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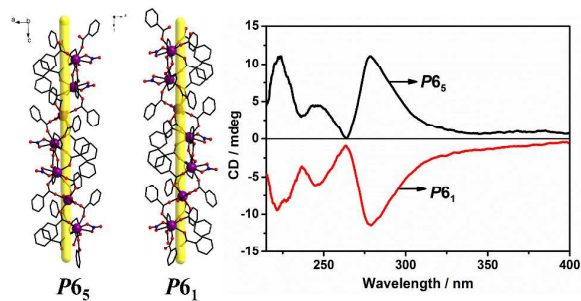
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A racemic helix chain  $Dy^{3+}$  compound **1** bridged by  $\mu_{1,3}$ -COO groups was synthesized, which showed slow magnetic relaxation behaviour.

## ARTICLE

Slow magnetic relaxation in a lanthanide helix chain compound  $[\text{Dy}(\text{HNA})(\text{NA})_2(\text{NO}_3)]_n$  (HNA = Nicotinic acid)

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A helix chain  $\text{Dy}^{3+}$  compound,  $[\text{Dy}(\text{HNA})(\text{NA})_2(\text{NO}_3)]_n$  (**1**, HNA = Nicotinic acid), was synthesized under solvothermal condition and fully characterized. The absolute configurations of the enantiomers in  $P6_1$  and  $P6_5$  space groups are characterized by single crystal X-ray diffraction and circular dichroism (CD). Magnetic studies reveal that compound **1** exhibits ferromagnetic interaction and slow magnetic relaxation at low temperatures with the energy barrier of 37 K under 900 Oe dc field.

## Introduction

Single-molecule magnets (SMMs) have attracted great attention owing to their potential applications in high-density information storage, quantum computing and spintronics.<sup>1</sup> Considerable efforts have been devoted to synthesize and characterize new molecular species to show SMM behavior with high blocking temperature towards practical applications.<sup>2</sup>  $\text{Ln}^{3+}$  ions, specifically for  $\text{Dy}^{3+}$  ion, have been proved to be good candidates for constructing new SMMs owing to their large uniaxial magnetic anisotropy originating from the large unquenched orbit moment and strong spin-orbit coupling.<sup>3</sup> Up to now, a large number of discrete Dy-SMMs have been reported.<sup>4</sup> Some of them have shown high effective energy barriers  $U_{\text{eff}}$  and/or high blocking temperatures.<sup>4b,4e</sup> However, the study of slow magnetic relaxation in one-dimensional (1D) Dy systems is much less and most of the magnetic studies on 1D compounds are limited to radical-containing systems<sup>5</sup> because it is difficult to obtain 1D chains with effective magnetic couplings between  $\text{Ln}^{3+}$  ions. And it is also hard to control and modify the local ligand field of central ion in a 1D system, which is crucial to the magnetic anisotropy of the central ion and the slow relaxation behaviour.<sup>6</sup> In addition, the intrachain  $\text{Dy}\cdots\text{Dy}$  coupling interaction existed in 1D chains plus single-ion effects always make the dynamic magnetic behaviours more complicated and hard to analyze.<sup>5d</sup> Therefore, the syntheses of 1D Dy-based systems and exploring their slow relaxation behaviours are quite challenging.

And, it is a trend to create new multifunctional magnetic materials which combine magnetism with other properties such as ferroelectricity, optical property or porosity.<sup>4c,7</sup> As the chiral compounds are an important class of materials due to their intriguing potential applications in the fields of enantioselective

separation, asymmetric catalysis, optical activity, and ferroelectrics, the survey of the combination of magnetism and chirality to construct chiral magnetic materials is also attractive.<sup>8</sup> Recently, magneto-chiral dichroism effect has been observed in a chiral single chain magnet, which provides an efficient model system to study the magneto chiral effect.<sup>9</sup>

With this in mind, herein, we report a Dy-based 1D helical chain in an enantiomeric pair compound  $[\text{Dy}(\text{HNA})(\text{NA})_2(\text{NO}_3)]_n$  (**1**, HNA = Nicotinic acid), which represents an example of 1D helix chain compound based on  $\text{Dy}^{3+}$  exhibiting SMM behaviour. Moreover, it displays well resolved relaxation process induced by a small applied dc field, which restrains the quantum tunnelling effect.

