Accepted Manuscript

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PII:	80277-5387(17)30016-5
DOI:	http://dx.doi.org/10.1016/j.poly.2017.01.011
Reference:	POLY 12415
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To appear in:	Polynearon
Received Date:	19 September 2016
Revised Date:	4 January 2017
Accepted Date:	7 January 2017



Please cite this article as: X. Gao, H. Li, P. Chen, W. Sun, P. Yan, A series of triple-stranded lanthanide(III) helicates: syntheses, structures and single molecular magnets, *Polyhedron* (2017), doi: http://dx.doi.org/10.1016/j.poly. 2017.01.011

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A series of triple-stranded lanthanide(III) helicates: syntheses, structures and

single molecular magnets

Xingrui Gao^a, Hongfeng Li^a, Peng Chen^{a,b,*}, Wenbin Sun^a and Pengfei Yan^{a,*}

Abstract. Bis- β -diketones have been proven to be effective for the construction of multiple-stranded helicates, where there commonly are two distinct Ln^{3+} centers with subtle geometric difference. In this study, a series of triple-stranded helicates $[Ln_2(BTB)_3(DME)_2] \cdot C_6H_{14}$ have been prepared with the ligand H₂BTB and trivalent metallic ions, respectively [Ln = La (1), Ce (2), Pr (3), Eu (4), Dy (5), Ho(6) andYb(7), $H_2BTB = 4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl)biphenyl and DME =$ dimethoxyethane]. All products have been fully characterized by IR spectroscopy, elemental analysis, thermogravimetric analysis, and single-crystal X-ray diffraction analyses. Structural analysis reveals that 1-7 are isostructurally crystallized in the orthorhombic space group of $Pna2_1$ and each Ln^{3+} ion is ligated to six O atoms of three BTB ligands and two O atoms of one DME molecule. Interestingly, DME molecule as a chelator to the Ln^{3+} centers has played a unique role in the crystallization of the triple-stranded helicate 1–7. Magnetic measurement shows that 5 displays significant single-molecule magnetic property, exhibiting magnetic slow relaxation. And the large separation between Dy³⁺ ions in the same helicates leads to two distinct magnetic relaxation processes.

Keywords: helicates, lanthanide, triple-stranded, magnetics

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Introduction

The design and synthesis of highly organized structures have achieved considerable attention in the supramolecular chemistry and material chemistry [1]. Helicates as the simplest structural motifs have received much interests since their formation process is the basis for the supramolecular architectures and device [2]. Various ligands with distinct geometries and coordination modes have been designed [3] and the bis- β -diketones have been proven to be qualified to construct the multiple-stranded helicates as well [4,5]. The control on the shape, flexibility and functionality of the ligands highlights the diversified structures of the helicates, while the substitution of the organic spacers provides an impetus for further investigation on their supramolecular architectures. The bis- β -diketones was initially utilized to construct transition metal-based complexes for their rigidity as excellent building units [6]. Thereafter, the bis- β -diketones have recently found their importance in the formation of multiple-stranded lanthanide-based helicates, while the enhanced emission with an unexpectedly high quantum yield is observed for the multiple-stranded helicates [4a].

Notably, the β -diketonate-Dy strategy has proven successful for the preparation of the single molecular magnets (SMM) with larger energy barrier [7], ever since Gao et al reported the structure and magnetic behavior of first β -diketonate-Dy SMM [8]. Commonly, the Dy³⁺ ions are approximately located in a D_{4d} symmetry, and it provides a good sample for the theoretical calculation on the easy axis of SMM [9]. It is well-known that the local magnetic anisotropy of the Dy³⁺ ions are sensitive to the subtle changes of the ligand field and local geometry. However, it is difficult to predict the potential magnetic behavior of the complexes in respect to the complex coordination environment of Dy³⁺ centers. A great deal of researches have been done

to extend the understanding on this subject and establish a proper synthetic strategy for the application [10].

We have been devoted to the design and syntheses of bis- β -diketone ligands with the aim of enforcing triple-stranded and quadruple-stranded topological patterns and introducing functionality aspects to the resulting complexes [5,11-13]. A variety of bis- β -diketones have been synthesized with diversified rigid and flexible spacers, which are used to ligate to the Ln³⁺ ions, producing multiple-stranded dinuclear helicates. In addition, triple-stranded and/or quadruple-stranded helicates could be produced, depending on the geometry of the ligands and the auxiliary moieties [5d]. The multiple-stranded dinuclear systems, featured by the similar coordination environments of the Dy³⁺ centers, could provide a way to tune the anisotropy axes to align the anisotropic axis with higher energy barrier for the spin reversal [10c].

