Two one-dimensional (1-D) chain complexes with pentagonal bipyramidal DyIII centers have been synthesized and magnetically characterized. Field-induced single molecule magnet behavior has been revealed in both compounds, which is still rarely reported in lanthanide SMMs, a ligand field of axial symmetries, such as pentagonal bipyramidal coordination geometry. Their crystal field parameters and orientations of the magnetic easy axes were obtained from the simulation of the magnetic data and the electrostatic model calculation.

Since the first discovery of the single-molecule magnet (SMM) behaviour of the sandwich complex \( [\text{Na}(\text{C}_6\text{H}_5)_3]_3[\text{LnPc}]_2 \) (\( \text{Ln} = \text{Tb}, \text{Dy} \)) in 2003,\(^1\) mononuclear SMMs, commonly termed as single-ion magnets (SIMs), have been intensively studied because of their potential applications in molecular spintronics\(^2\) and quantum-computing devices.\(^3\) These mononuclear systems provide excellent models for understanding the magnetic anisotropy, i.e., especially single-ion anisotropy.\(^4\) In lanthanide mononuclear SMMs, single-ion magnetic anisotropy depends on the competition between electrostatic crystal-field interaction and spin–orbit coupling.\(^5\) The large unquenched orbital moment of lanthanides gives rise to their large magnetic anisotropy, making lanthanides good candidates for the construction of SMMs. To suppress the quantum tunnelling of magnetization frequently observed in the lanthanide SMMs, a ligand field of axial symmetries, such as \( D_{4h}, D_{5h}, D_{6h}, S_8 \) and \( D_{6d} \), and so on, is usually preferred. For example, the following SMMs contain lanthanides of approximate \( D_{5h} \) local symmetry: \( [\text{PeC}_3\text{Ln}]^{11-} \), \( [\text{Ln}(W_5\text{O}_{18})_2]^{9-} \) (\( \text{Ln} = \text{Ho}, \text{Er} \)) and \( [\text{Ln}([\text{SiW}_{11}\text{O}_{39}])^{13-} \) (\( \text{Ln} = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb} \)),\(^7\) lanthanide \( \beta \)-diketone,\(^8\) and \( [\text{Ln}([\text{DOTA})[\text{H}_2\text{O}])^{-} \) (\( \text{Ln} = \text{Dy}, \text{Er}, \text{Yb} \)) \(^9\) systems.\(^9\) Organometallic double-decker lanthanide SMMs, \( [\text{Cp}^*\text{Er}-(\text{COT})_8\text{Er}(\text{COT})_8]^{-} \) (\( \text{Ln} = \text{Er}, \text{Dy}, \text{Ce} \)), have high rank rotation axes \( (C_{s}, S_6, C_6 \text{ axis}) \).\(^10\) Recently, strong magnetic anisotropy and SMM behaviour have been reported in \( [\text{Ln}[\text{SiMe}_3]_2]_3 \) (\( \text{Ln} = \text{Er}, \text{Dy} \)) and their related compounds with a \( C_{3v}, \text{symmetry} \).\(^11\)

In this regard, lanthanide complexes with pentagonal bipyramidal geometry \( (D_{5h}) \), especially for the Kramers DyIII \( (\text{E}_{8}^{1/2}) \) and ErIII \( (\text{E}_{8}^{3/2}) \) ions, are rarely reported to behave as SMMs, such as \( \text{Dy}^{12}, \text{Er}^{13}, \text{Dy}^{14}, \text{Zn}_2\text{Dy}^{15} \) and \( \text{Fe}_2\text{Dy}^{16} \) systems. In these systems, the pentagonal geometry of a five-fold axis played a predominant role in the suppression of the quantum tunnelling and resulted in the high energy barrier of 305 cm\(^{-1}\) (439 K) for the \( \text{ZnDyZn} \) compound compared to similar compounds of octahedral geometry.\(^15\) Also, an energy barrier of 319 cm\(^{-1}\) (459 K) is observed for the \( \text{FeDyFe} \) compound, which is the highest anisotropy barrier for 3d−4f SMMs.\(^16\) Previously, we adopted the pentadentate ligand to successfully design the 3d SMMs with quasi-\( D_{5h} \) symmetry.\(^17\) As these ligands can occupy the five equatorial coordination sites, a pentagonal bipyramidal geometry can be achieved if the axial positions are occupied by only two ligands. As an excellent pentadentate ligand, \( \text{H}_3\text{valdien} \) \((\text{N}_1, \text{N}_3\text{-bis(3-methoxysalicylidene)diethyl-triamine}) \) was widely used; and a series of SMMs based on this ligand were obtained, including the \( \text{Dy}_{2y}^{18}, \text{Dy}_{12z}^{19}, \text{CO}_{2}\text{Dy}_{2z}^{20} \) and \( \text{Ni}_2\text{Ln}_2 \) \((\text{Ln} = \text{ Tb}, \text{Dy} \) and \( \text{Ho} \)) compounds.\(^18\) But in these complexes, DyIII centres mostly adopted an eight-coordinate ligand environment. To lower the coordination number, bulky anions with large steric effects are available for constructing seven-coordinate complexes to obtain the pentagonal bipyramidal geometry \( (D_{5h}) \).

