

## The effect of two additional $\text{Eu}^{3+}$ lumophors in two novel trinuclear europium complexes on their photoluminescent properties†

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Two novel trinuclear europium complexes based on trisphen(1,3,5-tris(4-((1,10-phenanthroline-[5,6-d]imidazol-2-yl)phenoxy)methyl)-2,4,6-trimethyl-benzene) as a second ligand were designed, synthesized, and characterized by FT-IR, <sup>1</sup>H NMR, UV-visible, photoluminescence (PL) spectroscopy, elemental analysis (EA) and ESI-MS. The geometries of these two trinuclear europium complexes were predicted using the Sparkle/PM3 model and suggested a chemical environment of very low symmetry around the lanthanide ions ( $C_1$ ), which is in agreement with the luminescent spectra. CV analysis demonstrated that the trinuclear complexes possessed excellent electro-injection abilities. The effects of two additional  $\text{Eu}^{3+}$  lumophors in these trinuclear europium complexes on their photoluminescent properties were investigated in detail. The results indicated that these trinuclear europium complexes exhibited highly luminescent quantum efficiencies and experimental intensity parameters in the solid state. Especially, due to the contribution of the two additional  $\text{Eu}^{3+}$  lumophors in the trinuclear europium complexes, the quantum efficiency of the trinuclear complex  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$  was higher (ca. 34%) than the mononuclear europium complex  $\text{Eu}(\text{TTA})_3\text{imidazophen}$ .

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### Introduction

As one of the most promising next generation low-cost full-colour flat-panel displays, OLEDs have attracted much research interest since Tang and Van Slyke began the pioneering work in 1987.<sup>1</sup> For commercial applications, only three primary colors of red, green, and blue are required. Until now, the pure red luminescent material is still a challenge, although many metal complexes showing red emission have been reported.<sup>2–5</sup> Among those red light-emitting materials, europium complexes are particularly attractive, because they can emit highly monochromatic red light at around 612 nm with a 5–10 nm half peak bandwidth due to the electronic transitions of the central europium ion. In addition, they can offer 100% emission intrinsic quantum efficiency, theoretically, since this kind of transition is not restricted by the spin inhibition rule.

Unfortunately, the absorption coefficient of an europium ion is very low. To overcome the problem, organic ligands, which have much larger absorption coefficients, are usually coordinated to sensitize the europium complexes. So, in order to improve the luminescent properties of the europium complexes, the design and synthesis of organic ligands which have larger absorption coefficients is very important.

One efficient approach to increase the luminescent properties is to introduce ligands with multiple binding sites.<sup>6,7</sup> So far, organic europium complexes have been studied for twenty years. However, the majority of europium complexes studied are mononuclear and binuclear complexes.<sup>8–10</sup> There are few reports of the synthesis and properties for trinuclear europium complexes.<sup>11</sup> Some work<sup>6,7,12,13</sup> has shown that the quantum efficiencies of bi- and trinuclear europium complexes are higher (about 10%) than mononuclear ones, and the lifetimes of these europium complexes were longer than the mononuclear ones.

1,10-Phenanthroline (phen), a classic chelating bidentate ligand for transition metal ions, has played an important role in the development of coordination chemistry and still continues to be of considerable interest as a versatile starting material for organic, inorganic and supramolecular chemistry.<sup>14</sup> Phen is a rigid planar, hydrophobic, electron-accepting heteroaromatic system, whose nitrogen atoms are beautifully placed to act cooperatively in cation binding. These structural

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features determine its coordination ability toward metal ions. As is well-known, many studies have confirmed that 1,10-phenanthroline is an excellent second ligand for europium complexes, it can reduce the non-radiative decay of the excited states of the europium ion, improve the stability of the europium complexes, and increase the energy transfer efficiency from the ligands to the europium ion.

In this work, to further improve the luminescent properties of europium complexes, two novel trinuclear europium complexes, with trisphen as a second ligand, were designed and synthesized. The structures of the ligand and trinuclear europium complexes were characterized by FT-IR, UV-vis,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, ESI-MS and elemental analysis. The geometries were predicted using the Sparkle/PM3 model. The electrochemical properties were investigated by circle voltammetry (CV). The effects of two additional  $\text{Eu}^{3+}$  lumophors in these trinuclear europium complexes on their photoluminescent properties were investigated in detail by photoluminescent (PL) spectroscopy in solid state and in THF solution. We expect that these two novel trinuclear complexes can exhibit excellent luminescent properties.

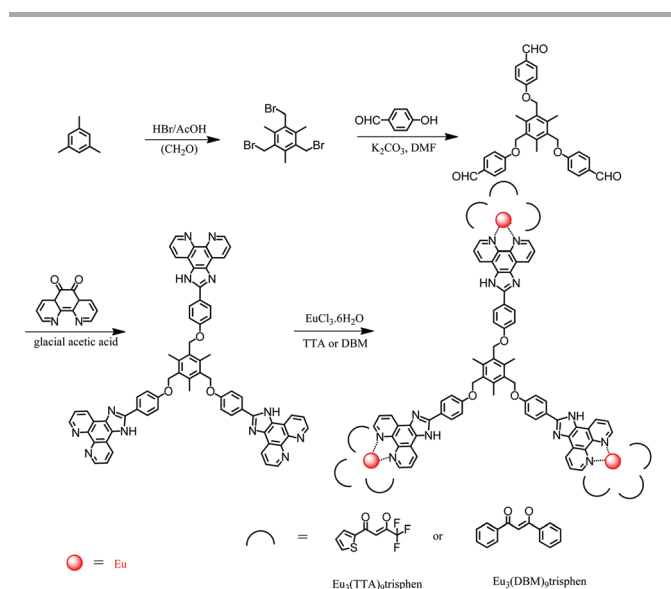
## Results and discussion

With the purpose of improving the properties of europium complexes, the trisphen ligand, with three binding sites, has been designed and synthesized, one trisphen molecule can efficiently coordinate with three europium ions and nine TTA (DBM) molecules. Then, two novel trinuclear europium complexes with trisphen as a second ligand were prepared by a simple method. We expect that these two novel europium complexes can exhibit excellent luminescent properties. The synthetic routes for trisphen and the trinuclear europium complexes are outlined in Scheme 1. The trisphen was readily

