Magnetic anisotropy provides directionality and stability to magnetization. It is the key ingredient to the coercive field and magnetic energy of bulk magnets, and to the performance of single-molecule magnets (SMMs), which has invoked intense interest in the field of spintronic devices and quantum computing. However, magnetic anisotropy is also the most difficult to manipulate, especially for lanthanides, which dominate the current SMM research studies. Theoretically, phenomenological crystal field methods have been used for decades to explain the magnetic properties of lanthanides. A popular version of this approach is the electrostatic point charge model, in which the charges are taken either as phenomenological parameters or extracted from DFT calculations. Fast progress of quantum chemistry methods and increased computational power made it possible to use nowadays fully ab initio methods to describe the anisotropy of relatively large complexes. In combination with the intuitive understanding that the axial (equatorial) ligand field favors the easy axis anisotropy of oblate (prolate) 4f electron distribution, these methods have permitted a full description of magnetic anisotropy in lanthanides.

Experimentally, anisotropy measurements on a wide range of transition metal and lanthanide complexes were reported and reviewed in the 1970s. Recently, angular-resolved magnetometry measurements have been proved to be very useful for magnetic anisotropy investigation of some lanthanide SMMs with one unique lanthanide center, including several DyIII, ErIII, and YbIII single-ion compounds. For TbIII-compounds, the angular-resolved experiment was also performed on the Tb-DOTA complex, which is unfortunately not an SMM. On the other hand, of all the lanthanide centers, the TbIII ion is of predominant importance. Although Tb-SMMs are less numerous compared to Dy-SMMs due to their non-Kramers nature, Tb-SMMs accounted for some of the most impressive results, including the first and most widely studied Ln-SMM (double-decker terbium complex [TbPc2]−). The first 3d–4f SMM ([CuL(Tb(hfac))2])15 the SMM with the highest energy barrier ([TbPc2]−, Ueff = 652 cm−1 = 938 K), and the highest blocking temperature ([(Me5Si)2N]2(THF)2[Tb]2[μ-N3], TbB = 14 K). Thus, knowledge of the anisotropy of TbIII-SMMs will be of great value for the design and construction of better SMMs.

Recently, we reported a tetranuclear [Cu(Tb)2-valpn] SMM where the TbIII ions were bridged solely by the end-on azides. Direct experimental confirmation of the easy axis using angular-resolved measurements was hindered by the small size of single crystals. Herein, we report the detailed characterization and magnetic pole determination of the TbIII ion in two enantiomorphic tetranuclear TbIII- SMMs [Cu2(valchxn)2(Tb2(N3)6)]2CH3OH (1-RR and 1-SS, H2valchxn = (R,R)-1,2-cyclohexanediylbis(2-iminomethylene-6-methoxy-phenol)). The magneto-structural relationship and the direction of the principal magnetic axis of this cluster have also been verified by detailed ab initio calculations.

The structures of 1-RR and 1-SS were very similar to the reported [Cu(Tb)2-valpn] compound (Fig. 1). Several points are worth mentioning. (1) They crystallized in the triclinic space group P1 with only one [CuTb]2 cluster in the unit cell; (2) the two phenolic oxygen bridged [CuTb] units were related to each
other by a pseudo-inversion center and bridged by two EO azides; and (a) the Tb\(^{3+}\) ions are in the bicapped trigonal prism environment with very long Tb–O bonds for the capping atoms (O3, O4, O7, and O8). These methoxy oxygen atoms bear much less negative charges compared to the deprotonated phenolic oxygen atoms and the nitrogen atoms of azides, leading to an axial negative charge distribution around the Tb\(^{3+}\) centers.

Compounds 1-RR and 1-SS show the same magnetic properties with negligible differences (ESI\(^\dagger\) for details), and we will only discuss the properties of 1-RR in detail. Upon cooling, the \(J_M T\) curve (Fig. S4, ESI\(^\dagger\)) decreases from the room temperature value 23.15 cm\(^3\) mol\(^{-1}\) K to a minimum at around 50 K, and increases again up to 2 K, suggesting the dominant ferromagnetic interactions between the phenolic oxygen bridged Cu–Tb and the azide bridged Tb–Tb pairs, consistent with the theoretical analysis (vide post) and the reported results.\(^{15,18,19}\)

The non-superposition of the \(M vs. H\) data to a single master curve and the low magnetization of 11.3 \(\mu_B\) at 7 T suggest the presence of significant magnetic anisotropy (Fig. S5 and S6, ESI\(^\dagger\)). Temperature and frequency dependencies of ac susceptibilities under a zero dc field (Fig. 2 and S7, ESI\(^\dagger\)) reveal a slow relaxation of magnetization. The analyses of the ac data using the generalized Debye model\(^{20}\) (Table S3, ESI\(^\dagger\)) and the Arrhenius law gave the following parameters: \(\alpha \leq 0.17\), \(U_{\text{eff}} = 27.6 \pm 0.2\) K (19.2 \(\pm 0.1\) cm\(^{-1}\)), and \(\tau_0 = (2.03 \pm 0.05) \times 10^{-5}\) s. Above 1.8 K, a thermally activated Orbach relaxation process with a narrow distribution of relaxation times was confirmed.