Based on the above consideration, we successfully synthesized a series of one-dimensional LnIII coordination polymers (experimental details in the ESI) by combining the pentadentate ligand valden and a bulky anion diphenyl phosphate \( ([\text{PhO})_2\text{P}=\text{O}]) \) (Scheme 1). Herein, we report the syntheses, crystal structures and magnetic properties of two 1D Dy...
monoclinic space group $P$$bnc$$a$.

Every valdien ligand in 1 uses both its coordination pockets (N$_3$O$_2$ and O$_4$ pockets) to embrace both the Dy$^{III}$ and Na$^+$ ions, in the orthorhombic space group $P$$bcn$.

The ligand H$_2$valdien and the bulky anion [[(PhO)$_2$PO$_2$]$^-$] acts as the coordination polymer. The chains in 1 are formed by the [DyNa(valdien)]$^+$ units bridged by the Cl$^-$ anions, while the chains in 2 are formed by the [Dy(valdien)]$^+$ units bridged by the O$^-$ anions. Although both compounds are one-dimensional coordination polymers, the chains are different depending on the deprotonated bases used in the reaction: the chains in 1 are formed by the [DyNa(valdien)]$^+$ units bridged by the Cl$^-$ anions, while the chains in 2 are formed by the [Dy(valdien)]$^+$ units bridged by the O–P–O group of diphenyl phosphate (Fig. 1a and b). Every valdien ligand in 1 uses both its coordination pockets (N$_3$O$_2$ and O$_4$ pockets) to embrace both the Dy$^{III}$ and Na$^+$ ions, respectively; while for 2, the O$_4$ pocket of the valdien ligand is empty. Interestingly, both Dy$^{III}$ centres in compounds 1 and 2 are seven-coordinate with a distorted pentagonal bipyramidal environment. The three nitrogen atoms and two oxygen atoms from the valdien ligands occupy the equatorial position of the Dy$^{III}$ center, while the axial positions are occupied by one oxygen atom from the [[(PhO)$_2$PO$_2$]$^-$] ligand and one chloride anion in 1 and two oxygen atoms from two [[(PhO)$_2$PO$_2$]$^-$] ligands in 2 (Fig. 1c and d). As the pentagonal bipyramidal geometry is distorted, the characteristic bond angles of the coordination geometry deviate from the ideal values for an ideal $D_{5h}$ symmetry (Table S3, ESI†). The axial bond angles (O$_5$–Dy$_1$–Cl$_1$ and O$_5$–Dy$_1$–O$_6$) are 162.87(7)$^\circ$ and 163.10(1)$^\circ$ for 1 and 2, respectively. Using the program SHAPE 2.1,$^{22}$ the continuous shape measures (CSHMs) of the Dy$^{III}$ centres relative to the ideal pentagonal bipyramid were calculated to be 0.775 and 0.496 for 1 and 2, respectively (Table S4, ESI†). Separated by the anions and the bulky ligands, the Dy$^{III}$ centres are isolated from each other: the shortest intra- and interchain Dy$^{III}...$Dy$^{III}$ distances are 8.3733(6) and 8.9941(5) Å for 1 and 2, respectively (Fig. S2, ESI†), which fall in the range of the Dy$^{III}...$Dy$^{III}$ distances in the reported 1D chain lanthanide SMMs.$^{23}$

