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# The role of ancillary ligand on regulating photoluminescence properties of Eu(III) helicates

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| ARTICLE INFO  | ABSTRACT  |  |  |  |
|---|---|--|--|--|
| Keywords:<br>Lanthanides<br>Complex<br>Luminescence<br>Ancillary ligands<br>Helicates | Three binuclear $Eu^{3+}$ helicates, $[Eu_2(OBTA)_3(H_2O)_3(CH_3COCH_3)] \cdot 1.5CH_3COCH_3 \cdot H_2O$ (1), $[Eu_2(OBTA)_3(Bpy)_2] \cdot 2CH_3COCH_3 \cdot CH_2Cl_2$ (2), $[Eu_2(OBTA)_3(Phen)_2] \cdot 2CH_3COCH_3$ (3) based a new bis- $\beta$ -diketone, 4,4'-bis(4,4,4-tri-fluoro-1,3-butanedione) diphenyl ether (OBTA) was prepared in order to insight into the effects of complexes structure on Ln <sup>3+</sup> ion emission properties. X-ray single crystal diffraction analyses confirmed the formation of binuclear triple-stranded helicates. The introduction of different ancillaries (Solvent molecular H <sub>2</sub> O and CH <sub>3</sub> COCH <sub>3</sub> ; 2,2'-bipyridine, Bpy and 1,10-phenanthroline, Phen) to helicates regulate the coordination environments around Eu <sup>3+</sup> ions, and lead to the obvious variations of photophysical properties. Combination the structural analyses and photophysical experiment results, the significance of spatial tension of helicate is embasized. |  |  |  |

#### 1. Introduction

Since the term "helicate" was firstly introduced by Lehn [1,2], this kind of helical metallosupramolecular architecture has received great attentions not only due to their fascinating structures, but also the accompanied optical [3–8], magnetic [9,10] and biomedical properties [11]. The generation of helicates need the ligand having a modest rigid, meanwhile the metal ions owning a predictable coordination direction. In this situation, the transition metals have markedly superiority to construct helicates due to their well coordination direction [12–14]. In contrast, the construction of lanthanide helicates is challenging in view of the large radii and undefined coordination geometries of Ln<sup>3+</sup> ions [15,16].

The motivation of preparing lanthanide helicates originated from their excellent luminescence properties [17,18]. In this realm, much efforts have been devoted by Piguet and Bünzli [19–22]. The stability and rigid of helicates generally endowed the complexes the higher luminescent quantum yields [23,24], while the supramolecular chirality arising from the helical twisting of ligand strands rendered the chiroptical properties of  $Ln^{3+}$  ion [25]. To insight into the effects of coordination structure on  $Ln^{3+}$  ion emission properties is the constant subject for lanthanide luminescence materials. The excellent structural stability of helicate provide a perfect platform to study the relationship between the coordination structure and luminescence properties.

Recently, bis- $\beta$ -diketones have been exploited as the excellent candidate to prepare lanthanide helicates [26,27]. The doubly negative charge of bis- $\beta$ -diketonate anion could strongly bonded to  $Ln^{3+}$  ion, by electrostatic and coordination interaction, and improve the thermodynamic stability of helicate. Additionally, the highly effective sensitizing capable of  $\beta$ -diketone on  $Ln^{3+}$  ion luminescence has also been well documented [28–30].

Herein, we designed a new bis- $\beta$ -diketone ligand, 4,4'-bis(4,4,4-trifluoro-1,3-butanedione) diphenyl ether, OBTA. The O-bridge between two  $\beta$ -diketonate units offers a modest rigid for ligand to wrap around Ln<sup>3+</sup> ion to form helicate. Upon self-assembly of OBTA and Eu<sup>3+</sup> in a 3:2 stoichiometric ratio, a triple-stranded binuclear Eu<sup>3+</sup> helicate was iso-[Eu<sub>2</sub>(OBTA)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>(CH<sub>3</sub>COCH<sub>3</sub>)]. lated with the formula, 1.5CH<sub>3</sub>COCH<sub>3</sub>·H<sub>2</sub>O (1). In order to investigate the effects of coordination environment on photophysical properties, two nitrogen-containing heterocycles, 2,2'-bipyridine (Bpy) and 1,10-phenanthroline (Phen) were selected as ancillary ligands to replace solvent molecules H<sub>2</sub>O and CH<sub>3</sub>COCH<sub>3</sub>. Single-crystal X-ray diffraction analyses confirmed the formation of [Eu<sub>2</sub>(OBTA)<sub>3</sub>(Bpy)<sub>2</sub>]·2CH<sub>3</sub>COCH<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub> (2)and [Eu<sub>2</sub>(OBTA)<sub>3</sub>(Phen)<sub>2</sub>]·2CH<sub>3</sub>COCH<sub>3</sub> (3). On the basis of the structure analyses and comprehensive photophysical experiments, it was concluded that the different spatial tension of helicates probably was the