For this reason, we decide to explore and prepare SMM by using different ligands furnished by the organic spacers. The ligand H₂BTB^a with 3,3'-substituted biphenyl as one of the simplest rigid spacers has accomplished a deeper insight into the crystallization of polymorphs and supramolecular isomers [5a,5e]. The efforts on the alternative substitution position of the biphenyl groups are still unknown, while 4,4'-substituted biphenyl in more rigid and lengthy geometry would result in a ligand in a distinct geometry in respect to H_2BTB^a . And it would lead to different local environments of the Dy^{3+} centers. Taking into account of our previous reports, we present the syntheses, structures and magnetic behavior of a series of triple-stranded helicates $[Ln_2(BTB)_3(DME)_2] \cdot C_6H_{14}$ [Ln = La (1), Ce (2), Pr (3), Eu (4), Dy (5), Ho(6) and Yb(7)],which assembled about bis-β-diketone ligand are а 4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl)biphenyl (H₂BTB). DME serves as a chelating

moiety to the lanthanide centers, while it has played a decisive role in the crystallization of this series of helicates. The result iterates the concerns on the crystal engineering for the crystallization of multiple-stranded helicates [5d]. Magnetic measurement shows that **5** displays significant single-molecule magnetic property, and the large separation between Dy^{3+} ions in the same helicates leads to two distinct magnetic relaxation processes.

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. MS detection was performed on an Agilent 6520 Q/TOF mass spectrometer with an ESI source and an AgilentG1607A coaxial sprayer (all from Agilent). The ¹H NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer in a CDCl₃ solution. The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-3 operating between 1.8 and 300 K for dc-applied fields ranging from -7 to 7 T, and ac susceptibility measurements were carried out under an oscillating ac field of 2 Oe and ac frequencies ranging from 1 to 1000 Hz. A diamagnetic correction was applied for the sample holder. The sample was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos, ULTRA AXIS DLD) with monochrome Al K α (hy = 1486.6 eV) radiation. All binding energies were calibrated by referencing to C 1s (284.6 eV). Xray powder diffraction data were collected on a Bruker D5005 X-ray diffractometer with Cu Ka radiation ($\lambda = 1.5406$ Å). Thermogravimetric analyses were obtained on an SDT Q600 thermogravimetric analyzer at a heating rate of 20

°C/min under air atmosphere in the temperature range of 25–780 °C. All measurements were carried out by using fresh crystals. Single crystals of 1-7 were selected for X-ray diffraction analysis on a Xcalibur, Eos diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The crystals were kept at room temperature during data collection. The structures were solved by the direct methods and refined on F^2 by full-matrix least-square using the ShelXL2014 program [14]. The Ln^{3+} ions were firstly located, and then non-hydrogen atoms (C, O and F) were placed from the subsequent Fourier-difference maps and refined anisotropically. The H atoms were introduced in the calculated positions and refined with fixed geometry with respect to their carrier atoms. In the case of 1-4, 6 and 7, F1-F3, F10–F12 and F16–F18 atoms have been modelled as disordered with the equivalent occupancy. In the case of 6, n-hexane molecules have been treated as a diffuse contribution to the overall scattering without specific atom positions by squeeze/platon [15], in respects with the cases of 1-5 and 7. The crystallographic formula has been modified to include the non-located atoms. The relatively larger Useq values of the *n*-hexane molecules in all cases might be owing to their higher thermal motion and flexible configuration. The experimental details for the structural determination are presented in Table 1. CCDC: 1478966-1478972 contained the supplementary crystallographic data for this paper.



Scheme 1 The structure and the synthetic route for the ligand H₂BTB.

Synthesis of 4,4'-diacetylbiphenyl

A 100-mL round-bottomed Schlenk flask was charged with anhydrous AlCl₃ (1.82 g, 13.6 mmol), dry dichloromethane (50 mL), and acetyl chloride (1.07 g, 13.6 mmol), resulting in a yellow transparent solution. A dry dichloromethane solution of biphenyl (1.00 g, 5.5 mmol) was added dropwise to the above solution at -20 °C. After kept 12 hours at room temperature, the resulting mixture was poured into 50 mL ice-water and alkalized to pH = 7 using the aqueous solution of NaOH. The resulting precipitate was then filtered. The crude product was crystallized with ethanol and dried under vacuum (0.93 g, 64 %). Anal. Calcd. for C₁₆H₁₄O₂ (238.10): C, 80.65; H, 5.92 wt%. Found: C, 80.61; H, 5.88 wt%. IR (KBr, cm⁻¹): 3446 (w), 1600 (s), 1590 (m), 1401 (m), 1363 (s), 1264 (s). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.08 (d, J = 8.4 Hz, 4H), 7.74 (d, J = 7.4 Hz, 4H), 2.67 ppm (s, 6H). The ¹H NMR spectra were shown in Figure S1–2.

Synthesis of H₂BTB

 H_2BTB was synthesized by the Claisen condensation of ethyl trifluoroacetate and 4,4'-diacetylbiphenyl in DME (dimethoxyethane). A mixture of sodium

methoxide (1.40 g, 20.0 mmol) and ethyltrifluoroacetate (2.90 g, 20.0 mmol) in 40 mL dry DME was stirred for 10 min, followed by the addition of 4,4'-diacetylbiphenyl (2.00 g, 8.4 mmol). Then, it was further stirred at room temperature for 24 h (Scheme 1). The mixture was poured into 100 mL ice-water and acidified to pH = 2–3 using hydrochloric acid (2.0 M), and the white precipitate was filtered and dried under vacuum. Recrystallization from acetone gave white flake crystals (2.5 g, 68 %). Anal. Calcd. for C₂₀H₁₂F₆O₄ (430.06): C, 55.83; H, 2.81. Found: C, 55.89; H, 2.84. IR (KBr, cm⁻¹): 3118, 1602, 1445, 1270, 1208, 1187, 1106, 1059, 792, 723, 709, 627, 577. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.09 (d, J = 8.53 Hz, 4H), 7.80 (d, J = 8.53 Hz, 4H), 6.64 ppm (s, 4H). ESI-MS m/z 430.0708 (M+H⁺).

