Herein, we reported two didysprosium single-molecule magnets constructed with (Dy(bbpen)(MeOH)) subunits and a \(\pi\)-conjugated tpb or non-conjugated tpcb bridging ligand. The former exhibits extremely weak luminescence that makes it difficult to simulate its emission spectra. However, the later shows obviously enhanced and well-resolved luminescence, which helps us to gain knowledge about the magneto-optical correlation and the relevant magnetic energy levels.

Single-molecule magnets (SMMs), exhibiting magnetic blocking at low temperatures, have been investigated for decades owing to their promising role in molecule-level information storage and processing.\(^1\)-\(^7\) In addition to the slow relaxation of magnetization, some SMMs had been reported with multifaceted behaviors, such as redox activity,\(^8\)-\(^11\) photochemical reaction,\(^12\)-\(^15\) ferroelectricity,\(^16\)-\(^19\) conductivity,\(^20\),\(^21\) spin crossover,\(^22\),\(^23\) and luminescence,\(^24\),\(^25\) where those properties are simply coexistent or display complicated synergy effects.

To comprehensively understand magnetic behaviours in multifunctional SMMs, energy levels relevant to the magnetic states are one of the most important information. In this regard, \textit{ab initio} calculations have been widely used as a powerful tool to obtain energy levels and further explain the magnetic relaxation mechanism reasonably.\(^31\)-\(^33\) Nevertheless, experimental evidence is crucial in verifying the result of \textit{ab initio} calculations. Taking advantages of the characteristic lanthanide luminescence, luminescent Ln-SMMs are regarded as a useful model for obtaining their magnetic sublevels of the ground crystal-field term in experiments.\(^24\),\(^25\) Moreover, luminescence spectra under a pulsed high magnetic field can even provide information about the Zeeman splitting.\(^34\),\(^35\)

Combining the magnetic measurements, specific lanthanide luminescence spectra and \textit{ab initio} calculations of the opto-magnetic systems can provide extremely valuable information on the magnetic sublevels.

On the one hand, for some Ln-SMMs, the f-f forbidden transitions of lanthanide ions and competitive fluorescence or phosphorescence of organic ligands reduce their luminescence, creating an obstacle to obtain energy levels from emission spectra. Therefore, it is required to select a suitable ligand as “antennas” for sensitizing the lanthanide ions.\(^36\),\(^37\)

On the other hand, to avoid the overlap of the fine structures of the luminescence spectra, the larger energy gap is very helpful for the unambiguous understanding of magneto-optical correlations. Therefore, the design and synthesis of Ln (\(n\)) SMMs with large crystal-field splitting should be also taken into consideration. It is believed that adequate coordination environments are critical for constructing high-performance Ln(\(n\)) SMMs,\(^38\),\(^39\) and aryloxides,\(^40\) cyclopentadienyls,\(^41\)-\(^45\) silanols,\(^46\),\(^47\) fluoride ion\(^48\) etc. are some of the good choices, whose electrostatic interaction offers a strong axial ligand field between the Ln(\(n\)) and the O-donor, leading to a large energy barrier (\(U_{\text{ct}}\)) and high blocking temperature (\(T_B\)).

In this context, we used the aryloxide ligand \(\text{H}_2\text{bbpen} (N_2\text{N}^\prime\text{-bis}(2-hydroxybenzyl)-N,N^\prime\text{-bis}(2-picolyl)ethylene diamine)\) as a strong axial ligand field and 1,2,4,5-tetra(pyridin-4-yl)benzene (tpb)\(^51\)-\(^54\) as a bridging ligand between the two highly magnetic anisotropic \{Dy[bbpen](MeOH)\} subunits. Then, a didysprosium SMM was successfully obtained, having the formula of \([\text{Dy}_2(\text{bbpen})_2(\text{tpb})(\text{MeOH})_2]\text{(BPh}_4)_2\text{·2MeOH}\) (1). Complex 1 exhibits high-performance SMM property with an effective barrier (666 K), whilst its luminescence is too weak to analyse its fine structure, which limits further study of its energy levels experimentally. After we changed the bridging ligand from the \(\pi\)-conjugated tpb to the non-conjugated 1,2,3,4-tetra(pyridine-4-yl)cyclobutane (tpcb)\(^55\) we obtained another didysprosium SMM, having the formula of \([\text{Dy}_2(\text{bbpen})_2(\text{tpcb})(\text{MeOH})_2]\text{(BPh}_4)_2\) (2). The luminescence becomes obviously enhanced.
and well-resolved. Based on the magnetic measurements, optical characterization and \textit{ab initio} calculations, we investigated the magneto-optical correlation and the energy levels of 2 in \textit{ab initio} calculations as well as in experiments.

