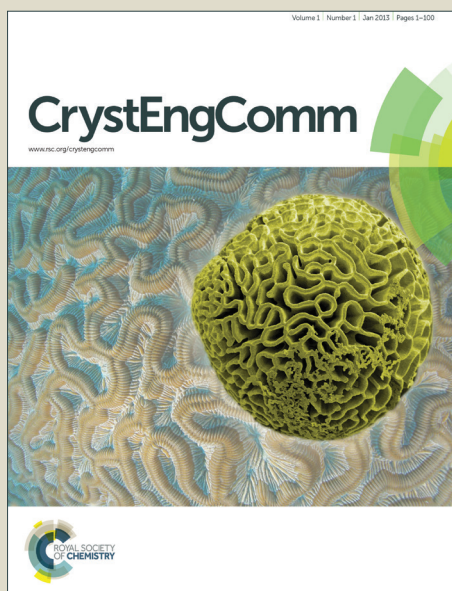


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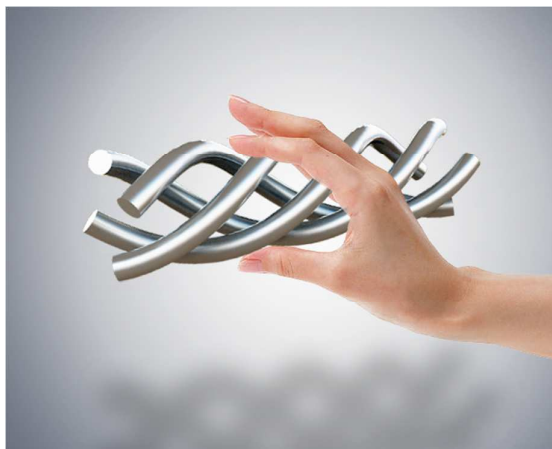
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Crystallization of Triple- and Quadruple-Stranded Dinuclear Bis- β -diketonate-Dy(III)

Helicates: Single Molecule Magnet Behavior

Peng Chen, Hongfeng Li, Wenbin Sun, Jinkui Tang, Lei Zhang and Pengfei Yan**



Quadruple-stranded Dy-containing helicates are crystallographically seized up through deliberate design on the bis- β -diketonate ligand. The triple-stranded helicates could be tuned by the incorporation of phenanthroline, which contributes to both tune the structure and strengthen the anisotropy barrier.



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Crystallization of Triple- and Quadruple-Stranded Dinuclear Bis- β -diketonate-Dy(III) Helicates: Single Molecule Magnet Behavior†

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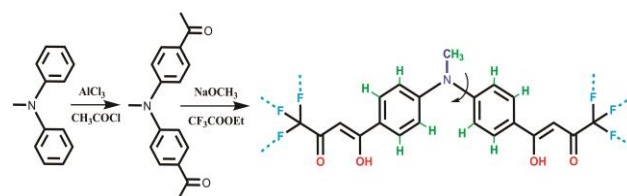
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Helical structures are vital in chemistry and biochemistry and its importance is reconsidered ever since DNA structure was revealed. In the past decades, the advantage of helical structures of bis- β -diketonate-based multiple-stranded Ln^{3+} complexes is speculated in respects to their unique structures. Based on our previous work, we have designed a V-shaped bis- β -diketone ligand H_2MBDA , which is utilized to crystallographically synthesize the triple-stranded and quadruple-stranded dinuclear Dy^{3+} complexes. In contrast to the absence of crystallographical results in previous studies, the successful crystallization in this work is contributed to the functionalization of the $-\text{CF}_3$ groups into the ligand as the termini, which have played a key role in the crystallization through the intermolecular weak interactions. Both complexes display slow magnetic relaxation. The auxiliary ligand phenanthroline contributes to both tune the structure and strengthen the anisotropy barrier.

