, explaining the lack of slow relaxation in zero magnetic field, while the tunnelling gap for **3-Tb** is much smaller (< 10<sup>-3</sup> cm<sup>-1</sup>) thus slow relaxation is observed under zero magnetic field. However, QTM is likely enhanced by transverse dipolar fields in the solid state, as observed for [Tb(Cp\*)<sub>2</sub>{μ-(Ph)<sub>2</sub>BPh<sub>2</sub>}],<sup>7b</sup> and is clearly sufficient to preclude open hysteresis in either compound. Therefore, the differences between **3-Tb** and **3-Dy** can be attributed to the non-Kramers nature of the former vs. the Kramers nature of the latter: the ground  $m_j$  doublet of Dy<sup>3+</sup> is resistant to direct mixing between the two projections, whereas there is no such restriction for Tb<sup>3+</sup>, thus efficient relaxation by QTM is facilitated in low symmetry environments.<sup>1,26</sup> Although the bis-Cp<sup>ttt</sup> framework engenders large magnetic anisotropy in **3-Tb**, it is apparent that high-symmetry environments are a requirement to prevent mixing between the opposing projections of the non-Kramers *pseudo*-doublets of Tb<sup>3+</sup> ions, unlike for Dy<sup>3+</sup> ions. Therefore, future strategies to achieve high temperature magnetic hysteresis in monometallic Tb<sup>3+</sup> SMMs may require symmetry-protection of the ground state by appropriate ligand design.<sup>26</sup>

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## Conflicts of interest

There are no conflicts to declare.

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