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Research paper







Scheme 1. Synthetic routes of the L and the corresponding lanthanide complexes 1-3.

crucial factor to affect non-radiative decay rate, intrinsic quantum efficiency, even the total luminescence efficiency.

#### 2. Experimental section

#### 2.1. Materials and instruments

All commercially available chemicals and the solvents were analytical reagent grade and used without further purification.

The IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region using KBr disks and a PerkinElmer Spectrum One spectrophotometer. UV/vis absorption spectra were measured with a PerkinElmer (Lambda 25) spectrometer. <sup>1</sup>H NMR spectra were measured by using a Bruker Avance 400 (400 MHz) spectrometer in CDCl<sub>3</sub>. Electrospray mass spectrometry (ESI-MS) mass spectra were taken on Bruker maXis mass spectrometers. X-ray crystal data for the complexes were collected on a Xcalibur, Eos, Gemini diffractometer with Mo Ka radiation. The structures were solved by direct methods and refined on  $F^2$  by full-matrix least-squares using the SHELXTL-2014 program [31]. The level B alerts in checkCIF file are caused by some reflections which are omitted due to beam stop or overflow. The luminescence spectra and luminescence lifetimes were done on an Edinburgh FSL-920 fluorescence spectrometer. The absolute quantum yields of Eu(III) ions emissions were measured by an absolute method using an Edinburgh Instruments integrating sphere equipped with the Edinburgh FLS-920 fluorescence spectrophotometer. The values reported are the average of three isolated determinations. The absolute quantum yield were measured by the following expression:

$$\Phi = \frac{\int L_{emisson}}{\int E_{reference} - E_{sample}}$$

Where  $L_{\text{emission}}$  is the emission spectrum of the sample, collected by the integrating sphere,  $E_{\text{sample}}$  is the spectrum of the incident light collected by the sphere, and  $E_{\text{reference}}$  is the spectrum of the light used for excitation with only the reference in the sphere.

#### 2.2. Synthesis of 4,4'-diacetyl diphenyl ether

Acetyl chloride (2.77 g, 35.28 mmol) and anhydrous AlCl<sub>3</sub> (4.70 g, 35.28 mmol) dissolved in anhydrous dichloromethane (30 mL) were added dropwise to a stirred solution of diphenyl ether (2.00 g, 11.76 mmol) in anhydrous dichloromethane (20 mL). The reaction was stirred at room temperature overnight and the resultant mixture was poured into 100 mL ice water. The resulting organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure to give a crude product, which was purified by recrystallization from ethanol and acetone to afford white flake crystals (2.42 g, 81%). Anal. calc. for C<sub>16</sub>H<sub>14</sub>O<sub>3</sub> (254.09): C, 75.57; H, 5.55. Found: C, 75.44; H, 5.42. IR (KBr, cm<sup>-1</sup>): 1601, 1228, 1172, 1109, 789. EI-MS m/z 254.09 M<sup>+</sup>.

## 2.3. Synthesis of 4,4'-Bis(4,4,4-trifluoro-1,3-butanedione) diphenyl ether (OBTA)

A mixture of sodium methoxide (1.44 g, 26.67 mmol) and ethyl trifluoroacetate (3.84 g, 27.00 mmol) in dry DME (70 mL) was stirred for 10 min, followed by the addition of 4,4'-Diacetyl diphenyl ether (2.54 g, 10.00 mmol), which was further stirred at room temperature overnight. The resulting solution was quenched with water and was acidified to pH 2–3 using hydrochloric acid (1 M solution). The resulting yellow precipitate was filtered and dried at room temperature. Recrystallization from cyclohexane gave yellow needle crystals (3.38 g, 72%). Anal. Calc. for  $C_{20}H_{12}F_6O_5$  (446.06): C, 53.82; H, 2.71. Found: C, 53.71; H, 2.65. IR (KBr, cm<sup>-1</sup>): 3075, 1588, 1501, 1239, 1201, 1168, 1108, 799, 576. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): 15.19 (s, 2H), 7.99 (d, 4H), 7.17 (d, 4H), 6.55 (s, 2H). ESI-TOF-MS *m/z* 501.0481 [M + CH<sub>3</sub>OH + Na]<sup>+</sup>.