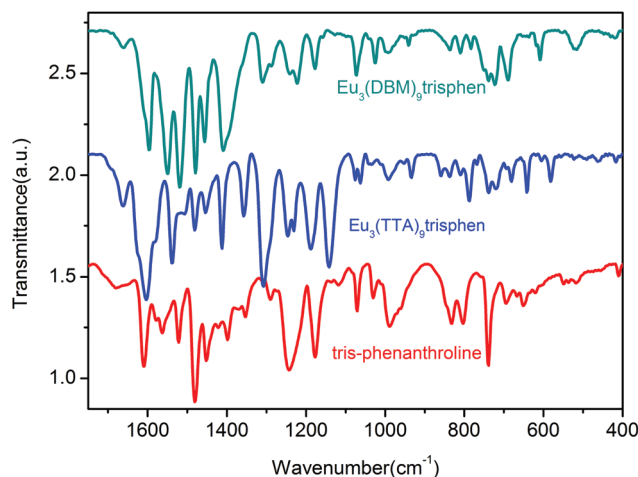
prepared in high yield (80%) from 1,3,5-tris[(4-formylphenoxy)methyl]-2,4,6-trimethylbenzene and 1,10-phenanthroline-5,6-dione. The trinuclear europium complexes are commonly synthesized by dissolving ligands in warm ethanol, neutralized pH = 7 with dilute sodium hydroxide solution, followed by the addition of the europium chloride solution.

We tried our best to obtain single crystals of the trinuclear europium complexes in our experiment, unfortunately, we failed. To deeply understand the complex structure, we optimized the molecular structures of the trinuclear europium complexes using the Sparkle/PM3 model,<sup>16</sup> and the optimized results are displayed in Fig. S1 and S2,<sup>†</sup> respectively. Every trinuclear Eu-complex consists of three parts with a small unit of europium complexes, where every unit was eight-coordinate and the coordination polyhedron can be approximately described as a distorted bicapped trigonal prism. The two trinuclear europium complexes belong to the  $C_1$  point-group. The spherical coordinates on the bonded oxygen and nitrogen atoms with respect to a coordinate system centred on the  $\text{Eu}^{3+}$  ion are given in Tables S1 and S2.<sup>†</sup> These structural data were consistent with a chemical environment of very low symmetry around the  $\text{Eu}^{3+}$  ions. An interesting point, predicted by the present structure optimization, is that the ligand DBM oxygen atoms were considerably closer to the  $\text{Eu}^{3+}$  ion than the TTA oxygen atoms in these trinuclear europium complexes. Further, the  $\text{Eu} \rightarrow \text{N}$  bonds with the trisphen ligand were longer than the  $\text{Eu} \rightarrow \text{O}$  bonds with the TTA (DBM) ligands, this result was in good agreement with the recently reported results in ref. 17.

The FT-IR spectra of trisphen and the trinuclear europium complexes are shown in Fig. 1. For complex  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$ , the characteristic stretching vibration absorption peaks of  $-\text{C}=\text{O}$  in the DBM ligand shifted from *ca.*  $1697\text{ cm}^{-1}$  to  $1629\text{ cm}^{-1}$ , and a new absorption peak was observed at  $1550\text{ cm}^{-1}$ , which is attributed to the  $-\text{C}=\text{C}$  stretching vibration of DBM coordinated to the europium ion. These results suggest that coordination bonds were formed between the DBM ligand and europium ion. The phenanthroline ring



**Scheme 1** Synthetic procedures of the trisphen ligand and trinuclear europium complexes.



**Fig. 1** FT-IR spectra of trisphen and the trinuclear europium complexes.

vibration of trisphen was observed at  $1520\text{ cm}^{-1}$ , although the intensity was relatively weaker. Meanwhile, two new absorption peaks were observed at *ca.*  $516\text{ cm}^{-1}$  and  $424\text{ cm}^{-1}$ , and were attributed to the stretching of  $\text{O} \rightarrow \text{Eu}$  and  $\text{N} \rightarrow \text{Eu}$ , respectively. For complex  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$ , the typical asymmetric vibrations of the carbonyl group of the TTA ligand were observed at about  $1600\text{ cm}^{-1}$  from the FT-IR spectra of the corresponding complexes, while the bond at about  $579\text{ cm}^{-1}$  revealed the presence of  $\text{O} \rightarrow \text{Eu}$ , which could not be observed in the ligands. Meanwhile, the peaks of phen at  $740\text{ cm}^{-1}$ , corresponding to the stretching vibration of C–H bonds, shifted to  $720\text{ cm}^{-1}$ . The FT-IR results further confirmed the conformation of the trinuclear europium complexes.

The UV-vis absorption spectra of the ligands and trinuclear europium complexes in THF solution ( $1 \times 10^{-5}\text{ mol L}^{-1}$ ) are shown in Fig. 2. Two main absorption bands of the trinuclear Eu-complex were easily observed, at  $284.2\text{ nm}$  and  $340.2\text{ nm}$  for complex  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$ , and at  $283.2\text{ nm}$  and  $351.6\text{ nm}$  for complex  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$ , respectively, which were attributed to the singlet-singlet  $\pi \rightarrow \pi$  enol absorption. Due to the formation of larger conjugated chelate rings in the trinuclear Eu-complexes, those main absorption bands shifted to longer wavelengths compared with corresponding ligands.

The  $^1\text{H}$  NMR spectra of trisphen and trinuclear europium complexes obtained at  $400\text{ MHz}$  in *d*-DMSO solutions were shown in Fig. 3. The  $^1\text{H}$  NMR spectrum of trisphen consisted of three singlet peaks at  $13.6$ ,  $5.23$  and  $2.42\text{ ppm}$ , three doublet peaks at  $8.90$ – $8.92$ ,  $8.27$ – $8.29$ , and  $7.25$ – $7.35\text{ ppm}$ , one triplicate peak at  $9.02$ – $9.03\text{ ppm}$ , and one multiplicate peak at  $7.81$ – $7.92\text{ ppm}$ . The singlet peaks at  $13.6$ ,  $5.23$  and  $2.42\text{ ppm}$  were attributed to the proton of the  $-\text{NH}$  group of the imidazole ring, three  $-\text{CH}_2-$  groups, and three  $-\text{CH}_3$  groups, respectively. The double peaks at  $8.90$ – $8.92$ ,  $8.27$ – $8.29$  and  $7.34$ – $7.35$  were attributed to the protons at the 3-, 4- and 6-positions of the phenanthroline ring and phenyl group with  $J = 8$ ,  $8.3$  and  $4\text{ Hz}$ . The peak at  $9.02$ – $9.03\text{ ppm}$  was attributed to the protons at the 2-position of the phenanthroline ring. The multiplicate

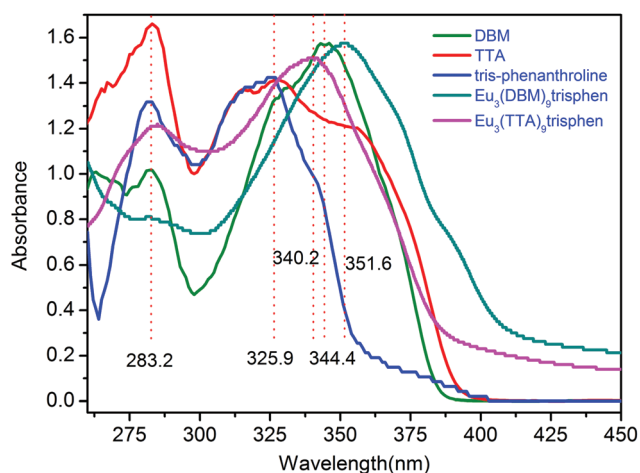


Fig. 2 UV-vis spectra of ligands and trinuclear europium complexes in THF solution ( $1 \times 10^{-5}\text{ mol L}^{-1}$ ).