The SMM behavior of 1-RR was confirmed by the hysteresis loops measured on a field-oriented single crystal (\(m = 0.93\) mg) on a conventional SQUID-VSM above 1.8 K (Fig. S13, ESI\(^\dagger\)) and on a \(\mu\)-SQUID down to 0.03 K (Fig. 3). At a field sweep rate of 0.14 T s\(^{-1}\), magnetic hysteresis is observed at temperatures up to 4.0 K. Above 1.4 K, the coercivities increase with decreasing temperature as expected for SMMs, reaching 4.6 kOe at 1.4 K. Quantum tunnelling of magnetization (QTM) is evidenced by the observation of temperature-independent loops below 1.4 K that remain strongly dependent on the field sweep rate.

In the zero-field cooling (ZFC) and field cooling (FC) experiments, a double step with coercivities of 0.43 mg at temperatures near 0.3 K (Fig. S16, ESI\(^\dagger\)) was observed. The hysteresis loops show hysteresis steps with coercivities of 0.8 kOe at 0.03 K (Fig. S17–S19, ESI\(^\dagger\)). Apparent strong magnetic anisotropy

Step-like features were clearly observed for the loops. As can be seen from the d\(M/dH\) curves (Fig. S14 and S15, ESI\(^\dagger\)), the critical fields at a higher field are proportional to the field sweep rates, while the critical field for the steps near zero field (0.8 kOe) is independent of the field sweep rate and the temperature, indicating that 1-RR is an exchange-biased SMM.\(^{22}\)

The Ising anisotropy of the cluster and the Tb\(^{3+}\) centers can be revealed by angular resolved magnetometry measurements based on the following two criteria: (1) 1-RR crystallizes in a triclinic space group with only one unique \([\text{CuTb}]_2\) unit in the unit cell, which guarantees the determination of the susceptibility tensor of the whole \([\text{CuTb}]_2\) unit.\(^{11–13}\) (2) The Cu\(^{2+}\) ions contribute little to the molecule’s magnetic anisotropy and the two ferromagnetically coupled Tb\(^{3+}\) centers are related by a pseudo-inversion center, which ensures the rough colinearity of the easy axis of each Tb\(^{3+}\) with that of the whole molecule. The angular dependence of magnetic susceptibility was measured on a face-indexed single crystal (\(m = 0.43\) mg, Fig. S16, ESI\(^\dagger\)) mounted on a L-shaped Cu:Be support from 1.8 to 15 K (Fig. 4 and Fig. S17–S19, ESI\(^\dagger\)). Apparent strong magnetic anisotropy
The Ising anisotropy of the ground doublets was confirmed by Table S9, ESI†. The effective Ising Hamiltonian for the low-lying multiplets (eqn (S2), ESI†) was obtained from the ab initio calculations. The experimental curves were upscaled by 10%.

was observed at all temperatures. The positions of the maxima of the curves were found to shift considerably below 2.5 K. This phenomenon is most likely connected to the low-temperature magnetic hysteresis, which generates a non-equilibrium situation during rotation.12 The susceptibility tensors and their principal values were extracted by simultaneously fitting the angular dependence data to the three rotation functions and subsequent diagonalizing the susceptibility tensors (solid lines in Fig. 4, Table S5, ESI†). At 3 K, the largest principal value of the susceptibility tensor is 23.54 cm3 mol−1 while the other two are close to 1 cm3 mol−1, confirming the strong Ising anisotropy of the [CuTb]2 cluster. This Ising anisotropy is evident at all temperatures, as can be seen from the big difference of the J\textsubscript{ab} vs. T plots along different principle axes (Fig. S20, ESI†). The obtained orientation of the molecular easy axis is shown in Fig. 1 as a blue dashed line, which has a deviation of 11.9° in the ab initio direction (vide post).