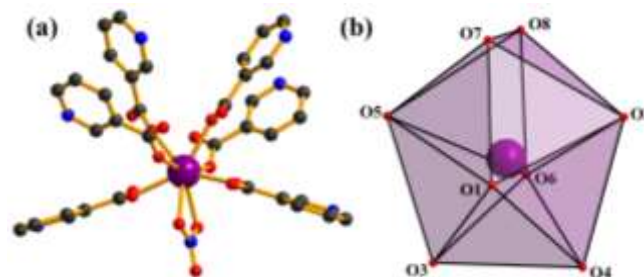
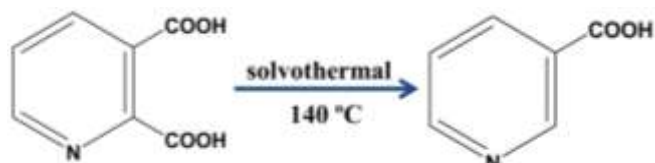


Fig. 1 (a) The coordinated environments of  $\text{Dy}^{3+}$ ; (b) quasi- $D_{2d}$  symmetry polyhedron of  $\text{Dy}^{3+}$  ion. All hydrogen atoms were omitted for clarity.

## Results and discussion

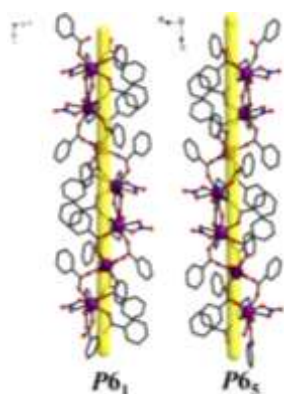
The reaction of  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , pyridine-2,3-dicarboxylic acid and 1*H*-1,2,4-triazole in  $\text{CH}_3\text{CN}$  in the presence of  $\text{Et}_3\text{N}$ , yields yellow microtube-shaped crystals of compound **1**. It is worth to note that pyridine-2,3-dicarboxylic acid is transformed into HNA in the process of the solvothermal reaction (Scheme 1),

which is a typical *in-situ* decarboxylation.<sup>10</sup> And the introduction of 1*H*-1,2,4-triazole plays an important role in the isolation of compound **1**, although it does not appear in the final product because without 1*H*-1,2,4-triazole, **1** could not be obtained. Similar phenomena were usually encountered in the reported literatures,<sup>11</sup> which might have a synergistic action with other materials in the system, though the detailed mechanism was not well understood. Single crystal X-ray diffraction analysis reveals that compound **1** is similar with the isostructural Eu, Gd and Tb analogies.<sup>12</sup> However, the reactants, synthetic method as well as the crystal shapes are quite different from the reported ones.



**Scheme 1** *In situ* decarboxylation of pyridine-2,3-dicarboxylic acid occurs to give nicotinic acid.

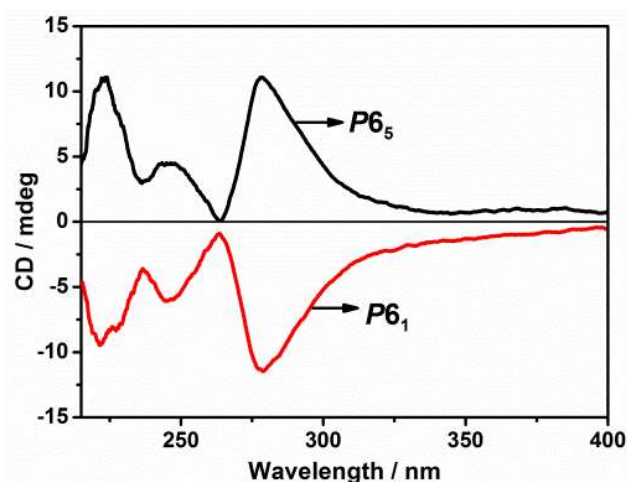
**Crystal structure of 1.** Single crystal X-ray diffraction analysis reveals that compound **1** crystallizes in a chiral space group of  $P6_1$  or  $P6_5$ . The asymmetric unit consists of one crystallography independent  $Dy^{3+}$  ion, two  $NA^-$  anions, one HNA and one nitrate anion. Each  $Dy^{3+}$  ion is eight coordinated by one bischelate  $NO_3^-$  and six carboxyl oxygen atoms from six  $NA^-$  ligands, forming a triangular dodecahedral geometry with quasi- $D_{2d}$  symmetry, which is measured by program SHAPE 2.0<sup>13</sup> (Fig. 1, Table S3, see ESI†). The Dy–O bond lengths range from 2.252(7) Å to 2.4581(7) Å. The carboxylic groups of the  $NA^-$  and the HNA ligands connect adjacent  $Dy^{3+}$  ions by 1,3-bridging mode affording an 1D infinite helix chain with intrachain Dy...Dy distance of 4.7909(6) Å (Fig. 2, Fig. S1, see ESI†).