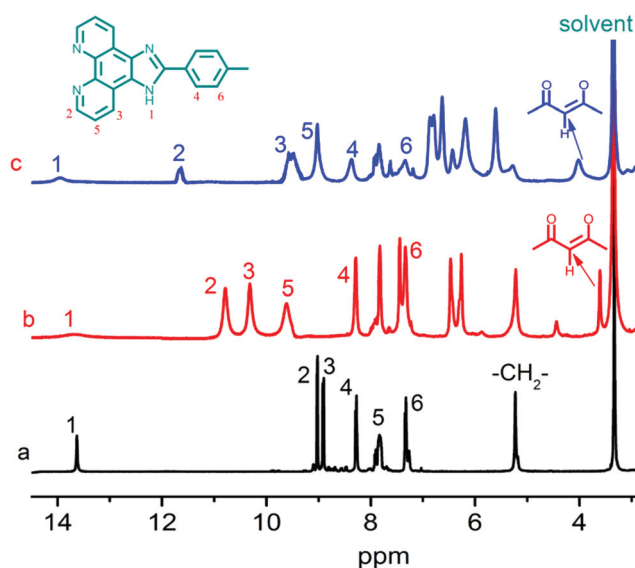
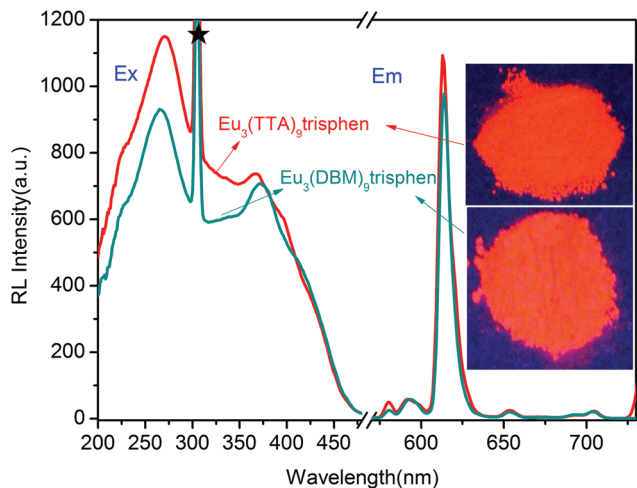


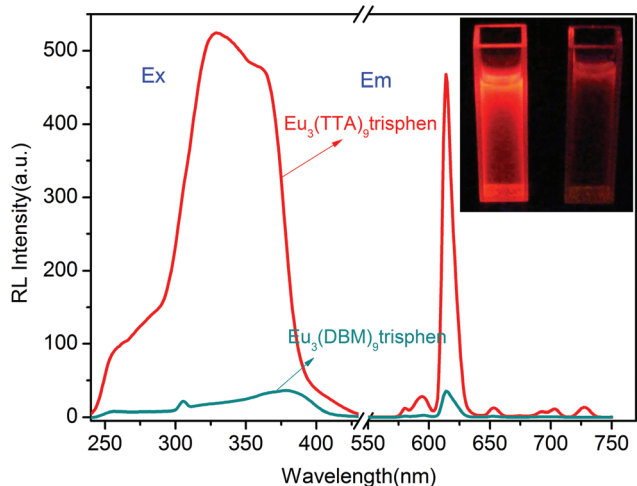
Fig. 3  $^1\text{H}$  NMR spectra of trisphen and trinuclear europium complexes in  $\text{DMSO-d}_6$ : (a) trisphen, (b)  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$ , (c)  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$ .

peak at  $7.81$ – $7.92\text{ ppm}$  was attributed to the protons at the 5-position of phenanthroline ring. The lanthanide-based complexes were well-known as shift reagents due to the paramagnetism of the lanthanide ion. Therefore, the peaks of trisphen in the trinuclear europium complexes were very different with free tris-phenanthroline. The obvious difference was the line broadening of certain peaks close to the paramagnetic europium ion. For complex  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$ , compared with free tris-phenanthroline, the proton of the  $-\text{NH}$  group is shifted from  $13.6$  to  $13.72\text{ ppm}$ , and the peak was broad. The peaks for the protons at the 2-, 3-, 5-positions shifted from  $9.04$  to  $10.79\text{ ppm}$ ,  $8.91$  to  $10.33\text{ ppm}$ , and  $7.85$  to  $9.58\text{ ppm}$ , respectively. The single peak at  $3.62\text{ ppm}$  was attributed to the protons at the  $\alpha$ -position (COCHCO) of the nine TTA ligands. For complex  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$ , the obvious change in the  $^1\text{H}$  NMR spectrum for trisphen was the peaks for the 2-, 3-, 5-positions shifted from  $9.04$  to  $11.66\text{ ppm}$ ,  $8.91$  to  $9.55\text{ ppm}$ , and  $7.85$  to  $9.03\text{ ppm}$ . The single peak for the proton of the  $-\text{NH}$  group shifted from  $13.6$  to  $13.97\text{ ppm}$ . The single peak at  $3.62\text{ ppm}$  was attributed to the protons at the  $\alpha$ -position (COCHCO) of the nine DBM ligands. In addition, the signal for the protons at the 4-positions shifted from  $8.26$  to  $8.39\text{ ppm}$ , where the doublet peak changed to a broad singlet peak.

The luminescent properties of the trinuclear europium complexes, in the solid state and in THF solution, were investigated in detail at room temperature. The excitation spectra of all complexes in the solid state and in THF solution were obtained by monitoring the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition of the europium ion, which are shown in Fig. 4 and 5, respectively. For the solution excitation spectra, there was one intense broad band at  $245$ – $425\text{ nm}$ , while in the solid state excitation spectra, it can be seen clearly that intense broad bands between  $200\text{ nm}$  and  $475\text{ nm}$  dominate a large portion of the excitation



**Fig. 4** The PL spectra of trinuclear europium complexes in the solid state. (Left) Excitation spectra ( $\lambda_{em} = 614$  nm for all complexes). (Right) Emission spectra [ $\lambda_{ex} = 367$  nm for  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$ ,  $372$  nm for  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$ ]. (Inset) Luminescent image from powder of trinuclear europium complexes excited at  $365$  nm ( $\star$ : false peak).