Introduction

The self-assembly of lanthanide compounds with desired functional groups and controlled structural motifs has been the subject of many studies,¹ while the helices have been the focus in respect to their simplicity and significance as the basic structural motif in chemistry and biochemistry.² Besides geometrical remarks, intriguing magnetic and luminescent behaviors have been revealed with nonequivalent g -tensor and improved sensitivity, respectively.³ And various ligands in different lengths and sequences have been designed in pursuit of multiple-stranded helicates,⁴ while Piguet and Bünzli have greatly contributed to the development of this field.^{1g,2b,2f,5}

The β -diketones as versatile ligands are qualified to ligate to lanthanide ions, and the bis- β -diketones have recently been utilized to construct multiple-stranded helicates.^{4f} Pikramenou has shown the advantage of multiple-stranded helicates in enhancing the emission with higher quantum yield,⁶ but the proposed multiple-stranded complexes are not crystallographically characterized as those reported.⁷ The absence of crystallographical evidence would stem the further studies on the relationship of structure and



Scheme 1 Synthetic route for the ligand H_2MBDA and the schematic representation of the potential functionalization in the ligand. (Black: The rigid and lengthy spacers separate the binding units; Red: The binding sites allow the coordination to Dy^{3+} ions; Blue: N-methyl group undergoes the helication and avoids the formation of mesocates; Green and light blue: H atoms and $-\text{CF}_3$ groups give the weak C–H...F and F...F interactions.)

properties. In the past decade, advances in the design of the ligands have been achieved, but rare examples of lanthanide helicates assembled about bis- β -diketones are known. The crystallization of such helical structures comprises coordination interactions between ligands and metal centers as well as subtle control of intermolecular interactions between helical units.^{2f,5,8} Less consideration on the intermolecular interactions results in the poor crystallization of bis- β -diketonate- Ln^{3+} helicates, while most solution-based studies have imposed that a combination of rigidity, length and flexibility of the ligand is responsible for the coordination interaction.⁹ On account of the previous aspects on the crystallization of lanthanide helicates and the structural features in the crystallization of triple-stranded helicates in our previous work,^{2f,8} the $-\text{CF}_3$ groups are introduced as well to enrich and strengthen the intermolecular interactions to facilitate the crystallization of bis- β -diketonate-based helicates. In addition, the multiple-stranded bridged dinuclear lanthanide systems, featured

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by the similar coordination environment of the Dy^{3+} center, could provide a way to tune the anisotropy axes to align the anisotropic axis with higher energy barrier for spin reversal.^{3a}

Herein, we present the syntheses and crystallization of triple-stranded and quadruple-stranded helicates assembled about a V-shaped bis- β -diketone ligand N-methyl-4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl)diphenylamine (H_2MBDA) (Scheme 1). The coordination of four ligands to two Dy^{3+} ions at the termini gives rise up to the formation of quadruple-stranded **1**, while the employment of three ligands leads to outcome of triple-stranded helicate **2** in addition to two phenanthroline (phen) molecules. Interestingly, single molecular magnet (SMM) behavior is observed for **2** in respect to the slow relaxation of **1** under zero dc field, which is ascribed to the incorporation of phen as the auxiliary ligand in **2**.¹⁰

Results and discussion

Structural analysis revealed that **1** crystallizing in the monoclinic space group of $C2/c$, is a quadruple-stranded dinuclear helicate (Fig. 1). Each crystallographically distinct Dy^{3+} ion is eight-coordinated to O atoms from four MBDA ligands in the square antiprism geometry. The Dy–O bond lengths are in the range of 2.359(4)–2.433(4) Å, which are in accordance with the reported values. The geometry of each Dy^{3+} center is slightly different and detailed bond lengths are presented in Table S2. A cavity is therefore constituted up from the wrapping about two Dy^{3+} ions by four deprotonated ligands in a helical fashion, where a diethyl ether molecule residues during the crystallization. The dihedral angles between the two phenyl groups in each MBDA are in the range of 56.6(2)–66.4(2)°, indicative of the allowance to twist. The negative charge of $[\text{Eu}_2(\text{MBDA})_4]^{2-}$ is balanced by the protonated triethylamines. The Dy...Dy distance in the same helicate is 12.6 Å, which is comparable to that in the triple-stranded $\text{Eu}_2(\text{BTB})_3$.^{8a}

Having validated the crystallization of quadruple-stranded helicate **1**, we target an alternative strategy for the preparation of triple-stranded helicate **2** through the incorporation of neutral phen molecules. **2** crystallizing in the triclinic space group of $P-1$ is a triple-stranded dinuclear helicate. Each crystallographically independent Dy^{3+} ion is eight-coordinated to six O and two N atoms from three MBDA ligands and one phen in the square antiprism geometry as well. The Dy–O and Dy–N bond lengths are in the range of 2.277(2)–2.374(2) Å and 2.531(2)–2.573(3) Å, respectively. Similarly, three interwinding MBDA ligands around two Dy^{3+} centers result in the helical structures of **2**. The dihedral angles between the two phenyl groups in each MBDA are in the range of 51.8(10)–60.3(1)°. The Dy...Dy distance of 13.4 Å in **2** is slightly longer than in **1**, and it is far enough to exclude the intramolecular magnetic coupling for both cases.