#### 2.4. Synthesis of [Eu<sub>2</sub>(OBTA)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>(CH<sub>3</sub>COCH<sub>3</sub>)] · 1.5CH<sub>3</sub>COCH<sub>3</sub>·H<sub>2</sub>O

OBTA (0.20 g, 0.45 mmol) and NEt<sub>3</sub> (0.10 g, 0.99 mmol) were dissolved in methanol (20 mL), and the mixture was allowed to stir for 20 min. EuCl<sub>3</sub>·6H<sub>2</sub>O (0.11 g, 0.30 mmol) in methanol (5 mL) was added dropwise and stirred at room temperature for 24 h. The precipitate formed after the addition of water was filtered and washed with H<sub>2</sub>O (3 × 10 mL) and CH<sub>3</sub>OH (3 × 10 mL) and dried in vacuum. Yield: 85%. Anal. Calc. For C<sub>60</sub>H<sub>38</sub>Eu<sub>2</sub>F<sub>18</sub>O<sub>19</sub> (1708.06): C, 42.09; H, 2.55. Found: C, 42.02; H, 2.47. IR (KBr, cm<sup>-1</sup>): 1620, 1459, 1311, 1291, 1244, 1169, 793. ESI-TOF-MS *m*/*z* 1658.9395 [Eu<sub>2</sub>(OBTA)<sub>3</sub> + Na]<sup>+</sup>.

#### 2.5. Synthesis of $Eu_2(OBTA)_3L_2$ [L = 2,2'-bipyridine (2), 1,10-phenanthroline (3)]

 $[Eu_2(OBTA)_3(H_2O)_3(CH_3COCH_3)]\cdot 1.5CH_3COCH_3\cdot H_2O$  (0.854 g, 0.50 mmol) was dissolved in methanol (25 mL), co-ligand (1.0 mmol) in methanol (15 mL) was added and refluxed for 7 h. After cooling to room temperature, the resulting white precipitate was filtered and dried under vacuum.

 $[Eu_2(OBTA)_3(Bpy)_2] \cdot 2CH_3COCH_3 \cdot CH_2Cl_2 \quad (2): \text{ Yield: } 85\%. \text{ Anal.} \\ Calc. For C_{80}H_{46}Eu_2F_{18}N_4O_{15} \quad (1948.16): C, \quad 49.19; \text{ H}, \quad 2.65; \text{ N}, \quad 2.83. \\ \text{Found: C, } 49.11; \text{ H}, \quad 2.59; \text{ N}, \quad 2.88. \text{ IR (KBr, cm}^{-1}): \quad 1619, \quad 1312, \quad 1249, \\ 1168, \quad 793. \quad \text{ESI-TOF-MS } m/z \quad 1971.0735 \quad [Eu_2(OBTA)_3(Bpy)_2 + \text{Na}]^+. \\ \end{array}$ 

 $\label{eq:cost} \begin{array}{l} [Eu_2(OBTA)_3(Phen)_2]\cdot 2CH_3COCH_3 \ (3): \ Yield: \ 80\%. \ Anal. \ Calc. \ For \\ C_{84}H_{46}Eu_2F_{18}N_4O_{15} \ (1996.16): \ C, \ 50.41; \ H, \ 2.60; \ N, \ 2.77. \ Found: \ C, \\ 50.34; \ H, \ 2.52; \ N, \ 2.82. \ IR \ (KBr, \ cm^{-1}): \ 1618, \ 1505, \ 1312, \ 1248, \ 1168, \\ 791.ESI-TOF-MS \ m/z \ 2019.0701 \ [Eu_2(OBTA)_3(Phen)_2 + \ Na]^+. \end{array}$ 

#### 3. Results and discussion

#### 3.1. Synthesis and characterization of ligands and complexes

The synthesis procedures of the ligand OBTA and their corresponding Ln(III) complexes **1**, **2** and **3** are outlined in Scheme 1. The  $C_2$ symmetric achiral bis- $\beta$ -diketone 4,4'-bis(4,4,4-trifluoro-1,3-



Fig. 1. ESI-TOF mass spectra of complexes 1–3 with insets showing the simulated (Sim.) and observed (Obs.) isotopic pattern.