**Fig. 5** The PL spectra of trinuclear europium complexes in THF solution ( $1 \times 10^{-5} \text{ L}^{-1}$ ). (Left) Excitation spectra ( $\lambda_{em} = 614$  nm for all complexes). (Right) Emission spectra [ $\lambda_{ex} = 359$  nm for  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$ ,  $381$  nm for  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$ ]. (Inset) Luminescent image from THF solution of trinuclear europium complexes excited at  $365$  nm.

spectra for all europium complexes. From comparison of the UV-vis spectra in Fig. 2, these bands were attributed to the  $\pi \rightarrow \pi^*$  transitions of the ligands (trisphen, DBM or TTA). In comparison with the excitation broad bands of the ligands, the direct excitation peaks of the europium ion was much weaker. This suggested that the emission of europium by the ligands were much more efficient than direct excitation of the trinuclear europium complexes. Meanwhile, the strong bright-red emission of the trinuclear europium complexes in the solid state and in THF solution, upon illumination with a  $365$  nm excitation light provided by a  $12$  W ultraviolet lamp, can be easily observed by the naked eye (inset of Fig. 4 and 5).

The mechanism of the energy transfer from ligands to metal ions has been widely discussed to interpret the luminescence of lanthanide compounds.<sup>18</sup> From the results discussed above, we can presume that the energy gaps of the europium ions were comparable with the triplet state energy of the ligands trisphen, TTA or DBM, and that efficient energy transfer can take place from the ligands to the europium ions, we will discuss in detail the energy transfer progress below. These complexes exhibited the characteristic red emission of europium ions, by  $365$  nm excitation, which suggested that these complexes could be potential red fluorescent materials.

The emission spectra of these complexes in the solid state are shown in Fig. 4, and the characteristic europium ion emission was not observed. The lines were distributed mainly in the  $550$ – $710$  nm range, which were associated with the  $4f \rightarrow 4f$  transitions of the  $^5\text{D}_0$  excited state to the low-lying  $^7\text{F}_j$  ( $j = 0, 1, 2, 3$  and  $4$ ) levels of  $\text{Eu}^{3+}$  ions. No emission peaks from the ligands were observed under this excitation, further confirming that the energy transfer from the ligands to the europium ion center was quite efficient in all trinuclear europium complexes. As is well-known, the emissions of europium ions were usually employed as a sensitive probe to investigate the coordination and local environment around cations. The europium ion transitions that are observed in the emission spectrum occur *via* three main mechanisms: forced electric dipole (ED), magnetic dipole (MD), and dynamic coupling. From the emission spectra, we can see the emission bands at about  $580$  and  $653$  nm were very weak, since their corresponding transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_{0,3}$  were forbidden both in the MD and ED schemes. A prominent feature, that may be noted in these spectra, was the very high intensity of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition at  $614$  nm. It was well-known to us that the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition was a parity allowed MD and is non-sensitive to the local structure environment, while the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition was a typical ED transition and was sensitive to the coordination environment to the europium ion. When the interaction of the rare earth complex with its local environment was stronger, the complex became more non-symmetrical, and the intensity of the electric-dipolar transitions became more intense. As a result, the integration intensity ratio of the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition to  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition ( $I_2/I_1$ ) had been widely used as an indicator of europium ion site symmetry. The calculated results were shown in Table 1.

Whether in the solid state or in THF solution, the intensity ratios of these trinuclear complexes were very high. In the solid state, the intensity ratios ( $I_2/I_1$ ) of the complexes  $\text{Eu}_3(\text{TTA})_9\text{trisphen}$  and  $\text{Eu}_3(\text{DBM})_9\text{trisphen}$  were  $16.9$  and  $15.1$ , respectively, while in THF solution they were  $15.2$  and  $14.6$ , respectively. This ratio was only possible when the europium ion did not occupy a site with inversion symmetry. It was clear that strong coordination interactions occur between the organic ligands and europium ion. Further, the emission spectra of the complexes showed only one line for the  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition, indicating the presence of a single chemical environment around the europium ions.<sup>19</sup> In addition, no emission from the ligands was observed in Fig. 4, which

**Table 1** Solid state and solution luminescent data of trinuclear europium complexes

Complexes	In the solid state					In THF solution			
	$\tau^b$ (ms)	$A_{\text{rad}}$ (s <sup>-1</sup> )	$I_2/I_1$	$\eta$ (%)	$\Omega_2$ (10 <sup>-20</sup> cm <sup>2</sup> )	$\Omega_4$ (10 <sup>-20</sup> cm <sup>2</sup> )	$I_2/I_1$	$\tau^b$ (ms)	$\Phi$ (%)
Eu <sub>3</sub> (TTA) <sub>9</sub> trisphen	0.78	827.99	16.9	64.58	21.5	1.3	15.2	0.63	22.8
Eu <sub>3</sub> (DBM) <sub>9</sub> trisphen	0.67	730.62	15.1	48.95	13.8	1.1	14.6	0.39	3.55
Eu(TTA) <sub>3</sub> imidazophen <sup>a</sup>	0.37	837.2	12.31	30.67	—	—	11.47	0.24	10.83
Eu(DBM) <sub>3</sub> imidazophen <sup>a</sup>	0.29	797.6	18.56	23.13	—	—	15.53	0.13	1.69

<sup>a</sup> These two compounds were synthesized according to ref. 24. <sup>b</sup> The integrated intensity ratio of the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> transition to <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub>.

indicated that a very efficient energy transfer occurred from the ligands to the central europium ion.

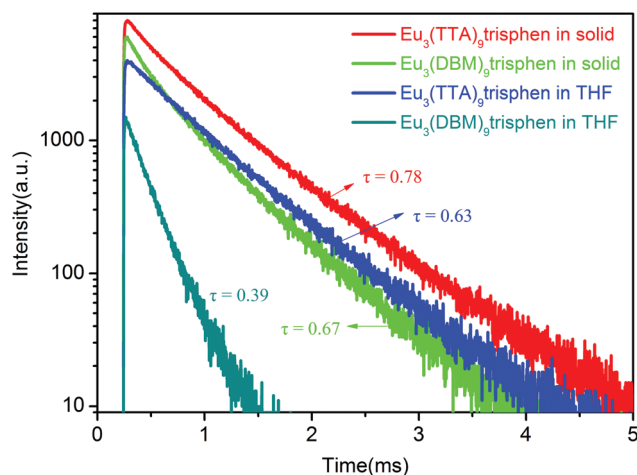
In addition to the emission spectra of solid complexes, the room temperature emission spectra of all the trinuclear europium complexes in THF solution were investigated (Fig. 5). Compared with the solid state, no great differences in the emission spectra for all complexes in THF solution were observed, except the emission intensity.