Syntheses of Ln₂(BTB)₃(DME)₂·C₆H₁₄

The synthetic methods for the triple-stranded helicates $Ln_2(BTB)_3(DME)_2 \cdot C_6H_{14}$ were similar and the preparation of 5 was given as an example. 0.29 g DyCl₃·6H₂O, 0.50 g H₂BTB and 0.24 g triethylamine were refluxed in MeOH (20 mL) for 3h, and the solution was kept stirred for extra 24 hours at room temperature. The addition of deionized water led to the precursor of white precipitates, which was filtered, collected and dried under vacuum. Single crystals of 5 suitable for X-ray analysis were obtained by the slow diffusion of *n*-hexane into its DME/CHCl₃ (1/3, v/v) solution in 7 days. Interestingly, it is found the crystallization of 1-7 is affected by the radius of lanthanide ions, the discrepancy of which is well-known arisen from the lanthanide contraction. Crystals in the larger size, better quality and higher

yields are obtained for the lighter lanthanides with larger radius than the heavier under the similar condition.

$La_2(BTB)_3(DME)_2 \cdot C_6 H_{14}(1)$

Yield: 76 %. Anal. Calcd. for C74H64La2F18O16 (1829.08): C, 48.59; H, 3.53

wt%. Found: C, 48.53; H, 3.49 wt%. IR (KBr, cm⁻¹): 2952, 1648, 1618, 1579.

1367, 1289, 1262, 1193, 1084, 1058, 1011, 785.

$Ce_2(BTB)_3(DME)_2 \cdot C_6H_{14}(2)$

Yield: 75 %. Anal. Calcd. for $C_{74}H_{64}Ce_2F_{18}O_{16}$ (1831.49): C, 48.53; H, 3.52 wt%. Found: C, 48.50; H, 3.49 wt%. IR (KBr, cm⁻¹): 2952, 1648, 1603, 1578, 1369, 1294, 1262, 1191, 1082, 1058, 1010, 785.

$Pr_{2}(BTB)_{3}(DME)_{2} \cdot C_{6}H_{14}(3)$

Yield: 70 %. Anal. Calcd. for C₇₄H₆₄Pr₂F₁₈O₁₆(1833.08): C, 48.49; H, 3.52 wt%.
Found: C, 48.44; H, 3.48 wt%. IR (KBr, cm⁻¹): 2953, 1643, 1606, 1579, 1366, 1294, 1261, 1191,1079, 1058, 1008, 786.

$Eu_2(BTB)_3(DME)_2 \cdot C_6H_{14}(4)$

Yield: 62 %. Anal. Calcd. for C₇₄H₆₄Eu₂F₁₈O₁₆ (1855.17): C, 47.91; H, 3.48 wt%. Found: C, 47.85; H, 3.41 wt%. IR (KBr, cm⁻¹): 2956, 1647, 1610, 1581, 1369, 1298, 1263, 1192, 1082, 1058, 1010, 785.

$Dy_2(BTB)_3(DME)_2 \cdot C_6H_{14}(5)$

Yield: 56 %. Anal. Calcd. for C₇₄H₆₄Dy₂F₁₈O₁₆ (1876.25): C, 47.37; H, 3.44 wt%. Found: C, 47.31; H, 3.41 wt%. IR (KBr, cm⁻¹): 2953, 1646, 1614, 1579, 1369, 1291, 1262, 1193, 1081, 1057, 1009, 786.

$Ho_2(BTB)_3(DME)_2 \cdot C_6H_{14}(6)$

Yield: 47 %. Anal. Calcd. for C₇₄H₆₄Ho₂F₁₈O₁₆ (1881.11): C, 47.25; H,3.43 wt%. Found: C, 47.21; H, 3.41 wt%. IR (KBr, cm⁻¹): 2952, 1645, 1610, 1579, 1369, 1298, 1263, 1192, 1080, 1060, 1009, 786.

$Yb_2(BTB)_3(DME)_2 \cdot C_6H_{14}(7)$

Yield: 36 %. Anal. Calcd. for C₇₄H₆₄Yb₂F₁₈O₁₆ (1897.33): C, 46.84; H,3.40 wt%. Found: C, 46.77; H, 3.38 wt%. IR (KBr, cm⁻¹): 2948, 1648, 1614, 1578, 1369, 1301, 1263, 1192, 1083, 1059, 1010, 786.