**Fig. 2** Enantiomeric pair of helix chains in  $P6_1$  and  $P6_5$  space groups. All H atoms are omitted for clarity.

**CD Spectra of 1.** As a mean to validate the absolute configurations of the two enantiomers, solid-state CD spectra of single crystals synthesized in the same reaction container were measured. As shown in Fig. 3, the CD spectra of **1** present an obvious Cotton effect. The crystals in  $P6_1$  and  $P6_5$  space groups

exhibit opposite Cotton effects at the same wavelengths (three peaks at 223, 245 and 279 nm), indicating the coexistence of left-hand and right-handed enantiomers in one pot, which confirms the spontaneous resolution during crystallization. To further demonstrate whether the enantiomeric excess exists in these chiral crystals, the bulk sample of **1** was measured by CD spectrum. However, bulk sample of **1** showed a silent CD spectrum (Fig. S2, see ESI†). All the results aforementioned confirmed that the resulting crystals of **1** were racemic mixtures.



**Fig. 3** Solid state CD spectra of the enantiomeric pair.

**Magnetic properties of 1.** Direct-current (dc) magnetic susceptibility studies of **1** were performed under a 1000 Oe dc field in the temperature range 300–2 K. As shown in Fig. 4, the room temperature  $\chi_M T$  value of 14.30  $\text{cm}^3 \text{K mol}^{-1}$  is in well agreement with the expected paramagnetic value (14.20  $\text{cm}^3 \text{K mol}^{-1}$ ) for one uncoupled  $Dy^{3+}$  ion with the ground state  $^6H_{15/2}$  and  $g = 4/3$ .<sup>14</sup> On cooling,  $\chi_M T$  gradually decreases to a minimum value of 13.01  $\text{cm}^3 \text{K mol}^{-1}$  at 14 K and then rises sharply to 13.95  $\text{cm}^3 \text{K mol}^{-1}$  at 2 K, indicating the presence of ferromagnetic interactions at the lower temperature, which were also found in a few of other  $Dy^{3+}$  compounds with  $\mu$ -O-C-O bridges.<sup>15</sup> The lack of saturation of the  $M$  versus  $H$  plot and non-superposition on  $M$  versus  $H/T$  curve at low temperature can be attributed to the presence of significant magnetic anisotropy and/or low lying excited states in **1** (Fig. S3–S4, see ESI†).<sup>1–2</sup>

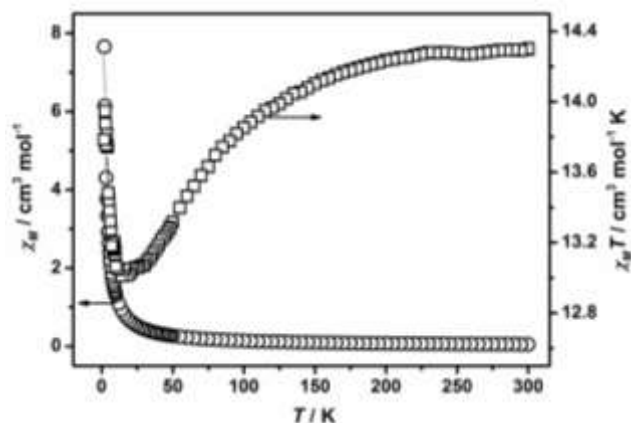


Fig. 4  $\chi_M T$  and  $\chi_M$  vs.  $T$  for **1**. Solid lines are eye guides.