Complexes 1 and 2 can be synthesized via the mixture of the [Dy(bbpen)NO$_3$] precursor,\textsuperscript{56–59} tpb or tpcb and NaBPh$_4$ in MeOH, and slow evaporation under ambient conditions (more details in ESI†). The single-crystal X-ray diffraction measurements were performed to reveal the crystallographic structures (Fig. 1). As described above, tpb and tpcb served as the bridging ligands to link two \{Dy(bbpen)(MeOH)\} subunits. Also, it should be mentioned that the \{Dy(bbpen)(MeOH)\} subunits in 1 are linked in \textit{cis}-position, whilst \textit{trans}-position in 2. Besides, the coordination environment of Dy(III) in 1 is slightly different, whilst that in 2 is crystallographically identical.

The multidentate bbpen$^{2-}$ encloses Dy(III) in the [N$_4$O$_2$] pocket (four N from amines/pyridines and two O from aryloxides) in both complexes. The Dy–O bond lengths range from 2.18 to 2.43 Å (1) and from 2.17 to 2.41 Å (2), where the shortest Dy–O is along the metal-aryloxide bond in both the complexes, which induces a strong axial ligand field, with the axial O–Dy–O bond angle of 158°/155° (1) and 156° (2). The Dy–N bonds range from 2.54 to 2.64 Å (1) and 2.54 to 2.62 Å (2). The intramolecular Dy–Dy distances are 16.4002(8) Å (1) and 13.467(1) Å (2), while the shortest intermolecular Dy–Dy distances are 9.6874(8) Å (1) and 10.1813(4) Å (2), which suggest that the possible dipolar interactions between the Dy ions are similar in 1 and 2. Using SHAPE 2.1,\textsuperscript{60,61} the values of continuous shape measures (CShM) for Dy(III) indicates the distorted square antiprism (D$_{4d}$) coordination geometry in 1 and the distorted triangular dodecahedron (D$_{3d}$) coordination geometry in 2 (Table S3†).

Variable-temperature direct-current (dc) magnetic susceptibilities were measured on the polycrystalline samples under 1 kOe dc field (Fig. S9†). At room temperature, the $\chi_M$T products of 1 and 2 are 28.03 and 27.82 cm$^3$ K mol$^{-1}$, respectively, which slightly deviate from the sum of two isolated Dy(III) (28.33 cm$^3$ K mol$^{-1}$, $^6$H$_{15/2}$, $g_f$ = 4/3). With the decrease in temperature, the $\chi_M$T value of both the complexes decreases slightly in the high temperature range, which is related to the large separated excited Kramers doublets from the crystal-field splitting of Dy(III). The $\chi_M$T product decreases more rapidly at a lower temperature, which suggests the existence of magnetic blocking. The field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibilities were measured under 1.2 kOe, which respectively show an obvious divergence at 7 K (1) and 8 K (2), confirming the occurrence of magnetic blocking.

To estimate the dynamic magnetic behavior for 1 and 2, variable-temperature and variable-frequency alternating-current (ac) magnetic susceptibilities were recorded. As depicted in Fig. S12 and S15,† the maximum peak of $\chi''_M$ at 999 Hz is located at 52 K (1) and 57 K (2) at the zero dc field. Upon cooling, the peaks of the frequency-dependent signals exhibit the behavior of shifting towards lower frequency, showing typical characteristics of SMMs.

The variable temperature relaxation times under 0 Oe and 1.2 kOe can be fitted with the Arrhenius law ($\tau = \tau_0 \exp(-U_{\text{eff}}/k_B T)$) at high temperatures, giving $U_{\text{eff}}/k_B = 666(23)$ K and $\tau_0 = 5(2) \times 10^{-10}$ under 0 Oe, $U_{\text{eff}}/k_B = 681(26)$ K and $\tau_0 = 4(2) \times 10^{-10}$ under 1.2 kOe for 1, $U_{\text{eff}}/k_B = 889(13)$ K and $\tau_0 = 2.7(6) \times 10^{-11}$ under 0 Oe, $U_{\text{eff}}/k_B = 869(15)$ K and $\tau_0 = 4(1) \times 10^{-11}$ under 1.2 kOe for 2 (Fig. S19†). To get more information about the magnetization blocking, magnetic hysteresis was measured on the polycrystalline samples (Fig. 2). The typical butterfly-shaped loop clearly remains open at the zero field up to 6 K (1) and 8 K (2) (using a cut-off criterion of >1% saturation magnetization).\textsuperscript{39}

To further investigate the magnetic anisotropy of complexes, \textit{ab initio} calculations were performed on the single-crystal structures of 1 and 2 using the OPENMOLCAS program (more details in ESI†).\textsuperscript{31–33} As shown in Fig. S20 and S21,† the magnetic anisotropy axes ($g_c$) of the ground doublet of all the Dy(III) sites are along the electron-donating aryloxides. As the Dy–O from aryloxides are the shortest, it is quite consistent with the oblate-like charge distribution of $|m_f = \pm 15/2, J = 15/2 \geq$ doublet for Dy(III).\textsuperscript{38,39} As revealed in Fig. S22 and S23,† it is predicted that the dominant relaxation path for 2 undergoes the 4$^{	ext{th}}$ Kramers doublets (KDs) (1238 K). However, the transition rates between 3$^{	ext{rd}}$ KDs are much larger. Therefore, it is also reasonable that 2 principally relaxes through the 3$^{	ext{rd}}$ KDs