As is well-known for europium ions, the sensitive ability of the ligand TTA was better than the ligand DBM, so the relative emission intensity of the corresponding trinuclear europium complex Eu<sub>3</sub>(TTA)<sub>9</sub>trisphen was stronger than complex Eu<sub>3</sub>(DBM)<sub>9</sub>trisphen under the same conditions. In particular, the emission intensity for <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> of Eu<sub>3</sub>(TTA)<sub>9</sub>trisphen was 13-fold stronger than the complex Eu<sub>3</sub>(DBM)<sub>9</sub>trisphen in THF solution.

For Eu<sub>3</sub>(TTA)<sub>9</sub>trisphen and Eu<sub>3</sub>(DBM)<sub>9</sub>trisphen, the Commission International de Éclairage (CIE) chromaticity coordinates from the emission spectra ( $\lambda_{\text{ex}} = 370$  nm for solid and  $\lambda_{\text{ex}} = 362$  nm in THF) were (0.66, 0.33) and (0.66, 0.33) in the solid state, (0.64, 0.32) and (0.56, 0.27) in THF solution, respectively (Fig. S3<sup>†</sup>), and indicated that they belong to the pure red emission. This result is very important because it indicated an advantage of rare-earth complexes for preparing OLEDs.

To better understand the luminescent properties of the trinuclear europium complexes in the solid state and THF solution, the room temperature (RT) luminescence decay curves of the <sup>5</sup>D<sub>0</sub> excited state were measured by monitoring the most intense emission lines (<sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub>) of the europium ion center at 614 nm, and under excitation of a 360 nm xenon lamp. As shown in Fig. 6, whether in the solid state or in THF solution, the decay curves of the complexes exhibited monoexponential behavior, indicative of the presence of a single chemical environment around the europium ion in these complexes, which was in agreement with the results of only one <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub> line in the emission spectra and the calculated results of Sparkle/PM3. The luminescent lifetime values ( $\tau$ ) of Eu<sub>3</sub>(TTA)<sub>9</sub>trisphen and Eu<sub>3</sub>(DBM)<sub>9</sub>trisphen were 0.78 ms and 0.67 ms in the solid state, and 0.63 ms and 0.39 ms in THF solution, respectively.

The intrinsic luminescent quantum efficiency ( $\eta$ ) of the <sup>5</sup>D<sub>0</sub> emission level in these trinuclear europium complexes at room temperature was obtained based on the luminescence data (emission spectra and emission decay curves of these



**Fig. 6** The decay curves of the trinuclear europium complexes in the solid state and in THF solution ( $\lambda_{\text{em}} = 614$  nm,  $\lambda_{\text{ex}} = 360$  nm).

complexes). Eqn (1) is a means to determine the  $\eta$  values from experimental spectroscopic data.<sup>20</sup>

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}} \quad (1)$$

where,  $A_{\text{rad}}$  and  $A_{\text{nrad}}$  are radiative and non-radiative transition rates, respectively. The denominator in eqn (1) is calculated from the lifetime of the emitting level ( $1/\tau = A_{\text{rad}} + A_{\text{nrad}}$ ). In the case of europium luminescence the value of  $A_{\text{rad}}$  can be estimated by spectral analysis with the help of eqn (2).<sup>21</sup>

$$A_{\text{rad}} = \frac{A_{0-1} h \omega_{0-1}}{S_{0-1}} \sum_{j=0}^4 \frac{S_{0-j}}{h \omega_{0-j}} \quad (2)$$

where,  $J$  represents the final <sup>7</sup>F<sub>0-6</sub> levels,  $S$  is the integrated intensity of the particular emission lines and  $h\omega$  stands for the corresponding transition energies.  $A_{0-1}$  is the Einstein coefficient of spontaneous emission between the <sup>5</sup>D<sub>0</sub> and the <sup>7</sup>F<sub>1</sub> Stark levels. The branching ratios for the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>5,6</sub> transitions must be neglected as they are too weak to be observed experimentally. Therefore, their influence can be ignored in the depopulation of the <sup>5</sup>D<sub>0</sub> excited state. The <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>1</sub> transition does not depend on the local ligand field seen by europium ions and, thus, may be used as a reference for the whole spectrum, *in vacuo*  $A_{0-1} = 14.65$  s<sup>-1</sup>.<sup>22</sup> An average refractive index equal to 1.5 was considered, leading to  $A_{0-1} \approx 50$  s<sup>-1</sup>.

According to the above discussion, the intrinsic luminescence quantum efficiency of these trinuclear europium complexes in the solid state can be determined, as shown in Table 1.

The solution luminescent yields of the trinuclear europium complexes were determined using quinine sulfate (dissolved in 0.5 M H<sub>2</sub>SO<sub>4</sub> with a concentration of 10<sup>-6</sup> M, assuming  $\Phi_{PL}$  of 0.55) as a standard.<sup>23</sup> The quantum yield is calculated according the following formula:

$$\Phi = \Phi_r \frac{A_r S n^2}{A S_r n_r^2} \quad (3)$$

where  $\Phi$  is the fluorescence quantum yield,  $S$  represents the area of the corrected emission fluorescence spectrum,  $A$  is the absorbance of the solution at the exciting wavelength, and  $n$  is the refractive index of the solvent used. The subscript  $r$  denotes the reference substance, of which the fluorescence quantum yield is already known. The calculated results were shown in Table 1.

Whether in the solid state or THF solution, these trinuclear europium complexes exhibited high luminescence quantum efficiencies or yields, indicating that the energy transfer from the ligands to the center europium ions was very efficient. From Table 1, we found that the trinuclear europium complexes based on TTA as a  $\beta$ -diketone ligand exhibited higher luminescence quantum efficiencies (yield) than the complexes based on DBM as the  $\beta$ -diketone ligand. This finding was in good agreement with the results from luminescent emission intensity. Especially in the solid state, due to the contribution of two additional Eu<sup>3+</sup> lumophors, the luminescent quantum efficiency of the trinuclear europium complexes Eu<sub>3</sub>(TTA)<sub>9</sub>trisphen and Eu<sub>3</sub>(DBM)<sub>9</sub>trisphen (64.58% and 48.95%, respectively) were higher than that of the mononuclear europium complexes Eu(TTA)<sub>3</sub>imidazophen (30.67%) and Eu(DBM)<sub>3</sub>imidazophen ( $\eta = 23.13\%$ ). In addition, the quantum yield of the trinuclear europium complexes in THF solution were higher (about 2-fold) than the corresponding mononuclear europium complexes. These results indicated that the introduction of ligands with multiple binding sites to the europium complex can effectively increase the quantum efficiency of the europium complexes.