Obviously, the understanding on the factors concerned with the crystal engineering would be of significant task for the synthesis of functional materials,¹¹ and it would provide deeper insight into the supramolecular assembly as well as their functional behavior arisen from the host-guest chemistry.¹² With respects to the crystallization of triple-stranded helicates based on bridging ligands containing two $-\text{CF}_3$ termini, we believe that some points are worth considered for the syntheses of the potential bis- β -diketone ligands for the crystallization of the quadruple-stranded helicates. Firstly, the rigid and lengthy moieties as the backbone enables it to sufficiently strand and chelate to two distinct metal ions (Scheme 1). With respect to the twisting plight of BTB in $\text{Eu}_2(\text{BTB})_3$, the flexibility is primary requirement as well for the ligand to constitute up the potential quadruple helicates, and a N-methyl group is therefore inserted between the two phenyl moieties.

In fact, it allows MBDA to twist around adopting a wide range of conformations and its asymmetric nature avoid the formation of mesocates as well.¹³ However, the flexibility permits the ligands to settle into conformations, disturbing the inter-ligand stacking. In comparison to the reported results, the salvation of the crystallization for the designing work may lie in the weak interactions, which always play a substantial role in driving the self-assembly. At last, the $-\text{CF}_3$ groups as the termini has been functionalized into the ligand that the fluorine has structural significance in the crystal engineering.¹⁴ As expected, extensive C...H...F and F...F interactions are detected for **1** and **2**, which steering the molecular orientation of the aromatic rings in the solid state.¹⁵ The rich bonds allow the complexes to crystallize from the solution without achieving identical conformation,¹⁶ since different conformers have been observed in **1** and **2** resulting from the easy rotation about the $\text{C}_{\text{phenyl}}-\text{N}$ single bond.

Phenanthroline is employed to satisfy the coordination geometry of Dy^{3+} ions in replacement of one MBDA in **2**, resulting in the tune-up of the structures.¹⁰ However, it could strengthen the magnetic energy barrier as well. Magnetic susceptibility measurements are carried out for **1** and **2** in an applied dc field of 500 Oe in the temperature range of 1.8–300 K. At room temperature, the χT values for **1** and **2** are 28.11 and 27.93 $\text{cm}^3 \text{K mol}^{-1}$, respectively, which are in good agreement with the expected value of 28.34 $\text{cm}^3 \text{K mol}^{-1}$ for two uncoupled Dy^{3+} ions ($S = 5/2$, $L = 5$, $^6\text{H}_{15/2}$, $g = 4/3$). The χT product remains relatively constant above 70 K before rapidly decreasing at lower temperatures reaching 20.25 and 19.72

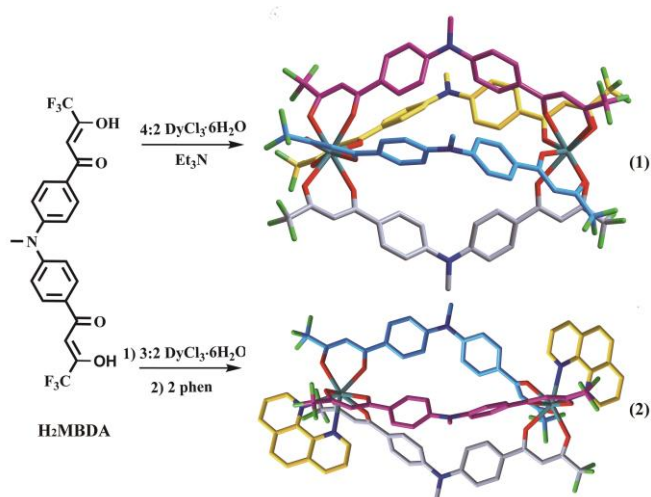


Fig. 1 The assemblies of quadruple-stranded **1** and triple-stranded **2** helicates. The C atoms in each ligand are marked in a different colour. H atoms and guest species have been omitted for clarity.