![a) b)](image-url)

**Fig. 1** The molecule structure of 1 (a) and 2 (b). Colour codes: Dy, orange; O, red; N, blue; C, grey. Hydrogen atoms and anion are omitted for clarity. Symmetry code (A): 1 – x, y, 3/2 – z.
(970 K), which is consistent with the experimental result (889 K). Moreover, later luminescence analysis further verifies that the relaxation transition is mainly through 3rd KDs (1015 K). However, the situation is more complicated in 1 because the asymmetric Dy(III) sites can undergo either the 2nd KDs or the 3rd KDs, giving rise to a lower effective barrier (666 K).

To get valuable information of the energy levels, photoluminescence spectra were measured for the polycrystalline samples. For comparing luminescence under the same conditions, both the complexes were excited at 322.7 nm around 6 K with the same instrumental parameter, i.e., slit width (Fig. 3, more details in ESI†). Unfortunately, complex 1 shows broad and weak peaks, which mainly originated from the tpb ligand (Fig. S7a and S8a†). Moreover, the fine structures of Dy(III) are largely smeared out (Fig. 3a), which hinder our further study on opto-magnetism correlation, even at the temperature as low as 6 K. It is known that the conjugation effect could decrease the energy of triplet state of the ligand, which reduces the energy transfer from the triplet state of the ligand to the F9/2 level of Dy(III).62 To reduce the conjugation of the ligand, we replaced the π-conjugated phenyl at the centre of tpb with non-conjugated cyclobutenyl. The emission spectrum of 2 exhibits three groups of characteristic sharp peaks of Dy(III) instead of the broad peak from the tpcb ligand (Fig. S7b and S8b†), which is quite different from that of 1, suggesting that the “antenna effect” of tpcb is stronger than tpb. In addition, the crystal packing effects on luminescence cannot be ignored and emission phenomena can be modified by molecular rotation.63–65 Then, the quantum yields were calculated and the results further support that the luminescence of 1 is particularly weak (ca.0% for 1 and 2.7% for 2). These peaks of 2 correspond to the f-f transitions, including the peaks around 475 nm (21 000 cm⁻¹, F9/2 → H15/2), 575 nm (17 400 cm⁻¹, F9/2 → H13/2), and 670 nm (15 000 cm⁻¹, F9/2 → H11/2) (Fig. 3a). In this study, we focus our attention on the F9/2 → H13/2 transition with a well-resolved structure (Fig. 3b), involving the lowest-lying energy levels related to the magnetic dynamics of Dy(III). To simulate the spectrum, Lorentz function fit was conducted, and it exhibits eight tran-
Fig. 4  Energy levels simulated by the luminescence spectra of 2, reversal barrier determined by the magnetic measurements and the energy levels calculated by ab initio calculations. The unidirectional arrows correspond to the f–f transition.

sitions attributed to the Stark splitting of $^6H_{15/2}$ sublevels (Fig. 4), which are commonly observed in the Dy(m) ion. The 2nd excited state is well-separated from the ground state by 1015 K, which is close to the experimental result (889 K from Arrenius law) and the ab initio calculations (970 K). As depicted in Fig. 4, the first two excited state levels obtained from the ab initio calculations (513 K for the 1st excited state, 970 K for the 2nd excited state) are comparable to the fitting results of optical spectrum (574 K for the 1st excited state, 1015 K for the 2nd excited state), which supports the results of ab initio calculations in the experiment.

In summary, by utilizing the aryloxide ligand H$_2$bbpen, we synthesized two organic ligand-bridged (tpb and tpcb) novel Dy(m) SMMs [Dy$_2$(bbpen)$_2$(tpb)(MeOH)$_2$]([BPh$_4$])$_2$·2MeOH (1) and [Dy$_2$(bbpen)$_2$(tpcb)(MeOH)$_2$]([BPh$_4$])$_2$ (2). Magnetic measurements indicate that both the complexes have high reversal barriers of 666 K (1) and 889 K (2), with opening magnetic hysteresis up to 6 K (1) and 8 K (2), whose high energy barrier is induced by strong axial anisotropy bearing the strong electron-donation from aryloxide. The fine-tuning of lanthanide characteristic luminescence was realized in 2 by reducing the conjugation effect of the ligand (from tpb to tpcb), while 1 barely exhibits broad and weak peaks. This result facilitates the subsequent analysis of the magnetic sublevels of the ground state. The optical characterization and analysis provide accurate information about the energy level splitting of $^6H_{15/2}$, which corresponds well with the magnetic measurements and show quantitative agreement with the ab initio calculations. We hope this study can be beneficial to the investigation of magneto-optical correlation in well-performed lanthanide single-molecule magnets.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the NSFC (grant no. 21620102002, 21822508, 21821003) and the Pearl River Talent Plan of Guangdong [2017BT01C161].

Notes and references