To investigate the possible structural changes around the emitting center europium ion among these trinuclear complexes, the experimental intensity parameters  $\Omega_2$  and  $\Omega_4$  (the  $\Omega_6$  parameter was not determined because the  $^5D_0 \rightarrow ^7F_6$  transition could not be experimentally detected) can be calculated from the emission spectra as described in ref. 25. In particular,  $\Omega_2$  was more sensitive to the symmetry and sequence of ligand fields. To produce faster europium radiation rates, antisymmetrical europium complexes with large  $\Omega_2$  parameters needed to be designed. The spontaneous emission probability  $A_{0\lambda}$  ( $\lambda = 2, 4$ ) of the transitions were related to its dipole strength according to the equation:

$$A_{0\lambda} = (64\pi^4 \nu^3) / [3h(2J + 1) \langle |n(n^2 + 2)/9 [S_{(ED)} + S_{(MD)}] \rangle] \quad (4)$$

here,  $\nu$  is the average transition energy in cm<sup>-1</sup>,  $h$  is the Planck constant,  $2J + 1$  is the degeneracy of the initial state.  $S(ED)$  and  $S(MD)$  are the ED and MD strengths, respectively. Among all these transitions, the  $^5D_0 \rightarrow ^7F_{0,3,5}$  transitions are forbidden, both in MD and ED schemes ( $S_{(ED)}$  and  $S_{(MD)}$  are zero). In addition, the  $^5D_0 \rightarrow ^7F_1$  transition is an isolated MD transition, and has no ED contribution, which is practically independent of the lanthanide ions chemical environment and can be used as a reference. The experimental parameters  $\Omega_2$  and  $\Omega_4$  can be calculated according to the equation:<sup>26</sup>

$$\Omega_\lambda = \frac{3hc^3 A_{0-\lambda}}{4e^2 \omega^3 \chi \langle ^5D_0 || U^{(\lambda)} || ^7F_j \rangle^2} \quad (5)$$

where,  $e$  is the electronic charge.  $\chi = n_0(n_0^2 + 2)^2/9$  is a Lorenz local field correction. The square reduced matrix elements are  $\langle ^5D_0 || U^{(2)} || F_2 \rangle^2 = 0.0032$  and  $\langle ^5D_0 || U^{(4)} || F_4 \rangle^2 = 0.0023$ , and an average index of refraction equal to 1.5 was used. The  $\Omega_2$  and  $\Omega_4$  intensity parameters for all complexes are shown in Table 1. A point to be noted in these results was the relatively high  $\Omega_2$  parameter for these two trinuclear europium complexes. This might be interpreted as being a consequence of the hypersensitive behavior of the  $^5D_0 \rightarrow ^7F_2$  transition, indicating that the europium ion was in a highly polarizable chemical environment in these trinuclear complexes.

It was known that in lanthanide complexes, neutral ligands often play a role in absorbing and transporting energy to the other ligands or the center metal ions. According to absorption spectra of trisphen and TTA (DBM) (Fig. 7), it was found that there was a large area of overlap between the absorption peaks of trisphen and TTA (DBM), from 297 to 400 nm. This meant that nearly all the radiation from trisphen can be absorbed by TTA (DBM). This wide overlap showed the possibility of the highly efficient energy transfer from trisphen to TTA (DBM).

To demonstrate the energy transfer progress, the triplet energy of the ligand trisphen was calculated using the configuration interaction single (CIS) based on the intermediate

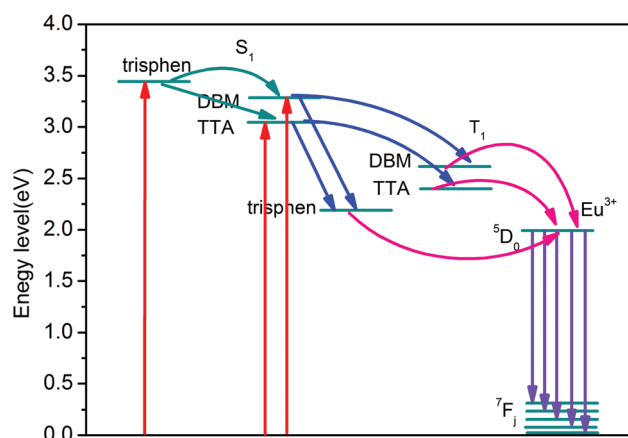


Fig. 7 Schematic energy level diagram and energy transfer processes for the trinuclear europium complexes.  $S_1$  represents the first excited singlet state and  $T_1$  represents the first excited triplet state.

neglect of differential overlap/spectroscopic (INDO/S)<sup>27</sup> method implemented in the ZINDO software.<sup>28</sup> The values of the triplet energy for TTA and DBM were obtained from ref. 29 and 30. The triplet energy levels of trisphen, TTA and DBM were 2.23, 2.35, and 2.53 eV, respectively. The singlet state energy levels of trisphen, TTA and DBM were estimated by referencing their absorbance edges, which were 3.45 eV, 3.12 eV and 3.25 eV, respectively. For comparison, the singlet and triplet state energy levels are illustrated in Fig. 7.

In Fig. 7, it can be seen that the S<sub>1</sub> energy level of trisphen matches that of TTA (DBM) and the <sup>5</sup>D<sub>0</sub> energy level of Eu<sup>3+</sup> ion. So the energy absorbed by trisphen could be transferred to TTA (DBM) or the Eu<sup>3+</sup> ion directly. However, it is known that the gap between the two energy levels should be intermediate, where being too big or small would decrease the efficiency of the energy transfer. The energy gap of the S<sub>1</sub> energy levels between trisphen and TTA or DBM were 0.33 eV and 0.20 eV, respectively. So it was appropriate to improve the energy transfer from the S<sub>1</sub> of trisphen to that of TTA or DBM. At the same time, due to the S<sub>1</sub> energy levels of TTA (DBM) being higher than the T<sub>1</sub> energy levels of trisphen, the energy transfer from the S<sub>1</sub> of TTA (DBM) to the T<sub>1</sub> of trisphen was fairly efficient. Meanwhile, as the T<sub>1</sub> state of trisphen was higher than the energy level of the <sup>5</sup>D<sub>0</sub> of Eu<sup>3+</sup> ion, so the efficient energy transfer from the T<sub>1</sub> of trisphen to the <sup>5</sup>D<sub>0</sub> of the Eu<sup>3+</sup> ion can occur, which can improve the ability of energy transfer from the ligands to the emitter Eu<sup>3+</sup> ions.