FT-IR spectra

The infrared spectra of 1–7 are similar, and 5 is selected as an example for further discussion. As shown in Figure S3, the vibration bands at 1646–1579 cm⁻¹ are attributed to the C=O stretching vibration of the ligands. In 5, the observation of the band shift by 20 cm⁻¹ compared with the free ligand reveals the coordination of Dy³⁺ ions to the O atoms of the ligand (Figure S4). The absence of the band at 3114 cm⁻¹ in 5 confirms the deprotonation of the bis- β -diketonate groups in H₂BTB as well. Due to the keto-enol tautomerization in the β -diketones, the C–O stretching vibrations could be observed at 1187 cm⁻¹ in the free ligand, while the corresponding intensity at 1193 cm⁻¹ is strengthened in respect to the incorporation of DME molecules. The C=C stretching vibrations of biphenyl are observed at 1579 cm⁻¹ and the vibration bands at 1262 cm⁻¹ are assigned to the C–C stretching vibrations of the diketonate moieties. The multiple bands observed around 2953 cm⁻¹ are attributed to the stretching vibration of DME to the Dy³⁺ ions in 5. Apart from the high frequency stretching vibrations of C–H, the in- and out-of-plane bending vibrations of C–H can also be

observed at 1369 and 1009 cm⁻¹. The peaks at 1081 and 1057 cm⁻¹ are attributed to the C–F stretching vibration.

Thermal behavior

The thermogravimetric analysis on the fresh crystals of **1–7** are conducted. For each compound, the first weight loss is clearly visible between 100 °C and 210 °C. It is attributed to the removal of *n*-hexane molecule, which fill out the intermolecular spaces. The second weight loss appears from 250 °C to 290 °C and it is assigned to the decomposition of two DME molecules attached to the Ln³⁺ centers. The following two steps are owing to the removal of BTB ligands and the final residue corresponds to the lanthanide oxide Ln₂O₃ for **1** and **4–7**, based on the observed and calculated values. However, it is well known that the oxide CeO₂ is formed upon the thermal decomposition of the cerium-based compound, and the final weight value is 18.74 wt% for CeO₂ (calcd. 18.79 wt%) in **2**. Pr₆O₁₁ is well-known formed at high temperature as well and the residue weight value agrees well with the theoretical values [16]. The detailed discussion on the thermogravimetric analyses are presented in the ESI (Figure S5).

Results and Discussion

Single crystal X-ray diffraction analysis reveals that 1–7 are isostructurally crystallized in the orthorhombic space group of $Pna2_1$ (Figure S6). Therefore, a full description of 5 is given as a representative example. As shown in Figure 1, 5 is a triple-stranded dinuclear helicate. In the asymmetric unit of 5, there are two Dy³⁺ centers, three BTB ligands, two DME and one *n*-hexane molecule. Each crystallographically distinct Dy³⁺ ion is eight-coordinated to six O atoms of three

BTB ligands and two O atoms of one DME molecule in the square antiprism geometry (Figure 1) [17]. It gives rise to the formation of the triple-stranded helicate, where three deprotonated BTB are wrapped about two Dy³⁺ ions. The structural analysis reveals that each dinuclear complex has homochiral Dy^{3+} centers in either left-handed $\Lambda - \Lambda$ or right-handed $\Delta - \Delta$ helix. The Dy–O distances are in the range of 2.271(9)–2.562(10) Å, which are in agreement with the reported values (Table S2) [5a]. The geometry of each Dy^{3+} center is slightly different and detailed bond lengths are listed in Table S1. The dihedral angles between the two phenyl groups in each BTB are in the range of $13.9-29.7^{\circ}$, while the phenyl groups of BTB^a twist more with the dihedral angles in the range of 40.3–65.3° [5a]. The Ln. Ln distance in the same helicate is 14.401(1) Å for 1 down to 14.210(1) Å for 7, in accordance with the lanthanide contraction effect (Table 2). The results are larger than the reported values [5a]. As far as we know, no cavity could be constituted up by three ligands to accommodate the guest species in the triple-stranded system. The *n*-hexane molecules are found among the helicates, filling up the intermolecular space [5a,5e]. In the structures of 1-7, plenty of weak intermolecular C-H...F and F...F interactions have been observed among the helicates and the guest molecules, which are of helps to the stability of the whole structures (Figure 2, Table S2) [18]. And it iterates the importance of the termini $-CF_3$ groups in the crystallization of the helicates, and guides the design and synthesis for the potential ligand [5].



Figure 1 The molecular structure of triple-stranded helicate **5** (The C atoms in each ligand are marked in a different colour. H atoms and guest species have been omitted



Figure 2 The packing diagram of **5** shows the weak C–H...F intermolecular interactions, viewed along the *b* axis. Detailed bond lengths are listed in Table S2.