The temperature dependence of alternating-current (ac) magnetic susceptibilities was measured under zero applied dc field for **1** (Fig. S5, see ESI†). Both in-phase ( $\chi'$ ) and out-of-phase ( $\chi''$ ) signals of ac magnetic susceptibility show obvious frequency dependence below 8 K, but no peak is observed, which can be attributed to the presence of a fast relaxation of the magnetization through quantum tunnelling mechanism.<sup>1-2</sup> The application of a dc field may remove the ground state degeneracy and fully or partly suppress the quantum tunnelling process.<sup>16</sup> Therefore, the variable-frequency ac susceptibility at 1.8 K were measured with application of dc fields ranging from 300 Oe to 3900 Oe for checking quantum tunnelling effects (Fig. S6, see ESI†). A well resolved peak is observed above 10 Hz and shows the typical shift in peak position resulted by the collective effect of quantum tunnelling and direct process.<sup>15</sup> The optimum field is extracted to be 900 Oe by plot of  $\tau$  versus  $H$ . Under 900 Oe dc field, both the temperature (Fig. 5) and frequency dependence (Fig. 6) of out-of-phase ac susceptibilities signal are observed. The parameter  $\phi = (\Delta T_p / T_p) / \Delta(\log \nu) = 0.23$  calculated by the data extracting from the temperature dependence of in-phase ac susceptibility, excludes the possibility of spin-glass behaviour ( $0.01 < \phi < 0.08$ ).<sup>17</sup> Compound **1** relaxes slowly over the temperature range 1.8 to 4.2 K under a 900 Oe applied field. However, the corresponding plot of  $\ln(\tau)$  vs.  $1/T$  shows obvious deviations from linearity (Fig. 7), indicating the multiple pathways existed for relaxation of the magnetizations. In this condition, only a few of the high temperature points can be fitted to extract a value of the relaxation barrier and provide an estimate of  $\Delta/k_B$ . To quantitatively compare the respective influences of the other possible spin-lattice relaxation mechanisms, namely the quantum tunneling (QTM), Raman and direct processes, equation (1) was introduced to fit the entire range of temperature-dependent relaxation.<sup>18</sup> In equation (1), the first, second, third, and last terms account for the temperature-dependence of QTM, direct, Orbach, two-phonon Raman processes, respectively. And the first attempting involving all the relaxation processes yielded the negligible value for  $\tau_Q^{-1}$  ( $2.44 \times 10^{-20} \text{ s}^{-1}$ ) and related small value of  $C$  ( $6.00 \times 10^{-4} \text{ s}^{-1} \text{ K}^{-7}$ ) precluding the contributions from QTM and two-phonon

Raman processes. So, to avoid overparametrization, the QTM and two-phonon Raman processes were precluded from the final fits. The successful fitting (Fig. 7) was achieved using the sum of Orbach and direct processes with the best-fit parameters as follows:  $A = 208.29 \text{ s}^{-1} \text{ K}^{-1}$ , the effective energy barrier  $\Delta/k_B = 37 \text{ K}$  and pre-exponential factor  $\tau_0 = 5.27 \times 10^{-8} \text{ s}$ , which lie in the usual range of SMMs.<sup>1-2</sup> The result reveals that the relaxation occurs largely via the coefficient of Orbach and direct processes, in which the former process dominates the higher temperature range while the latter rules the lower.

$$\tau^{-1} = \tau_Q^{-1} + AT^m + \tau_0^{-1} \exp(-\Delta_{\text{eff}} / k_B T) + CT^n \quad (1)$$

The data of Cole-Cole plots can be fitted by the generalized Debye model and yields  $\alpha$  parameter of 0.45–0.30 in the temperature range from 1.8 to 5 K (Fig. S7, Table S4, see ESI†). The relatively high  $\alpha$  values imply a wide range distribution of relaxation times and more than one relaxation processes are occurring.<sup>2a,19</sup> The range distribution of  $\alpha$  parameters may attribute to the presence of two enantiomeric  $\text{Dy}^{3+}$  centres in  $P6_1$  or  $P6_5$  local environment, the dipolar interaction among the  $\text{Dy}^{\text{III}}$  centers as well as the coefficient of Orbach and direct processes mentioned above.<sup>1c,3,5,20</sup> But the accurate origin of the relaxations is unclear, which needs detailed *ab initio* calculations.