The electrochemical properties of the trinuclear europium complexes were investigated by cyclic voltammetry (CV) at 298 K in acetonitrile solutions *versus* the saturated calomel electrode (SCE) (Fig. 8), and the reduction peaks of these trinuclear complexes were easily observed, the values of the reduction potential (*E*<sub>red</sub>) were -1.57 eV for Eu<sub>3</sub>(TTA)<sub>9</sub>trisphen, and -1.42 eV for Eu<sub>3</sub>(DBM)<sub>9</sub>trisphen, respectively, but their oxidation peaks disappeared. The oxidation potential (*E*<sub>ox</sub>) had to be estimated based on the energy gap (*E*<sub>g</sub>) and *E*<sub>red</sub>, in

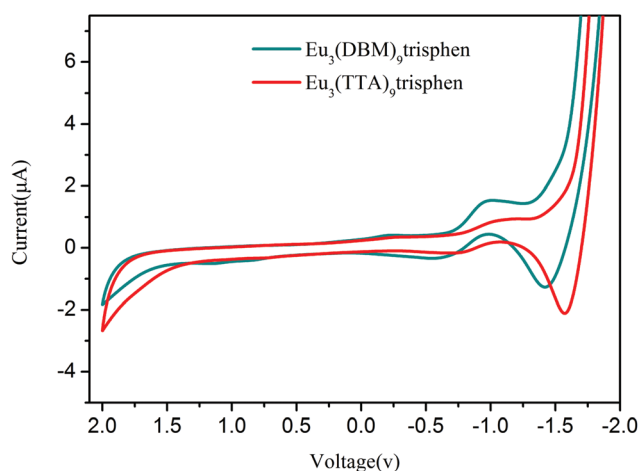


Fig. 8 Cyclic voltammogram of the trinuclear europium complexes measured in acetonitrile solution, containing 0.1 M Bu<sub>4</sub>NClO<sub>4</sub> at 298 K. Scans rate: 50 mV s<sup>-1</sup>.

Table 2 Electrochemical data of the europium complexes

Complexes	<i>E</i> <sub>ox</sub> <sup>a</sup> (V)	<i>E</i> <sub>red</sub> <sup>b</sup> (V)	<i>E</i> <sub>HOMO</sub> <sup>c</sup> (eV)	<i>E</i> <sub>LUMO</sub> <sup>d</sup> (eV)	<i>E</i> <sub>g</sub> <sup>e</sup> (eV)
Eu <sub>3</sub> (TTA) <sub>9</sub> trisphen	1.76	-1.57	-6.14	-2.81	3.33
Eu <sub>3</sub> (DBM) <sub>9</sub> trisphen	1.71	-1.42	-6.09	-2.96	3.13
Eu(TTA) <sub>3</sub> phen <sup>e</sup>	1.53	-1.5	-6.3	-3.27	3.03
Eu(DBM) <sub>3</sub> phen <sup>f</sup>	1.25	-1.95	-5.63	-2.42	3.21

<sup>a</sup> Estimated according to the reduction potential and the UV-vis absorption spectra. <sup>b</sup> Measured in DMF solution at 298 K. <sup>c</sup> *E*<sub>HOMO</sub> = -(*E*<sub>ox</sub> + 4.38) eV. <sup>d</sup> *E*<sub>LUMO</sub> = -(*E*<sub>red</sub> + 4.38) eV. <sup>e</sup> These values for Eu(TTA)<sub>3</sub>phen were reported in ref. 32. <sup>f</sup> These values for Eu(DBM)<sub>3</sub>phen were reported in ref. 33.

which the *E*<sub>g</sub> was estimated based on the UV-vis absorption edge. Thus, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels (*E*<sub>HOMO</sub> and *E*<sub>LUMO</sub>) of the trinuclear europium complexes were calculated according to the empirical relationship formula: *E*<sub>HOMO</sub> = -*e* (*E*<sub>ox</sub> + 4.38) and *E*<sub>LUMO</sub> = -*e* (*E*<sub>red</sub> + 4.38) eV, proposed by the Brédas group.<sup>31</sup> The electrochemical data of the trinuclear europium complexes are listed in Table 2. The HOMO and LUMO energy levels of the trinuclear complexes Eu<sub>3</sub>(TTA)<sub>9</sub>trisphen and Eu<sub>3</sub>(DBM)<sub>9</sub>trisphen are -6.14 and -2.81 eV, and -6.3 and -2.96 eV, respectively. Compared to the corresponding mononuclear europium complexes Eu(TTA)<sub>3</sub>phen and Eu(DBM)<sub>3</sub>phen, these two trinuclear europium complexes exhibited a decrease in the HOMO and LUMO energy levels. As is well-known, the decreased LUMO energy levels were available to facilitate electro injection and transportation from the cathode to the emitters of the europium complexes. Therefore, two additional Eu<sup>3+</sup> ions in the trinuclear europium complexes may significantly tune the electrochemical and transporting property of the europium complexes.

## Conclusions

In this work, two new trinuclear europium complexes were designed and synthesized, and their luminescent properties were carefully studied. Their ground state geometries were obtained from the Sparkle/PM3 model and pointed to a chemical environment of very low symmetry around the Eu<sup>3+</sup> ions. Whether in the solid state or in THF solution, all trinuclear complexes exhibited strong luminescent intensities and long luminescent lifetimes. The results of the decay curves and emission spectra of the trinuclear complexes indicated that there was only one luminescence centre, and the europium ion was located in a polarized chemical environment. Most importantly, due to the contribution of the two additional Eu<sup>3+</sup> lumophors in the trinuclear europium complexes, these two complexes exhibited much longer lifetimes and higher intrinsic quantum efficiencies than the corresponding mononuclear europium complex. These results indicated that the introduction of ligands with multiple binding sites to europium complexes could effectively increase the luminescent properties of the europium complexes. Further investigation indicated that

trisphen has a mezzo first triplet excited energy level ( $T_1$ ) between the first  $T_1$  of TTA (DBM) and the  $^5D_0$  of the  $\text{Eu}^{3+}$  ion, which may support one more additional energy transfer routine from the  $T_1$  energy level of trisphen to the  $^5D_0$  of the  $\text{Eu}^{3+}$  ion, and consequently results in the improvement of energy transfer in these trinuclear europium complexes.