Direct-current (dc) magnetic susceptibilities of both 1 and 2 were determined on polycrystalline samples in the temperature range of 2.0–300 K under 1000 Oe (Fig. 2a and b). The $\chi_M$ values at 300 K for 1 and 2 are 13.87 and 14.53 cm$^3$ mol$^{-1}$ K, respectively, which are close to the expected values (14.17 cm$^3$ mol$^{-1}$ K) for an isolated Dy$^{III}$ ion ($S = 5/2, L = 5, J = 15/2, \hbar = 15/2, g = 4/3$). Upon cooling, the $\chi_M$ values for 1 and 2 gradually decrease to 8.67 and 8.92 cm$^3$ mol$^{-1}$ K at 2.0 K. This behaviour is mainly due to the thermal depopulation of the Dy$^{III}$ Stark sublevels. The magnetization of both 1 and 2 at 2 K increases up to 5.26 and 5.56$\mu_B$ at 70 kOe (Fig. 2a and b, inset), respectively, which is clearly lower than the expected saturation value for one uncorrelated Dy$^{III}$ centre (10$\mu_B$), indicating the presence of magnetic anisotropy and/or low-lying excited states.

To understand the magnetic anisotropy of the Dy$^{III}$ ion for both 1 and 2, their magnetic susceptibility and magnetization data (Fig. 2a and b) were analysed simultaneously with the crystal field theory using the PHI program.$^{24}$ The Crystal-Field Hamiltonian is expressed in the equation as follows:

$$\hat{H}_{CF} = \sum_{l=1}^{N} \sum_{k=2,4,6} \sum_{q=-k}^{k} \sigma_{l}^{2} \beta^{2} \theta_{k} \hat{O}_{k}^{q} $$  (1)
where $a_i^k$ are the orbital reduction parameters, $B_{ij}^k$ are the crystal field parameters (CFPs) in Steven's notation, $\delta_k$ are the operator equivalent factors, and $\Omega_k^i$ are the operator equivalents. Considering the slightly distorted pentagonal bipyramidal geometry of $D_{5h}$ symmetry, only the parameters ($B_{ij}^0$, $B_{ij}^1$ and $B_{ij}^2$) are adopted to avoid overparametrization.\(^{15,25}\) The CFPs ($B_{ij}^0$, $B_{ij}^1$ and $B_{ij}^2$) and the anisotropy $g$-factors ($g_x$, $g_y$ and $g_z$) were employed to fit the magnetic susceptibility and magnetization data. As can be seen in Fig. 2, both the susceptibility and the magnetization data in the whole temperature range and up to the highest magnetic field can be fitted well with one set of parameters (Table S3, ESI†). With the obtained fitting parameters (CFPs and $g$-factors), the magnetic data of 1 and 2 are simulated to obtain the energy-levels, the eigenstates and $g$-tensors. From the simulation of the ground state multiplet $^5H_{15/2}$ (energy-levels are listed in Table S6, ESI†), the energy gap between the ground state Kramers doublets ($m_l = \pm 13/2$) and the first excited states ($m_l = \pm 11/2$) are 41.63 cm\(^{-1}\) for 1 and 45.65 cm\(^{-1}\) for 2, respectively. The local $g$-tensors on the ground doublets of the Dy sites show large $g_z$ values, $g_z = 15.46$ for 1 and $g_z = 17.44$ for 2 (ideally $g_x = g_y = 0$, $g_z = 20$), indicating the easy axial magnetic anisotropy of both compounds.\(^{23,26}\)

To probe the slow magnetic relaxation, the temperature and frequency-dependent ac susceptibilities were determined in the temperature range of 1.8–10 K for 1 and 2. Under a zero dc field, no out-of-phase ac susceptibility ($\chi''$) signal was observed above 1.8 K for both compounds, probably due to the fast QTM (Fig. S3 and S4, ESI†). However, to suppress the QTM effect, the 1000 Oe dc field was applied and both the in-phase ($\chi'$) and out-of-phase ($\chi''$) for 1 and 2 showed obvious temperature and frequency dependence (Fig. 3, S5 and S6, ESI†), indicating that the slow magnetic relaxation originated from the single-ion magnetic behaviour of the Dy\(^{III}\) ion, as observed for other 1D or 2D Dy\(^{III}\) compounds with SMM behavior.\(^{23}\)