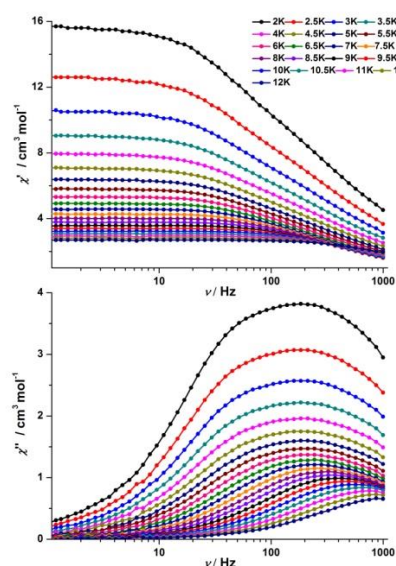


Fig. 2 Frequency dependence of the real (top) and imaginary (bottom) components of the ac magnetic susceptibilities for **2** under zero dc field in the temperature range of 2–12 K.

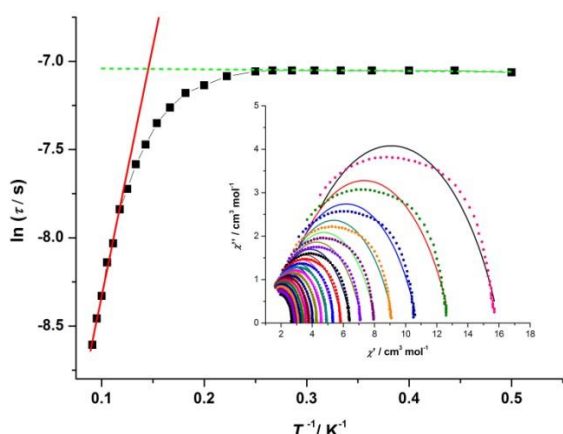


Fig. 3 The relaxation time is plotted as $\ln(\tau)$ vs T^{-1} for **2** under zero dc field. The red line is fitted using the Arrhenius law. Inset shows the Cole-Cole plots of **2** under zero dc field (2–12 K, an interval of 0.5 K).

$\text{cm}^3 \text{ K mol}^{-1}$ at 2 K for **1** and **2**, respectively. The decline of the χT product is generally indicative of intramolecular antiferromagnetic coupling of the metal centers. However, due to the large distance between the Dy^{3+} ions, this behavior is attributed to the thermal depopulation of the Stark sub-level and/or from the presence of large anisotropy in this system. The magnetization plots, M vs. H/T , for **1** and **2** show field dependence of the magnetization, which does not saturate at low temperature and high magnetic fields. The result reveals the existence of significant magnetoanisotropy and/or low lying excited states.

In order to study the possible SMM behavior, ac magnetic susceptibility measurements are carried out under zero dc field. No maxima of the characteristic frequency dependence of the out-of-phase signal, χ'' , is found for **1** below 14 K, indicative of obvious QTM. And it reveals the SMM behavior of **2** that a maximum at 10 K is detected (Fig. 2). Below 4 K, the relaxation of **2** becomes

temperature-independent, indicative of the quantum regime. Analysis on frequency-dependent data between 9.5 and 12 K by using Arrhenius law [$\tau = \tau_0 \exp(U_{\text{eff}}/K_B T)$, $\tau = 1/2\pi f_{\text{max}}$] gives a relaxation barrier of $U_{\text{eff}} = 28 \text{ K}$ and $\tau_0 = 1.4 \times 10^{-5} \text{ s}$ for **2**. The relatively smaller barrier is ascribed to the presence of QTM (Fig. 3).

To quench the quantum tunnelling effect of **1** and **2**, ac susceptibility measurements as a function of the frequency at different temperatures are carried out under dc field of 2000 Oe, where the quantum tunnelling is minimized (Fig. 4–5). The data

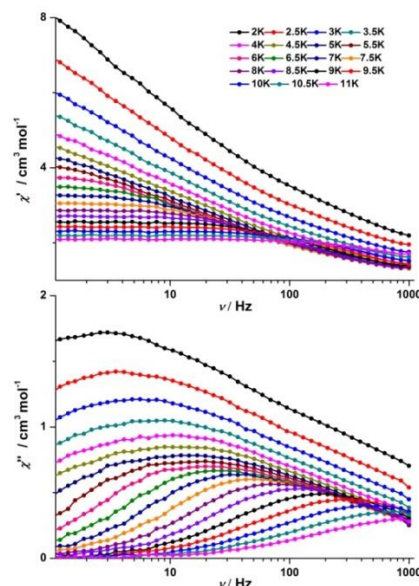


Fig. 4 Frequency dependence of the real (top) and imaginary (bottom) components of the ac magnetic susceptibilities for **1** under an applied field of 2000 Oe in the temperature range of 2–11 K.