Empirical formula $C_{x4}H_{ab}C_{x4}C_{x5}P_{x0}C_{x5}$ $C_{x4}H_{ab}P_{x4}P_{x0}C_{x5}$ $C_{x4}H_{ab}P_{x4}P_{x4}P_{x0}C_{x5}$ $C_{x4}H_{ab}P_{x4}P_{x4}P_{x4}$ $C_{x4}H_{x4}P_{x4}P_{x4}$ $A_{x4}P_{x4}$ $A_{x4}P_{x4}$ $A_{x4}P_{x4}P_{x4}P_{x4}P_{x4}P_{x4}$ $A_{x4}P$	Code	1	2	3	4	5	6	7
Formula weight 1829.07 1831.49 1833.08 1855.17 1876.25 1881.11 1897.33 Crystal system Orthorhombic Ana21 Pau21 Pau21 <t< td=""><td>Empirical formula</td><td>$C_{74}H_{64}F_{18}La_2O_{16}\\$</td><td>$C_{74}H_{64}Ce_2F_{18}O_{16}$</td><td>$C_{74}H_{64}F_{18}O_{16}Pr_2$</td><td>$C_{74}H_{64}Eu_2F_{18}O_{16}\\$</td><td>$C_{74}H_{64}Dy_2F_{18}O_{16}\\$</td><td>$C_{74}H_{64}F_{18}Ho_2O_{16}\\$</td><td>$C_{74}H_{64}F_{18}Yb_2O_{16}\\$</td></t<>	Empirical formula	$C_{74}H_{64}F_{18}La_2O_{16}\\$	$C_{74}H_{64}Ce_2F_{18}O_{16}$	$C_{74}H_{64}F_{18}O_{16}Pr_2$	$C_{74}H_{64}Eu_2F_{18}O_{16}\\$	$C_{74}H_{64}Dy_2F_{18}O_{16}\\$	$C_{74}H_{64}F_{18}Ho_2O_{16}\\$	$C_{74}H_{64}F_{18}Yb_2O_{16}\\$
Crystal systemOrthorhombicOrthorhombi	Formula weight	1829.07	1831.49	1833.08	1855.17	1876.25	1881.11	1897.33
space group Pma21	Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	<i>a</i> (Å)	43.4625(6)	43.5356(7)	43.4491(13)	43.2419(6)	43.2398(7)	43.2208(8)	43.1122(11)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	<i>b</i> (Å)	10.1303(2)	10.0879(2)	10.1166(3)	10.04000(10)	10.0112(4)	10.0045(2)	10.0010(4)
Volume (Å3)7750.0(3)7676.2(3)7730.2(4)7563.35(18)7517.9(4)7502.2(3)7465.7(4)Z4444444444Limiting indices $575/c55$ $582/c53$ $575/c56$ $495/c54$ $535/c51$ $555/c55$ $-12 \leq K \leq 13$ $-13 \leq K \leq 10$ $-13 \leq K \leq 10$ $-12 \leq K \leq 2$ $-12 \leq K \leq 2$ $-12 \leq K \leq 2$ $-22 \leq 22$ $-16 \leq 22$ $-21 \leq 21$ $-21 \leq 21$ $-21 \leq 22$ $-21 \leq 22$ Reflec, collec. 73471 22575 25516 75592 2592 33220 25368 /mique18216111491597115411107231407815519 R_{m} 0.05020.02630.03160.03220.04380.03100.0306 $R_1 [I > 2\sigma(I)]$ 0.09420.04600.09420.05130.0971 $wR_1 [I > 2\sigma(I)]$ 0.19080.09540.20280.09080.10400.11180.2584 R_1 (al data)0.10290.06020.10370.05880.06320.05330.1201 wR_2 (al data)0.19500.10230.20750.09440.10810.11660.2812GOF of I^2 1.1421.0761.1341.1621.1381.1341.079	<i>c</i> (Å)	17.6022(4)	17.4784(4)	17.5863(6)	17.4211(3)	17.3671(5)	17.3501(4)	17.3151(6)
Z44444444Limiting indices $-575h\leq59$ $-575d\leq55$ $-585d\leq53$ $-575d\leq56$ $495d\leq4$ $535d\leq41$ $555d\leq53$ $-125K\leq13$ $-135K\leq10$ $-135K\leq10$ $-125K\leq6$ $-125K\leq12$ $-125K\leq12$ $-125K\leq92$ $-225d\leq22$ $-16d\leq22$ $-21d\leq21$ $-15d\leq23$ $-21d\leq21$ $-21d\leq20$ $-21d\leq22$ Reflec. collec. 73471 22575 25516 7592 25992 33200 25368 Amique 82164 11149 15971 15411 10723 14078 13519 R_{mit} 0.0502 0.0263 0.0316 0.0322 0.0438 0.0310 0.0306 $R_1[I > 2\alpha(I)]$ 0.0942 0.0942 0.0517 0.0539 0.0453 0.0971 $wR_2[I > 2\alpha(J)]$ 0.1029 0.0602 0.1037 0.0588 0.0632 0.0533 0.1201 wR_2 (all data) 0.1950 0.1023 0.2075 0.0944 0.1081 0.1166 0.2812 GOF of F^2 1.142 1.076 1.134 1.162 1.138 1.134 1.079	Volume (Å ³)	7750.0(3)	7676.2(3)	7730.2(4)	7563.35(18)	7517.9(4)	7502.2(3)	7465.7(4)
Limiting indices $-575/re59$ $-555/re55$ $-585/re55$ $-575/re56$ $-495/re54$ $575/re54$ $-555/re55$ $-125K \le 13$ $-135K \le 10$ $-135K \le 10$ $-125K \le 6$ $-125K \le 12$ $-125K \le 9$ $-225/22$ $-165/re52$ $-215/re51$ $-215/re52$ $-215/re52$ $-215/re52$ $-215/re52$ Reflec. collec. 73471 22575 25516 7592 25992 33200 25368 Anique 00502 0.0263 0.0316 0.0322 0.0438 0.0310 0.0306 $R_{1}[I > 2\alpha(I)]$ 0.9942 0.0942 0.0517 0.0539 0.0453 0.0971 $wR_{2}[I > 2\alpha(J)]$ 0.1020 0.0602 0.1037 0.0688 0.0632 0.0333 0.1201 $wR_{2}(all data)$ 0.1950 0.1023 0.2075 0.0944 0.1081 0.1166 0.2812 GOF of F^3 1.142 1.076 1.134 1.162 1.138 1.134 1.079	Ζ	4	4	4	4	4	4	4