Fig. 2. Ball-and-stick representation of the crystal structures of 1 (a), 2 (b), 3 (c).

dioxobutyl) diphenyl ether (L) was prepared via two steps, the first was the Friedel – Crafts acylation of diphenyl ether, then followed with a Claisen condensation of 4,4'-diacetyl diphenyl ether and ethyl trifluoroacetate. The corresponding intermediate and ligand were characterized by ESI-MS, ESI-TOF-MS and <sup>1</sup>H NMR (Figs. S1–S3).

The complex  $[Eu_2(OBTA)_3(H_2O)_3(CH_3COCH_3)]\cdot 1.5CH_3COCH_3\cdot H_2O$ (1), was isolated by stirring a 3:2 mixture of OBTA with the corresponding LnCl<sub>3</sub>·6H<sub>2</sub>O salts (Ln = Eu, Gd) with a triethylamine as base in Table 1 Shape analysis of Eu(III) complexes 1, 2 and 3 by SHAPE 2.1 software.

| Complexes | Square<br>antiprism (D <sub>4d</sub> ) | Triangular<br>dodecahedron (D <sub>2d</sub> ) | Biaugmented trigonal prism $(C_{2v})$ |  |
|-----------|--|---|---------------------------------------|--|
| 1         | 2.376                                  | 0.408   | 2.250                                 |  |
| 2         | 0.722                                  | 1.578   | 2.178                                 |  |
| 3         | 1.859                                  | 0.856   | 1.395                                 |  |



Fig. 3. UV–visible absorption spectra of OBTA, and complexes 1, 2 and 3 in CH\_3OH (1.0  $\times$   $10^{-5}$  M).

CH<sub>3</sub>OH. While the complexes  $[Eu_2(OBTA)_3(Bpy)_2] \cdot 2CH_3COCH_3 \cdot CH_2Cl_2$ (2) and  $[Eu_2(OBTA)_3(Phen)_2] \cdot 2CH_3COCH_3$  (3) were obtained by adding 2.0 equivalent of 2,2'-bipyridine or 1,10-phenanthroline into the solution of **1** in refluxing condition. High resolution ESI-TOF-MS analyses affirmed the successful preparation of triple-stranded helicates. From Fig. 1, three clusters of peaks with m/z at 1658.9395, 1971.0735 and 2019.0701 corresponding to  $[M + H]^+$  molecule ion peaks of three helicates,  $[Eu_2(OBTA)_3(H_2O)_3(CH_3COCH_3)] \cdot 1.5CH_3COCH_3 \cdot H_2O$ ,  $[Eu_2(OBTA)_3(Bpy)_2] \cdot 2CH_3CO CH_3 \cdot CH_2Cl_2$  and  $[Eu_2(OBTA)_3(Phen)_2] \cdot 2CH_3COCH_3$ , respectively, could be clearly observed. The assignments were further affirmed by comparing the isotopic distributions of the experimental with simulated results.

#### 3.2. X-ray crystallographic analysis

The dinuclear triple-stranded helical structures of three complexes were affirmed by single crystal X-ray diffraction analyses (Table S1). The complex 1 crystallized in the monoclinic space group  $P2_1/c$ , while the complexes **2** and **3** both crystallized in the monoclinic space group C2/c. In complex 1, each  $Eu^{3+}$  ion was eight coordinated to six O atoms from three  $\beta$ -diketone chelate units and two O atoms from solvent molecules H<sub>2</sub>O or CH<sub>3</sub>COCH<sub>3</sub> (Fig. 2(a)). The Eu–O (bis-β-diketonate) distances fall in the range of 2.361-2.411 Å, which are slightly shorter than those of Eu-O bond lengths of coordination solvent molecules, 2.435 and 2.472 Å. In complexes 2 and 3, the eight coordinated geometry of Eu<sup>3+</sup> ion was saturated by six O atoms of  $\beta$ -diketones and two N atoms from ancillary ligands Bpy or Phen, as shown in Fig. 2(b) and (c). The Eu–O distances are in range of 2.342–2.391 Å and 2.324–2.414 Å for complexes 2 and 3, respectively, while the Eu-N distances obviously lengthened, reaching to 2.554-2.568 Å in Bpy and 2.546-2.582 Å in Phen complexes. It was rational to consider that the O atoms had the stronger affinity than N atoms.