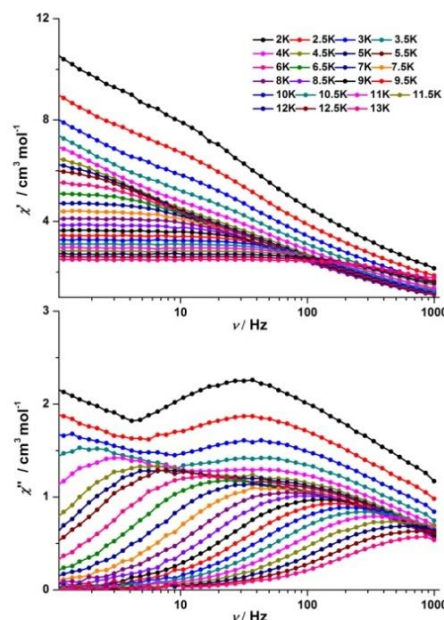


Fig. 5 Frequency dependence of the real (top) and imaginary (bottom) components of the ac magnetic susceptibilities for **2** under an applied field of 2000 Oe in the temperature range of 2–13 K.

plotted as Cole-Cole plots of **1** in the temperature range of 2–12 K shows symmetrical shape and can be fitted to the generalized Debye model.¹⁷ The relaxation time is extracted from the frequency-dependent data between 8–10.5 K and the Arrhenius plot obtained from these data is given in Fig. S16. Above 8.5 K, the relaxation follows a thermally activated Orbach mechanism with an energy gap of 81 K and a preexponential factor τ_0 of 1.0×10^{-7} s. Meanwhile, the occurrence of two distinct peaks for the out-of-phase ac signals (χ'') is evident at higher frequencies, revealing the possibility of a multiple relaxation process.¹⁸ The Cole-Cole plot of **2** in the temperature range of 2–13 K exhibits a unique double-ridge structure. The anisotropic energy gaps are calculated to be 59 K (1.6×10^{-6} s) and 9 K (3.7×10^{-4} s) for the low temperature and high temperature domains (Fig. S19), respectively. It is noted that the τ_0 values are larger than the expected values for SMM,¹⁹ which is probably enhanced by the presence of QTM.

Conclusions

The crystallization of triple-stranded and quadruple-stranded Dy-based helicates has been achieved through delicate ligand design, in respect to the advantage of weak interactions and the intrinsic geometric elements. The weak but attractive F...F and C-H...F interactions steer the molecular orientation to supramolecular self-assembly. The present work demonstrates the promise of bis- β -diketonate as excellent chelators for the synthesis of Dy-SMM, while **2** exhibits SMM behavior. Furthermore, it is believed that the 4f-based multiple helicates would be promising candidate for use in separation, catalysis and photocatalysis process in respect to their chiral nature.

Acknowledgements

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Experimental Section

Materials and instrumentation

Elemental analyses were performed on an Elementar Vario EL cube analyzer. FT-IR spectra were obtained on a Perkin-Elmer Spectrum One spectrophotometer by using KBr disks in the range of 4000–370 cm^{-1} . The ^1H NMR spectra were recorded on a Bruker Avance III 400MHz spectrometer in DMSO- d_6 solution. Magnetic susceptibility measurements were performed with the crystals of **1** and **2** in the temperature range 2–300 K, using a Quantum Design MPMS-3 SQUID magnetometer equipped with a 7 T magnet. The dc measurements were collected from 2 to 300 K and the ac measurements were carried out in a 2.0 Oe ac field oscillating at various frequencies from 1 to 1000 Hz and with a zero dc field. The diamagnetic corrections for the compounds were estimated using Pascal's constants, and magnetic data were corrected for diamagnetic contributions of the sample holder. MS detection was performed on an Agilent 6520 Q/TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer (all from Agilent). Thermogravimetric analyses were conducted on an SDT Q600 thermogravimetric analyzer at a heating rate of 20 $^\circ\text{C min}^{-1}$ under air atmosphere in the temperature range of 50–780 $^\circ\text{C}$.