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	Limiting indices	-57≤h≤59	-57≤h≤55	-58 <i>≤h</i> ≤53	-57 <i>≤h</i> ≤56	-49≤h≤54	-53≤h≤41	-55≤h≤55
$-22 \le 22$ $-16 \le 22$ $-21 \le 21$ $-15 \le 23$ $-21 \le 12$ $-21 \le 20$ $-21 \le 22$ Reflec. collec.73471225752551675592250923322025368/unique18216111491597115411107231407813519 R_{int} 0.05020.02630.03160.03200.04380.03100.0306 $R_i [I > 2\sigma(I)]$ 0.09420.05170.05390.04530.0971 $wR_2 [I > 2\sigma(I)]$ 0.1980.09540.20280.09080.10400.11180.2584 R_1 (all data)0.10290.06020.10370.05880.06320.05330.1201 wR_2 (all data)0.19500.10230.20750.09440.10810.11660.2812GOF of F^2 1.1421.0761.1341.1621.1381.1341.079		-12≤K≤13	-13 <i>≤K</i> ≤10	-13 <i>≤K</i> ≤6	-13 <i>≤K</i> ≤10	-12 <i>≤K≤</i> 6	-12≤ <i>K</i> ≤12	-12 <i>≤K</i> ≤9
Reflec, collec.73471225752551675592259923322025368/unique18216111491597115411107231407813519 R_{mt} 0.05020.02630.03160.03220.04380.03100.0306 $R_1 [J > 2\sigma(I)]$ 0.09420.04600.09420.05170.05390.04530.0971 $wR_2 [J > 2\sigma(J)]$ 0.19080.09540.20280.09080.10400.11180.2584 R_1 (al data)0.10290.60620.10370.05880.06320.05330.1201 wR_2 (al data)0.19500.10230.20750.09440.10810.11660.2812GOF of F^2 1.1421.0761.1341.1621.1381.1341.079		-22 <i>≤l≤</i> 22	-16 <i>≤l≤</i> 22	-21 <i>≤l</i> ≤21	-15 <i>≤l</i> ≤23	-21 <i>≤l</i> ≤12	-21 <i>≤l</i> ≤20	-21 <i>≤l≤</i> 22
Junique18216111491597115411107231407813519 R_{int} 0.05020.02630.03160.03220.04380.03100.0306 $R_1 [I > 2\sigma(I)]$ 0.09420.04600.09420.05170.05390.04530.0971 $wR_2 [I > 2\sigma(I)]$ 0.19080.09540.20280.09080.10400.11180.2584 $R_1 (al data)$ 0.10290.06020.10370.05380.06320.05330.1201 $wR_2 (all data)$ 0.19500.10230.20750.09440.10810.11660.2812GOF of F^2 1.1421.0761.1341.1621.1381.1341.079	Reflec. collec.	73471	22575	25516	75592	25992	33220	25368
X_{mat} 0.05020.02030.05100.05220.04530.05100.0500 R_1 [$I > 2\sigma(I)$]0.09420.04600.09420.05170.05390.04530.0971 wR_2 [$I > 2\sigma(I)$]0.19080.09540.20280.09080.10400.11180.2584 R_1 (all data)0.10290.06020.10370.05880.06320.05330.1201 wR_2 (all data)0.19500.10230.20750.09440.10810.11660.2812GOF of F^2 1.1421.0761.1341.1621.1381.1341.079	/unique	18216	11149	15971	15411	10723	14078	13519
$M_1[1 > 20(1)]$ 0.0542 0.0500 0.0542 0.0511 0.0533 0.0433 0.0511 $wR_2[I > 2\sigma(I)]$ 0.1908 0.0954 0.2028 0.0908 0.1040 0.1118 0.2584 R_1 (all data) 0.1029 0.0602 0.1037 0.0588 0.0632 0.0533 0.1201 wR_2 (all data) 0.1950 0.1023 0.2075 0.0944 0.1081 0.1166 0.2812 GOF of F^2 1.142 1.076 1.134 1.162 1.138 1.134 1.079	R_{int}	0.0942	0.0203	0.0942	0.0517	0.0539	0.0310	0.0971
Rr (all data) 0.1029 0.0602 0.1037 0.0588 0.0632 0.0533 0.1201 wR2 (all data) 0.1950 0.1023 0.2075 0.0944 0.1081 0.1166 0.2812 GOF of F ² 1.142 1.076 1.134 1.162 1.138 1.134 1.079	$K_{I} \left[I > 20(I) \right]$	0.1908	0.0450	0.0942	0.0008	0.0539	0.0433	0.0971
A1 (an data) 0.1023 0.0012 0.1033 0.0034 0.1081 0.1166 0.2812 GOF of F ² 1.142 1.076 1.134 1.162 1.138 1.134 1.079	$R_{1} \text{ (all data)}$	0.1020	0.0507	0.1037	0.0588	0.0632	0.0533	0.1201
WA (all data) 0.1550 0.1025 0.2013 0.0044 0.1001 0.1100 0.5512 GOF of F ² 1.142 1.076 1.134 1.162 1.138 1.134 1.079	$W_{R_{2}}$ (all data)	0.1950	0.1023	0.2075	0.0944	0.1081	0.1166	0.2812
	$GOF \text{ of } F^2$	1 142	1.076	1 134	1 162	1 138	1 134	1.079
		Ç						