As previously reported by us and others [32-37], the coordination geometry around Eu<sup>3+</sup> ions have been proved to relate to their emission



Fig. 4. Solid state emission spectra of 1–3 with excitation at 374 nm.

properties. Therefore, the coordination geometries around  $Eu^{3+}$  ions in three complexes were calculated based on the crystal data by employing the SHAPE 2.1 software (Fig. S4). The smaller of calculated value, it was closer to the perfect coordination polyhedra. From the calculated values (Table 1), the coordination geometries of complexes 1 and 3 were suggested to fulfill an eight-coordinated triangular dodecahedral structure with the  $D_{2d}$  symmetry. In complex 2, a high symmetry eight-coordinated square antiprismatic structure (8-SAPR,  $D_{4d}$ ) should be more reasonable.

#### 3.3. Photophysical properties of helicates

The absorption spectra of free ligand OBTA and its corresponding  $Eu^{3+}$  complexes 1, 2 and 3 are shown in Fig. 3. They all display two clear bands in ranges of 250-300 nm and 300-380 nm, respectively. The low energy bands with maxima at about 330 nm could be attributed to the ILCT transition from benzene ring to  $\beta$ -diketone units. While the high energy bands are ascribed to the  $\pi$ - $\pi$ \* transitions localizing at benzene ring of ligand, 2,2'-bipyridine (Bpy) and 1,10-phenanthroline (Phen). In comparison with free ligand, the complexes all show a shoulder at about 354 nm, which was an exciton coupling feature usually observed in β-diketone complexes. It originated from the spatial proximity of three strand ligands. In addition, we also estimated the possible transition characters of ligand OBTA by DFT calculation with the Gaussian 09 package (basis set, B3LYP/6-31 + g(d,p)). From the optimized electron structure (Fig. S5), it can be observed that the electron cloud of HOMO orbital mainly locates at the diphenyl ether moiety, while in LUMO orbital the electron cloud spreads to diketone units. This result indicates that the electron transitions in the ligand probably have ILCT character.

Fig. 4 show the emission curves of three helicates upon excitation at 374 nm, the maxima value of excitation bands (Fig. S6). In the spectra, five emission bands at 580, 594, 611, 651 and 702 nm were observed, which corresponds to the  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  (J = 0–4) transitions of Eu $^{3+}$  ion. In these bands, the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition is hypersensitive transition, its

emission intensity is far higher than those of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1,3-6}$  transitions. In fact, according to the Judd–Ofelt theory [38–40], this transition is strictly forbidden if a Eu<sup>3+</sup> ion locate at a site with an inversion center. Therefore, the larger  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  emission intensity generally means the stronger the distortion of the Eu<sup>3+</sup> site from a highly symmetric coordination polyhedron. The integrated intensity ratio of  $I({}^{5}D_{0} \rightarrow {}^{7}F_{2})/I$  ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ) was often employed as a probe to infer the coordination geometry symmetry of Eu<sup>3+</sup> ion [41–47]. Here, the intensity ratios reach to 16.82, 16.66 and 16.96 for complexes 1, 2 and 3, respectively. It indicated the presence of a low symmetry around the metal ions, which were in line with the coordination geometries calculated from crystal structures.

The luminescence quantum yields (QYs) experiments showed that three helicates all present the excellent luminescence efficiencies, with the absolute QYs reaching up to 33%, 39% and 47% for  $[Eu_2(OBTA)_3(H_2O)_3(CH_3COCH_3)]$ ·1.5CH<sub>3</sub>COCH<sub>3</sub>·H<sub>2</sub>O,

[Eu<sub>2</sub>(OBTA)<sub>3</sub>(Bpy)<sub>2</sub>]·2CH<sub>3</sub>COCH<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub> and [Eu<sub>2</sub>(OBTA)<sub>3</sub>(Phen)<sub>2</sub>]· 2CH<sub>3</sub>COCH<sub>3</sub>. The lower value of complex 1 compared with 2 and 3 were easily understood as the consideration of solvent molecules ligated on one metal center. Generally, the replacement of coordination solvents with ancillary ligands would markedly enhance the Ln<sup>3+</sup> center emission [48–52]. Herein, the enhanced degree of luminescence for two substituted complexes were different, 3 display an increase of 14%, while 2 only give a 6% enhancement. This result demonstrates that the introduction of ancillary ligand is an effective strategy for lanthanide complexes, but the enhanced extent was not only determined by the reduction or disappearance of high energy oscillators, such as N-H and O-H vibrations. Herein, the bidentate ancillary ligands, Bpy and Phen have similar electron structures and the same coordination fashion. It is suggested that the luminescence properties of  $\mathrm{Ln}^{3+}$  center should relate to the coordiantion geometry around Eu<sup>3+</sup> ion. The different split patterns of  ${}^5D_0{\rightarrow}{}^7F_2$  and  ${}^5D_0{\rightarrow}{}^7F_1$  transitions in complexes  ${\bf 2}$  and  ${\bf 3}$  also reflected their different coordination environment [53–56].