Syntheses

H_2MBDA was synthesized by the Claisen condensation of ethyl trifluoroacetate and N-methyl-4,4'-diacetyldiphenylamine in DME (ethylene glycol dimethyl ether). A mixture of sodium methoxide (0.606 g, 11.22 mmol) and ethyl trifluoroacetate (1.328 g, 9.35 mmol) in 30 mL dry DME was stirred for 20 min, followed by the addition of N-methyl-4,4'-diacetyldiphenylamine (1.00 g, 3.74 mmol). Then, it was further stirred at room temperature for 24 h. The resulting mixture was poured into 100 mL ice-water and acidified to pH = 2–3 using hydrochloric acid (2 M), and the resulting white precipitate was filtered and dried in vacuum. Recrystallization from acetonitrile gave yellow flake crystals (1.3 g, 77 wt %). Anal. Calc. for $\text{C}_{21}\text{H}_{15}\text{F}_6\text{NO}_4$ (459.34): C, 54.91; H, 3.29; N, 3.05 wt%. Found: C, 54.93; H, 3.30; N, 3.05 wt%. IR (KBr, cm^{-1}): 3122 (w), 1582(s), 1487 (s), 1282 (s), 1202(s), 1158 (s), 1058 (s), 791 (m), 661 (w), 580 (m). ^1H NMR (400 MHz, DMSO- d_6 , 25 $^\circ\text{C}$, TMS): δ = 8.13 (d, J = 8.88 Hz, 4H), 7.31 (d, J = 8.88 Hz, 4H), 6.95 ppm (s, 2H), 3.50 ppm (s, 3H). ESI-MS m/z : 460.0939 ($\text{M}+\text{H}^+$).

$[\text{C}_6\text{H}_{16}\text{N}]_{3.5}[\text{Dy}_2(\text{MBDA})_4] \cdot 1.5\text{Cl} \cdot 2\text{CH}_3\text{CN} \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{C}_4\text{H}_{10}\text{O}$ (**1**) To a methanol solution (15 mL) of H_2MBDA (0.500 g, 1.089 mmol), triethylamine (0.220 g, 2.2 mmol), $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (0.199 g, 0.544 mmol) were consequently added and the mixture was further stirred for 24 h at room temperature. The precipitate was filtered and dried in vacuum. Single crystals of **1** suitable for single-crystal X-ray diffraction study were obtained by slow diffusion of diethyl ether into its (0.010 g) $\text{CH}_3\text{CN}/\text{acetone}$ (6 mL/8 mL) solution in 7 days (Yield: 35 %). Anal. Calc. for $\text{C}_{116}\text{H}_{130}\text{Cl}_{1.5}\text{Dy}_2\text{F}_{24}\text{N}_{9.5}\text{O}_{18}$ (2779.47): C, 50.13; H, 4.71; N, 4.79 wt%. Found: C, 50.05; H, 4.63; N, 4.80 wt%.

$[\text{Dy}_2(\text{MBDA})_3(\text{phen})_2] \cdot 0.5\text{CH}_3\text{CN} \cdot \text{C}_3\text{H}_6\text{O} \cdot \text{C}_4\text{H}_{10}\text{O}$ (**2**) A mixture of H_2MBDA (0.500 g, 1.089 mmol) and NaOH (0.087 g, 2.177 mmol) in methanol solution (15 mL) was stirred for 15 min at room temperature. Then, $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ (0.274 g, 0.73 mmol) in methanol solution (10 mL) was added dropwise and the resultant mixture was further stirred 12h. Finally, the auxiliary phenanthroline was added into the mixture, which was kept refluxing 4–5 h. The precipitate was filtered and dried in vacuum. Single crystals of **2** suitable for single-crystal X-ray diffraction study were obtained by slow diffusion of diethyl ether into its (0.010 g) $\text{CH}_3\text{CN}/\text{CHCl}_3/\text{acetone}$ (1 mL/6 mL/9 mL) solution in 7 days (Yield: 23 %). Anal. Calc. for $\text{C}_{95}\text{H}_{72.5}\text{Dy}_2\text{F}_{18}\text{N}_{7.5}\text{O}_{14}$ (2210.10): C, 51.63; H, 3.31; N, 4.75 wt%. Found: C, 51.59; H, 3.22; N, 4.99 wt%.

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