The relaxation time ($\tau$) can be obtained from the frequency-dependent ac susceptibility data ($\chi'$ and $\chi''$), and the corresponding Cole–Cole plots exhibit asymmetrically semi-circular shapes in the high frequency region and irregular curves in the low frequency region, respectively (Fig. S7, ESI†). According to the generalized Debye model for the high frequency region,\(^{27}\) the Cole–Cole plots at 1.8–4.0 K of 1 and 1.8–5.0 K of 2 (Fig. S7, ESI†) can be fitted well, with $\alpha$ values in the range of 0.10–0.22 for 1 and 0.07–0.14 for 2 (Tables S7 and S8, ESI†), respectively, indicating a relatively narrow distribution of the relaxation processes. To estimate the anisotropy energy barrier ($U_{\text{eff}}$), the high temperature data (Fig. 4) were fitted according to the Arrhenius law $\tau^{-1} = \tau_0^{-1} \exp(-U_{\text{eff}}/k_BT)$. The effective energy barrier $U_{\text{eff}}$ was estimated to be 14.23 cm\(^{-1}\) (20.48 K) and 13.70 cm\(^{-1}\) (19.70 K) for 1 and 2, respectively, with $\tau_0 = 2.56 \times 10^{-7}$ s for 1 and $\tau_0 = 6.12 \times 10^{-7}$ s for 2. It is noteworthy that the plots of ln($\tau$) versus 1/$T$ exhibit multiple relaxation processes under 1000 Oe field. In general, $n = 9$ for Kramers ions, smaller $n$ values in the range of 1–6 can be considered as reasonable for an optical acoustic Raman process.\(^{28}\) Considering the spin-lattice relaxation of both Raman and Orbach processes at low temperatures,\(^{29}\) we could fit all the magnetic data with eqn (1) $\tau^{-1} = C T^n + \tau_0^{-1} \exp(-U_{\text{eff}}/k_BT)$, giving $C = 100.9$ s\(^{-1}\) K\(^{-1}\), $n = 3.5$, $U_{\text{eff}} = 49.94$ cm\(^{-1}\)$, $\tau_0 = 1.50 \times 10^{-8}$ s for 1 and $C = 505.0$ s\(^{-1}\) K\(^{-2}\), $n = 2.0$, $U_{\text{eff}} = 53.25$ cm\(^{-1}\)$, $\tau_0 = 3.03 \times 10^{-8}$ s for 2 (Fig. 4), which are close to the obtained energy gap from
the calculated values (vide supra). The results indicate that the Raman relaxation process could significantly influence the Orbach relaxation process on reducing the thermal energy barrier of the slow magnetic relaxation.\textsuperscript{29a}

To determine the magnetic anisotropy of the crystal field in both 1 and 2, the orientation of the magnetic easy axes was estimated by an electrostatic model using the program MAGELLAN (Fig. 5a and b).\textsuperscript{30} It is shown that the orientation of the magnetic easy axes in both 1 and 2 deviated remarkably from the pseudo-C5 axes of the pentagonal bipyramidal geometry ($D_{5h}$) of Dy\textsuperscript{III} centres. This deviation is reasonable considering the fact that the pentagonal bipyramid of the Dy\textsuperscript{III} centres are distorted and there is no real 5-fold axis, not to mention that the distribution of the negative charges has an even lower symmetry. Also, the arrangement of magnetic axes could be related to the dynamic magnetic behavior in both the compounds.\textsuperscript{31} This result emphasizes that one needs to consider more on the negative charges of the coordination atoms for the rational design of lanthanide SMMs in a specific symmetry.

In summary, these results demonstrate that the Dy\textsuperscript{III} compounds with pentagonal bipyramidal Dy\textsuperscript{III} centres can be rationally designed and synthesized. Due to the individual isolated system between the Dy\textsuperscript{III} ions, the two one dimensional Dy\textsuperscript{III} coordination polymers display single molecule magnet behavior with the Raman process significantly affecting the Orbach relaxation process in this system. The fitting and simulating magnetic data in the crystal field parameters have been analysed to gain insight into the possible mechanism of the slow magnetic relaxation. The method represents a potentially new design strategy leading toward the construction of a new class of SMMs. Future efforts will be devoted to the development of other heptacoordinate Dy\textsuperscript{III} SMMs by controlling the single-ion anisotropy and/or the crystal field environment.

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Notes and references