Table 1 Crystal data and structure refinement for 1–7.

Codes	Ln-O (Å)	Ln-O ^{BTB} (Å)	Ln-O ^{DME} (Å)	LnLn (Å)
1	2.364(1)-2.637(1)	2.364(1)-2.461(1)	2.550(9)-2.637(1)	14.401(1)
2	2.362(2)-2.662(3)	2.362(2)-2.476(2)	2.567(2)-2.662(3)	14.410(1)
3	2.370(1)-2.642(1)	2.370(1)-2.452(1)	2.558(8)-2.642(1)	14.398(1)
4	2.304(7)-2.597(7)	2.304(7)-2.406(6)	2.480(5)-2.597(7)	14.296(1)
5	2.271(1)-2.562(9)	2.271(9)-2.379(8)	2.446(6)-2.562(9)	14.266(1)
6	2.262(3)-2.561(7)	2.262(3)-2.373(3)	2.448(2)-2.561(3)	14.259(1)
7	2.242(4)-2.558(5)	2.242(4)-2.351(4)	2.418(4)-2.558(5)	14.210(1)

Table 2 Interatomic Ln-O and Ln...Ln distance ranges in 1-7

As we have previously discussed, the insufficiency in the flexibility of the 4,4'-substituted BTB ligand would result in the formation of triple-stranded helicate in respect to the 3,3'-substituted BTB^a ligand [5a]. Besides of six O atoms from three BTB ligands, the Ln³⁺ centers are believed to coordinated to two extra O atoms from water/methanol, which allow for the possibility to be replaced with proper solvent molecules. The solvents are well known to have significant impacts on the crystallization and polymorphs. And it has illustrated the unique role of the diversified solvents to the crystallization. We have previously prepared three complexes $[Dy_2(BTB^a)_3(CH_3OH)_4] \cdot 3CH_3OH,$ $[Dy_2(BTB^a)_3(DME)_2]$ and $[Dy_2(BTB^a)_3(DOA)(H_2O)_2] \cdot 4.5DOA$ (BTB^a 3,3'-bis(4,4,4-trifluoro-1,3dioxobutyl)biphenyl, DOA =1,4-dioxane) by using various solvents under the similar condition [5a]. The results have deepened our understandings on the factors concerned with the crystallization of the multiple-stranded bis-β-diketonate-Ln helicates, and similar synthetic strategy has been carried out in this work. Various solvents (methanol, ethanol, DOA and DMF etc) have been mixed with CHCl₃ to

dissolve the precursor, but we failed to crystallize the helicate, except for DME [19]. The structural analyses on **1–7** reveal that each DME molecule chelates to one Dy^{3+} center, replacing the water/methanol molecules. It is noted that the auxiliary ligands in the similar coordination modes (2,2'-bipyridine and 1,10-phenanthroline) are not helpful for the crystallization. All of the lanthanide elements are commonly known to have the +3 oxidation state. The relative ease to remove the 4th electron would lead to the separation of Ce⁴⁺ compounds in the basic condition. We are interested in the oxidation state of cerium, which has not been included in any multiple-stranded bis- β -diketonate helicates. Structural analysis indicates that **2** is isostructural to **1** and **3–7**, revealing the +3 oxidation state of cerium in **2**. X-ray photoelectron spectroscopy is employed as well to confirm the trivalence of cerium ions in **2**, as it is proposed by the structural analysis (Figure S7). Two strong peaks centered at 885 and 903 eV binding energy of Ce $3d_{3/2}$ and Ce $3d_{3/2}$ are observed, respectively [20].