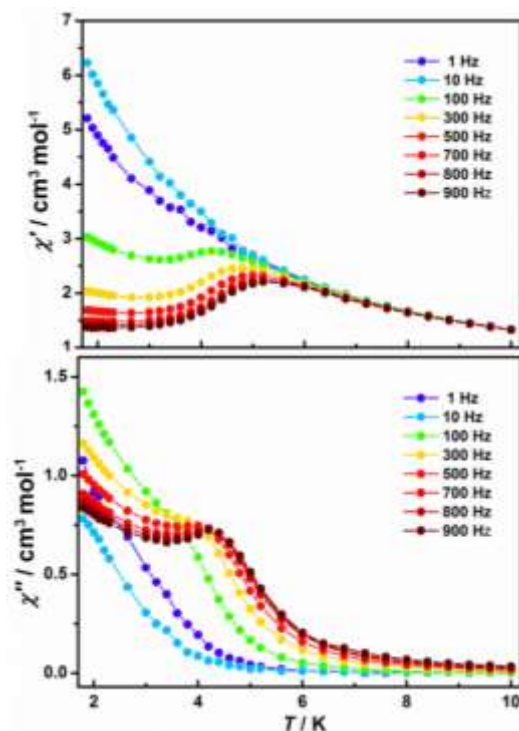


Fig. 5 Temperature dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility for **1** under 900 Oe dc field with an oscillation of 2.5 Oe.



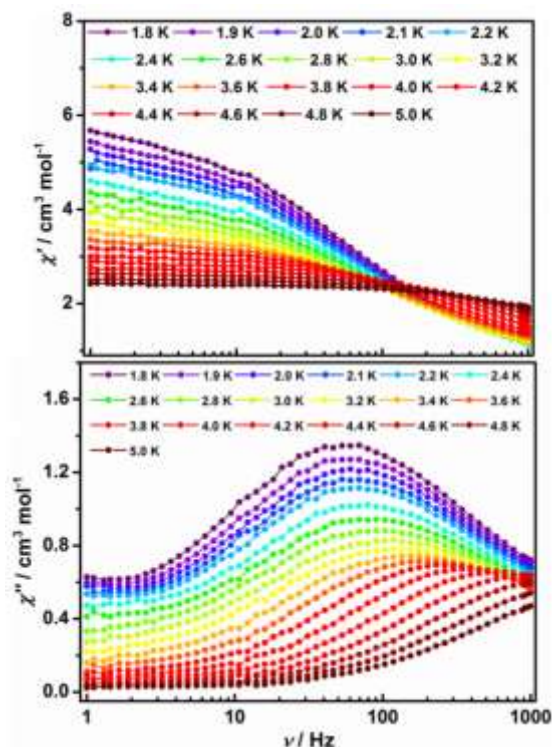


Fig. 6 Frequency dependence of the in-phase (top) and out-of-phase (bottom) ac susceptibility for **1** under 900 Oe dc field with an oscillation of 2.5 Oe.

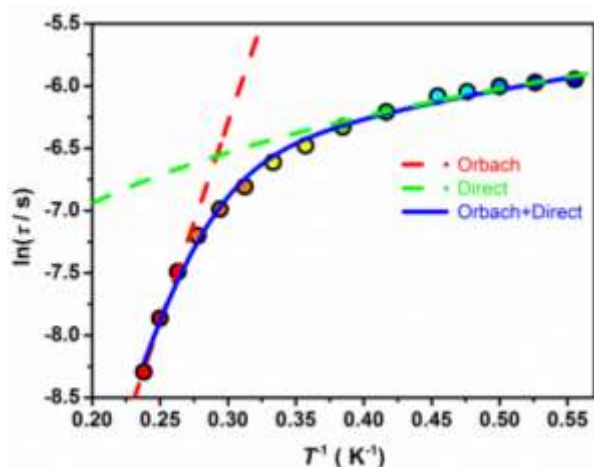


Fig. 7 Plot of  $\ln(\tau)$  vs.  $1/T$  for **1**, obtained under an applied field of 900 Oe over the temperature range 1.8–4.2 K. The blue line represents the fit to the experimental data using equation 1 (main text). Red and green dashed lines represent individual Orbach and Direct processes fits, respectively.