## Experimental section

Starting materials were of reagent grade and used without further purification, unless otherwise stated. All solvents were purified with conventional methods before use. Mesitylene, dibenzoylmethane (DBM) and 2-thenoyltrifluoroacetone (TTA) were purchased from Aldrich Chemical Company.  $\text{Eu}_2\text{O}_3$  (99.99%) was purchased from a Chinese company, Beijing Founder.  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  was obtained by dissolving  $\text{Eu}_2\text{O}_3$  in concentrated chlorohydric acid.

FT-IR spectra were carried out using a Tensor 27 (Bruker) Fourier Transform Infrared Spectrometer. Elemental analysis data were obtained from a Vario EL elemental analyzer. NMR spectra were taken on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer with TMS as an internal standard. UV-vis absorption spectra were determined on a Shimadzu spectrophotometer (UV 2550). CV measurements were performed on a computer-controlled CHI600D electrochemical analyzer with a Pt working electrode, a Pt plate counter electrode, and an SCE reference electrode immersed in 0.1 M  $\text{Bu}_4\text{NClO}_4$  in dry acetonitrile purged with dried argon. The scanning rate was  $50 \text{ mV s}^{-1}$ , and all electrochemical potentials were calibrated with the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) standard. The photoluminescence (PL) measurements in the solid state and in the THF solutions were conducted in a Hitachi F-4600 fluorescence spectrophotometer. Luminescence lifetimes were obtained with a FLS920 steady state spectrometer with a pulsed xenon lamp.

### Synthesis of 1,3,5-tris{4-((1,10-phenanthroline-[5,6-*d*]imidazol-2-yl)phenoxy)methyl}-2,4,6-trimethylbenzene (trisphen)

Trisphen was prepared according to the procedure described in the literature with some modification.<sup>15</sup> A mixture of 1,3,5-tris[(4-formylphenoxy)methyl]-2,4,6-trimethylbenzene (0.76 g, 1.5 mmol), 1,10-phenanthroline-5,6-dione (0.94 mg, 4.5 mmol), and  $\text{NH}_4\text{Ac}$  (8.79 g, 114 mmol) in 90 mL glacial acetic acid was heated to  $125^\circ\text{C}$  for 6 h. After cooling to room temperature, the solution was diluted with 1 L ice water. Neutralization of the solution with aqueous ammonia solution gave a yellow precipitate. The precipitate was then filtered and subsequently washed with ethanol and ethyl ether, respectively, affording the desired product as a yellow solid. Yield: 1.31 g (80%).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  2.42 (s,  $-\text{CH}_3$ , 9H), 5.23 (s,  $-\text{CH}_2-$ , 6H), 7.33 (d,  $J = 7.3$  Hz, phenyl, 6H), 7.85 (dd,  $J = 7.9, 4.3$  Hz, phenanthroline ring, 6H), 8.26 (d,  $J = 8.4$  Hz, phenyl, 6H), 8.89 (d,  $J = 8.0$  Hz, phenanthroline ring, 6H), 9.02 (d,  $J = 4.8$  Hz, phenanthroline ring, 6H), 13.60 (s,  $-\text{NH}$ , 3H) ppm. ESI-MS:  $m/z$  1093.4 ( $\text{M} + \text{H}$ )<sup>+</sup>. Elemental anal. Found:

C 75.83, H 4.61, N 15.39; Calcd for  $\text{C}_{69}\text{H}_{48}\text{N}_{12}\text{O}_3$ : C 75.81, H 4.43, N 15.38. FT-IR/ $\text{cm}^{-1}$ , 3122 (NH), 1609, 1480, 1243, 1179, 986. UV-vis (nm), 283, 326.

### General procedure of syntheses of europium complexes

Trisphen (1 mmol), DBM or TTA (9 mmol), and sodium hydroxide (9 mmol) were dissolved in 60 mL THF under stirring. Then the solution was heated to  $70^\circ\text{C}$ , and 40 mL anhydrous ethanol with 3 mmol  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  was added dropwise to the solution, and kept at this temperature for 5 h. The mixed solution was cooled to room temperature and the solvents removed to give the crude product. The complexes were purified by reprecipitation from cyclohexane and washed three times with 50 mL ethanol every time to give the desired trinuclear europium complexes.

$\text{Eu}_3(\text{TTA})_9\text{trisphen}$  was synthesized as a yellow-white powder in 75% yield.  $\text{Eu}_3\text{C}_{141}\text{H}_{84}\text{N}_{12}\text{O}_{21}\text{S}_9$  found (calc.): C 47.59 (47.84), H 2.41 (2.39), and N 4.63 (4.75). ESI-MS: 3677.9.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  13.65 (s,  $-\text{NH}$ , 3H), 10.78 (s, phenanthroline ring, 6H), 10.32 (s, phenanthroline ring, 6H), 9.64 (s, phenanthroline ring, 6H), 8.29 (s, phenyl, 6H), 7.83 (d,  $J = 7.5$  Hz, Th-H, 9H), 7.34 (d,  $J = 7.5$  Hz, phenyl, 6H), 6.47 (br, s, Th-H, 9H), 6.26 (br, s, Th-H, 9H), 5.22 (s,  $-\text{CH}_2-$ , 6H), 3.61 (br, s, COCHCO, 9H), 2.43 (s,  $-\text{CH}_3$ , 9H) ppm. FT-IR/ $\text{cm}^{-1}$ , 1603, 1539, 738, 578, 464. UV-vis (nm), 283, 344.

$\text{Eu}_3(\text{DBM})_9\text{trisphen}$  was synthesized as yellow-white powder in 67% yield.  $\text{Eu}_3\text{C}_{204}\text{H}_{129}\text{N}_6\text{O}_{18}$ , found (calc.): C 68.9 (68.86), H 3.92 (4.16), and N 4.83 (4.72). ESI-MS: 3702.5.  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  13.98 (s,  $-\text{NH}$ , 3H), 11.64 (br, s, phenanthroline ring, 6H), 9.56 (br, s, phenanthroline ring, 6H), 9.04 (s, phenanthroline ring, 6H), 8.37 (br, s, phenyl, 6H), 7.85 (s, phenyl, 6H), 7.34 (s, phenyl, 9H), 6.79–6.87 (d,  $J = 5.8$  Hz, phenyl, 18H), 6.63 (s, phenyl, 18H), 6.43 (s, phenyl, 9H), 6.19 (s, phenyl, 9H), 5.61 (s, phenyl, 9H), 5.28 (s,  $-\text{CH}_2-$ , 6H), 4.02 (br, s, COCHCO, 9H), 2.47 (s,  $-\text{CH}_3$ , 9H) ppm. FT-IR/ $\text{cm}^{-1}$ , 1603, 1550, 1519, 738, 516, 424. UV-vis (nm), 283, 352.

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