Magnetic properties of 5

The direct-current (dc) magnetic measurements are performed in an applied magnetic field of 1000 Oe (Figure 3) for **5** in the temperature range of 1.8–300 K. At the room temperature, the value of χ T is 28.14, which are close to the expected value for two independent Dy³⁺ ions (28.34 cm³ K mol⁻¹): Dy³⁺ (S = 5/2, L = 5, ⁶H_{15/2}, g = 4/3, C =14.17 cm³ K mol⁻¹). The χ T product remained constant down to 75 K on lowering the temperature before dropping rapidly down to 24.50 cm³ K mol⁻¹ at 1.8 K. The decrease of χ T is likely due to crystal-field effects (i.e. thermal depopulation of

the Ln(III) Stark sublevels) and/or the possible antiferromagnetic dipole-dipole interaction between the molecules and, even if magnetic anisotropy might also



Figure 3 Plot of $\chi T vs T$ for 5 in an applied dc field of 1000 Oe in the temperature



Figure 4 Magnetization as a function of *H/T* for 5.

partially affect low temperature susceptibility. Magnetization (M) data for 5 are collected in the 0–7 T field range below 5K (Figure 4). The magnetization versus H/T data at different temperatures show nonsuperposition plots, and a gradual increase of 16

the magnetization at high fields, without a saturation even at 7 T, revealing the presence of a significant magnetic anisotropy and/or low-lying excited states.

The dynamics of the magnetization for 5 are investigated using alternating current susceptibility measurements. A temperature dependent increase of the in-phase signal with the appearance of an out-of-phase signal is observed for 5 (Figure S8). The increasing of χ' and χ'' below 6 K is indicative of the quantum tunnelling of the magnetization (QTM) at a zero dc field, which is typical properties for the lanthanide-based SMMs (Figure S9). To suppress the QTM effect, ac susceptibility measurements are performed under a static dc field of 2000 Oe for 5 (Figure 5). As expected, the QTM was suppressed obviously and the full peaks of temperature dependence of ac susceptibility are observed. The frequency-dependent data in the temperature range of 2–12 K for 5 display the intensity of the χ '' increases with decreasing the temperature and frequency. Moreover, it is worth noting that the two frequency dependent χ'' peaks are observed for 5, which is indicative of double relaxations processes. Multiple relaxation processes have been observed in some reported f-based SMMs mostly due to the existence of different anisotropic centers or isomers and conformers in the crystal. In respect to the structures of 5, there are two crystallographically independent Dy^{3+} centers, which should be responsible for the observation of two relaxations processes (Figure S10). The presence of two relaxation processes is further examined using a graphical representation, χ ' versus χ '. The Cole–Cole plots of 5 in the temperature range of 2-10 K exhibits a unique double-ridge shape and the data can be fitted very well via using the sum of two

modified Debye functions [21]. The two distinct peaks of the out-of-phase ac signals (χ'') at higher frequencies is evident, which reveals the occurrence of a double relaxation process deriving from two crystallographically independent Dy³⁺ centers in **5** [22]. The relaxation time is extracted from the frequency-dependent data based on the Arrhenius law [$\tau = \tau_0 \exp(U_{eff}/K_BT)$, $\tau = 1/2\pi f_{max}$] and the Arrhenius plot obtained from these data is given in Figure 6. The anisotropic energy barriers are calculated to be 12.4 K ($\tau_0 = 1.26 \times 10^{-5}$ s) and 35.6 K ($\tau_0 = 2.82 \times 10^{-6}$ s) for the low temperature and high temperature domains, respectively. It is noted that the τ_0 values are relatively larger than the expected values for SMM [23], which is probably due to the presence of quantum tunnelling magnetization.



Figure 5 Frequency dependence of the in-phase (χ' , top) and out-of-phase (χ'' , bottom) ac susceptibilities for **5** under 2000 Oe dc field in the temperature range of 2–11 K.



Figure 6 The relaxation time is plotted as $ln(\tau)$ vs T^1 for **5**. The solid lines are fitted using the Arrhenius law (blue: low temperature domain; red: high temperature

domain).

Conclusions

In summary, a series of triple-stranded helicates $[Ln_2(BTB)_3(DME)_2] \cdot C_6H_{14}$ incorporating various trivalent lanthanide ions (Ln = La³⁺, Ce³⁺, Pr³⁺, Eu³⁺, Dy³⁺, Ho³⁺ and Yb³⁺) have been prepared with a rigid bis- β -diketone ligand 4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl)biphenyl. The synthetic works have revealed that DME molecules have played unique role in the crystallization of 1–7, while the weak interaction are responsible to the crystallization as well. The intramolecular magnetic coupling could be excluded between the Dy³⁺ centers owing to their large separation in the same helicates, so the structure of the bis- β -diketonate-Dy SMM can be divided as two distinct single ion magnets. Therefore, we believed that the multiple-stranded dinuclear Dy³⁺ systems, featured by the subtle coordination environment of the Dy³⁺ centers, could supply an excellent sample for the chemists

and physicists to further understand the magneto-structural correlation. And it provides a way to tune the anisotropy axes to enhance the whole molecular magnetic anisotropy with higher energy barrier for the spin reversal.

Supporting Information

Electronic Supplementary Information (ESI) available: ¹H NMR spectra, FT–IR spectra, TG curves, Ce 3d XPS spectrum and the magnetic data are presented as Figure S1–S10. Selected bond lengths are given as Table S1–S2.

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Acknowledgements

The authors acknowledge financial support from the NSFC (21572048, 21102039, 21272061 and 51302068).

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A series of triple-stranded β-diketonate-Ln helicates have been assembled, where Acction dimethoxyethane molecules have played a unique role in the crystallization.