The above experimental results were further confirmed and rationalized by the ab initio calculations performed on the complete molecular structure of 1-RR (Fig. S21, see ESI† for details). As can be seen in Table S7 (ESI†), the calculated ground doublets of the Tb3+ ions are both well separated from the first excited states located at the energy of 200 cm\textsuperscript{−1} higher. The Ising anisotropy of the ground doublets was confirmed by the very large g\textsubscript{e} values (17.90, Table S8, ESI†) of the ground doublets. Furthermore, the calculated easy axes of the individual Tb3+ centers were almost parallel to each other (Fig. 1), consistent with the presence of the pseudo-inversion center. The magnetic interactions in 1-RR were simulated using a pseudospin exchange Hamiltonian (eqn (S1), ESI†). Simultaneous simulation of J\textsubscript{ab} vs. T and M-H curves (Fig. S4 and S5, ESI†) provides the following coupling parameters: J\textsubscript{Cu-Tb} = 25.3 cm\textsuperscript{−1}, J\textsubscript{Tb-Tb} = 4.3 cm\textsuperscript{−1}, J\textsubscript{Cu-Cu} = −3.2 cm\textsuperscript{−1}, entering the effective Ising Hamiltonian for the low-lying multiplets (eqn (S2), Table S9, ESI†). With these exchange parameters obtained, the exchange spectrum of the cluster was calculated and is shown in Table S10 (ESI†). As we can see, the resulting exchange spectrum shows negligible tunnelling splitting for all exchange doublets, thus outlining a barrier of blocking of magnetization of ca. 25 cm\textsuperscript{−1}, which is in good agreement with the experimental value. This is further confirmed by the construction of the blocking barrier of magnetization following a recently proposed methodology.25 The relaxation path of magnetization was found by connecting the exchange states with the largest transition moments (Fig. 5). It contains intense spin–phonon transitions 1± ↔ 4± and 4± ↔ 7±, and a temperature-assisted QTM 7− ↔ 8± → 7+ which becomes possible in the presence of internal magnetic fields bringing in resonance the states 7 and 8. This analysis shows that the observed blocking barrier is of exchange origin.

Moreover, due to the relatively strong ferromagnetic exchange interaction between the terbium and (isotropic) copper centres, the local magnetic moments of Cu2+ in the ground exchange doublet are aligned along the main magnetic axes of terbium (Fig. 1). These results allow concluding that the extracted anisotropy axis of the complex coincides with the calculated anisotropy axes on the two Tb3+ sites. The angular dependence of the magnetic susceptibility of 1-RR at 3 K was also calculated ab initio and depicted in Fig. 4 by dashed lines. For the curves rotating around the y axis, the experimental and calculated curves match very well with a small difference in the absolute values, which is reasonable considering the small mass of the single crystal. For the curves rotating along the x and z directions, the offset is about 10°, reflecting the deviation between the measured and calculated directions.

For the magnetostructural relationship, the main anisotropy axis of the Tb3+ ion is directed approximately perpendicular to the triangles of the bicapped trigonal prism, as in the case of other sandwiched Ln complexes.14,23 Furthermore, we can see...
that in the coordination geometry of the Tb\(^{3+}\) ion, there is a pseudo-mirror plane formed by atoms Tb1, N11 and N14 (Fig. S22, ESIF). According to Neumann’s principle,\(^{24}\) the easy axis of Tb\(^{3+}\) should be related to a symmetry operation, i.e., lie within the mirror plane, as confirmed by experimental and \textit{ab initio} analysis. These conclusions were also reproduced by a simple electrostatic crystal field calculation involving point charges on coordination atoms taken as Mulliken charges obtained from DFT calculations (see ESIF).\(^{7,c,d}\) The direction of the main anisotropy axis in these calculations coincides with the direction of the lowest energy in the electrostatic potential energy surface (Fig. S22, ESIF). However, the deviation of this axis from the measured one amounts to 20.8°, twice larger than for the \textit{ab initio} calculated anisotropy axis. This shows the limitation of the electrostatic model that does not take into account the metal–ligand covalency effects in the crystal (ligand) field of lanthanide, which are treated in angular-overlap models (AOMs).\(^{6,b,c}\) The latter models are expected to give results with similar accuracy for the direction of the main anisotropy axis, which is thus basically determined by the geometry of the surrounding ligand atoms rather than exclusively by their electrostatic charges. Comparison of \textit{ab initio} with simplified electrostatic crystal field calculations shows that all contributions to the ligand field have to be taken into account in order to obtain a deeper understanding of the magnetic anisotropy of the Ln complexes.

In summary, two enantiomorphetic tetraneuclear \([\text{CuTb}]_4\) SMMs were characterized and their magneto-structural relationship was carefully studied. Angular resolved magnetometry measurements and \textit{ab initio} calculations were performed on a multinuclear SMM for the first time, to establish the ising magnetic anisotropy of both the whole molecule and the Tb\(^{3+}\) centers. Further studies on the isostructural compounds with other 3d–4f combinations in the 

Notes and references