## Conclusions

In summary, a 1D helix  $\text{Dy}^{3+}$  chain has been synthesized via solvothermal method. Magnetic investigation reveals that compound **1** displays ferromagnetic coupling at low temperature and exhibits slow magnetic relaxation behaviour. Under a small applied dc field, the energy barrier  $\Delta/k_B = 37$  K with pre-exponential factors  $\tau_0 = 5.27 \times 10^{-8}$  s can be obtained via ac susceptibility study. Compound **1** is a rare example of a Dy-based helix chain exhibiting SMM behaviour. The result

reported here would enrich the available database in order to enhance the fundamental knowledge of the magnetic properties of Ln-based chains.

## Experimental

**General remarks.** All the materials and reagents are commercially available and were used without further purification. FT-IR spectrum was measured with a Bruker Tensor 27 Spectrometer on KBr disks in the 400–4000  $\text{cm}^{-1}$  region. Elemental analysis was performed on a Perkin–Elmer 240 C H N elemental analyzer. Thermal analysis (under  $\text{N}_2$  atmosphere, heating rate of  $10^\circ\text{C min}^{-1}$ ) was carried out in a Labsys NETZSCH TG 209 Setaram apparatus from room temperature to  $800^\circ\text{C}$ . Powder X-ray diffraction measurement (PXRD) was recorded on Ultima IV X-ray diffractometer using  $\text{Cu-K}\alpha$  radiation. The simulated powder pattern was calculated by using Mercury 2.0. Solid state circular dichroism (CD) spectra were measured on a JASCO J-715 spectropolarimeter with KBr pellets. The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-VSM operating between 1.8 and 300 K for dc-applied fields ranging from  $-7$  to  $7$  T. Dc analyses were performed on polycrystalline sample, while ac susceptibility measurements were carried out under an oscillating field of 2.5 Oe with ac frequencies ranging from 1 to 1000 Hz. Diamagnetic corrections were applied for the sample holder and Pascal's constant.

**X-ray crystallography.** Crystallographic data of **1** in space group of  $P6_1$  or  $P6_5$  was collected with a SuperNova, Single source at offset, Eos diffractometer with a  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Both the structures were solved by direct methods and refined anisotropically by full-matrix least-squares techniques based on  $F^2$  using the SHELXS-97 and SHELXL-97 programs contained on Olex 2.<sup>21</sup> Crystal data as well as details of data collection and refinement for the compounds are summarized in Table S1, and Table S2. CCDC: 1008253 and 1008252 for **1**- $P6_1$  and **1**- $P6_5$ , respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Synthesis of  $[\text{Dy}(\text{HNA})(\text{NA})_2(\text{NO}_3)]_n$  (**1**).** A mixture of pyridine-2,3-dicarboxylic acid (0.5 mmol, 0.0835 g),  $\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.2 mmol, 0.0912 g), 1*H*-1,2,4-triazole (0.2 mmol, 0.0140 g), a drop of  $\text{Et}_3\text{N}$  and 6 mL  $\text{CH}_3\text{CN}$  were sealed in a 25 mL Teflon-lined stainless steel container and heated to  $140^\circ\text{C}$  with increasing rate of  $1^\circ\text{C min}^{-1}$ , and maintained for 3 days under autogenous pressure, then cooled to room temperature with decreasing rate of  $5^\circ\text{C h}^{-1}$ . The microtube-shaped yellow crystals were obtained in 42% yield (based on Dy). Compound **1** crystallized in  $P6_1$  or  $P6_5$ , which are synthesized in one reaction container and unable to be separated by naked eyes. Elemental analysis calcd (%) for

$C_{18}H_{13}DyN_4O_9$  (FW: 590.82): C 36.53, H 2.21, N 9.47; found (%): C 36.32, H 2.60, N, 9.22. IR (KBr disk,  $\nu$   $cm^{-1}$ ): 1649.1 (m), 1595.1 (m), 1475.5 (m), 1425.4 (m), 1303.8 (m), 673.1 (s).

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## Notes and references

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† Electronic Supplementary Information (ESI) available: *structural characterizations, crystallographic information and magnetic property plots*. CCDC: 1008253 (1-P6<sub>i</sub>), 1008252 (1-P6<sub>s</sub>). See DOI: 10.1039/b000000x/

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