To get insight into the relationship between the coordination geometry and the luminescent properties, we estimated the related photophysical parameters, such as the excited state lifetimes, the intrinsic quantum yields ( $\Phi_{Ln}$ ) and sensitizing efficiency ( $\eta_{sen}$ ). For Ln<sup>3+</sup> complexes, the absolute luminescence quantum yields are proportional to the  $\Phi_{Ln}$  and  $\eta_{sen}$  by eq. (1):

$$\Phi_{overall} = \eta_{sen} \Phi_{Ln} \tag{1}$$

The intrinsic quantum yields  $(\Phi_{Ln})$  reflect the competition efficiency of radiative transition and nonradiative transition to deactivate the excited state (Eq. (2)). The values of radiative rate constant  $(k_r)$  and nonradiative constant  $(k_{nr})$  are the scale to assess the two transitions.

$$\Phi_{Ln} = \frac{k_r}{k_r + k_{nr}} = \frac{\tau_{obs}}{\tau_{rad}}$$
(2)

The radiative rate constant from  $\mathrm{Eu}^{3+}$  center can be estimated from Eq. (3):

$$k_r = \frac{1}{\tau_{rad}} = A_{MD,0} n^3 \left( \frac{I_{tot}}{I_{MD}} \right)$$
(3)

 $I_{tot}$  and  $I_{MD}$  represent the total integrated emission of  ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$  and  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transitions, respectively.  $A_{MD,0}$  is a constant (14.65 s<sup>-1</sup>), representing the spontaneous emission probability of  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ . With this equation, the  $k_{r}$  are calculated to be  $1.0 \times 10^{3} \text{ s}^{-1}$  for three complexes 1, 2 and 3. Calculated radiative lifetimes  $\tau_{rad}$  is the reciprocal of  $k_{r}$ , the values of  $\tau_{rad}$  are  $9.6 \times 10^{2}$ ,  $9.8 \times 10^{2}$  and  $9.5 \times 10^{2} \mu$ s, respectively. These values are almost equivalent, consequently we cannot build an empirical rule based on this result.

The non-radiative rate constants can be obtained by equation (2) after intrinsic quantum yields ( $\Phi_{Ln}$ ) being estimated. On the basis of the emission decay curves monitored within the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition (Fig. 4), the lifetimes of the complexes **1**, **2** and **3** were measured to be 3.8 × 10<sup>2</sup>, 4.4 × 10<sup>2</sup> and 4.7 × 10<sup>2</sup> µs, respectively (Figs. S7–S9). Based on the

#### Table 2

Radiative ( $k_r$ ) and nonradiative ( $k_{nr}$ ) decay rates, observed luminescence lifetime ( $\tau_{obs}$ ), calculated radiative lifetimes ( $\tau_{rad}$ ), intrinsic quantum yield ( $\Phi_{Ln}$ ), sensitization efficiency ( $\eta_{sen}$ ), overall quantum yield ( $\Phi_{overall}$ ) for complexes 1–3 at 298 K. Error in  $\tau_{obs}$  Eu: ±0.05 ms; 10% relative error in the other values.

| Complexes | I7F2/I7F1 | $k_{\rm r}  ({ m s}^{-1})$ | $k_{\rm nr}  ({\rm s}^{-1})$ | $\tau_{obs}$ (µs) | $\tau_{rad}$ (µs) | $\Phi_{Ln}$ (%) | η <sub>sen</sub> (%) | $\Phi_{\rm overall}$ (%) |
|-----------|-----------|----------------------------|------------------------------|-------------------|-------------------|-----------------|----------------------|--------------------------|
| 1         | 16.82     | $1.0	imes10^3$             | $1.6	imes10^3$               | $3.8	imes10^2$    | $9.6	imes10^2$    | 39              | 84                   | 33                       |
| 2         | 16.66     | $1.0	imes 10^3$            | $1.2	imes10^3$               | $4.4 	imes 10^2$  | $9.8 	imes 10^2$  | 45              | 86                   | 39                       |
| 3         | 16.96     | $1.0	imes10^3$             | $1.0	imes10^3$               | $4.7 	imes 10^2$  | $9.5	imes10^2$    | 50              | 93                   | 47                       |

calculated radiative lifetimes ( $\tau_{rad}$ ) and measured lifetimes,  $\Phi_{Fu}$  were calculated to reach up to 39%, 45% and 50% for complex 1, 2 and 3. With Eq. (2), the nonradiative rate constants  $(k_{nr})$  were calculated to be  $1.6 \times 10^{3}$ ,  $1.2 \times 10^{3}$  and  $1.0 \times 10^{3}$  s<sup>-1</sup> for complex **1**, **2** and **3**. The larger value for 1 was due to the effectively deactivated capable of O-H oscillator present in coordination water molecules. While the about 200  $\mathrm{s}^{-1}$  difference of  $k_{nr}$  values between **2** and **3** could bring their different  $\Phi_{Eu}$ , 45% and 50%. Because the excitation wavelength used to emission measurement was 374 nm, which beyond the absorbance region of ancillary ligands. Therefore, the participation of electron structure of Bpy or Phen on  $\mathrm{Eu}^{3+}$  ion emission could be excluded. Thus, the different  $k_{nr}$  values should originate from the slightly variation of helical structures caused by ancillary ligands. After focusing on the single crystal structure once again, we found that the Eu-Eu distances in one helicate were difference, with 13.469 Å for 2 and 14.108 Å for 3. The shorter distance implies 2 was slightly "fatter" than 3. In helicates, it indicates there are a little stronger pulling force between two metal centers. From the overlapped partial crystal structure (Fig. S10), one benzene ring on one helical strand of **3** was obviously away from the helical axis. This result demonstrated there was a larger tension in 2 than that in 3. On the other word, the smaller tension implies the more stable structure of 3 and the smaller contribution to the non-radiative decay.

From the Eq. (1), the sensitizing efficiency ( $\eta_{sen}$ ) was also calculated and listed in Table 2. The complex **3** present the highest  $\eta_{sen}$ , reaching up to 93%, and higher than the values of 86% for **2**, 84% for **1**. In Eu<sup>3+</sup> complexes, the energy level difference  $\Delta E (T_1 - {}^5D_0)$  between the triplet states ( $T_1$ ) of ligands and  ${}^5D_0$  energy level of Eu<sup>3+</sup> ion usually determines the sensitizing efficiency. An empirical energy gap to realize a highly effective energy transfer was in range of 2500–5000 cm<sup>-1</sup> for Eu<sup>3+</sup> complexes [57–60]. By virtue of phosphorescence spectra of the Gd<sup>3+</sup> complexes (Figs. S11–S13), the  $\Delta E$  were estimated to be 3377, 3247 and 3161 cm<sup>-1</sup> for the complexes **1**, **2** and **3**, It is interesting to note that although three complexes were constructed by one ligand, the excited state energy level of **L** still present a slight variation. On the basis of the  $\Delta E$ , it maybe explains the higher sensitizing efficiency ( $\eta_{sen}$ ) in **3**.

#### 4. Conclusion

In summary, three binuclear triple-stranded Eu<sup>3+</sup> helicates composed of the same bis- $\beta$ -diketone (OBTA) and different ancillary ligands were successfully prepared, and their structures were confirmed by single crystal X-ray crystallographic analyses. The photoluminescence experiments showed that the substitution of coordination solvent molecules by N-containing heterocyclic ring Bpy and Phen markedly improved the luminescence quantum efficiencies (QYs) of  $Eu^{3+}$  ion. Moreover, Phen substituted complex **3** showed the larger QY (47%) than complex 2 (39%). According to comprehensive photophysical experiments we found that non-radiative transition rates played an important role on influencing the luminescence efficiency of complexes. In combination with the single crystal structure analyses, we proposed that the large spatial tension existing in helicate would increase the non-radiative transition rate constant and lead to the decrease of QYs of helicates. This work proved that the effects of ancillary ligands on luminescence properties of Ln<sup>3+</sup> complexes were complicated, but the partial experiment results have referential value for designing the excellent lanthanide luminescence materials.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120495.

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