

# Synthesis and optical character of novel Eu(III) ternary complexes with $\beta$ -diketone and imidazo[5,6-f]phenanthroline

XIAOMING REN, CHANGPING WEI\*, GUO CHENG

*Collage of Materials Science and Engineering, Changchun University of Science and Technology, Weixing Road 7186, Changchun 130022, Jilin Province, China*

In this paper, the ternary complexes of Eu (III) with 1,3-diphenylpropane-1,3-dione (DBM), 1-(4-bromophenyl)-3-phenylpropane-1,3-dione (Br-DBM) and imidazo[5,6-f] phenanthroline (IP) have been synthesized. The new complexes were characterized by elemental analysis, infrared spectroscopy and thermal stability analysis. Their compositions were  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$ . Fluorescence spectra demonstrated that the complexes could emit narrow emission bands that arise from the  ${}^5\text{D}_0\text{-}{}^7\text{F}_J$  ( $J=1-4$ ) transition of the  $\text{Eu}^{3+}$  ion, and the fluorescence intensity of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  was obviously higher. In addition, the luminescence decay curves of the complexes fit a single-exponential decay law. The values of quantum efficiencies of the emitting  ${}^5\text{D}_0$  level for the complexes  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$  were 28% and 24%, respectively.

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## 1. Introduction

Europium (III) complexes with  $\beta$ -diketones ligands having good fluorescence properties, which have been found important application in light conversion events, are primarily thought to be due to both the unique electronic structure of  $\text{Eu}^{3+}$  ions and the antenna effect of the ligands [1-3]. As light conversion materials, ultraviolet (UV) light is firstly absorbed by  $\beta$ -diketone ligands, then the absorbed energy is transferred from the lowest triplet state energy level of the ligand to the resonance level of  $\text{Eu}^{3+}$  ions and make them send out their characteristic light[4-6]. Many  $\beta$ -diketone type ligands and their Eu (III) ternary complexes have been investigated due to their strong coordination capability to the  $\text{Eu}^{3+}$  ions and enhanced luminescence of Eu (III) complexes by providing some proper conjugate absorption groups suitable for energy transfer [7-10]. Besides, many studies show that rare earth luminescence enhancement can be facilitated in complexes by adding aromatic rings possessing a nitrogen atom, such as 1,10-phenanthroline or pyridine[11-14].

With an aim to develop novel optical materials, our group prepared Eu (III) ternary complexes with 1,3-diphenylpropane-1,3-dione(DBM),1-(4-bromophenyl)-3-phenylpropane-1,3-dione (Br-DBM) and imidazo[5,6-f] phenanthroline (IP). In addition, the optical properties of the complexes in solid state were investigated in detail.

## 2. Experimental

### 2.1. Materials

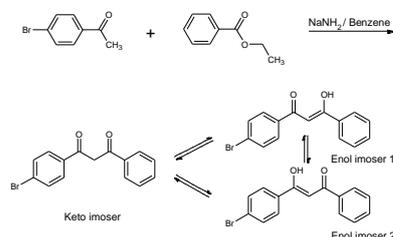
Europium chloride ( $\text{EuCl}_3$ ) ethanol solution (EtOH) was prepared by dissolving  $\text{Eu}_2\text{O}_3$  in concentrated hydrochloric acid (HCl). DBM and other materials were of AR grade. Solvents were purified with conventional methods.

### 2.2. Instrumentation

Elemental analysis (C, H, N) was performed on an Elemental vario EL elemental analyzer. The lanthanide content was determined by EDTA titration. Infrared spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer between KBr plate.  ${}^1\text{H}$  NMR spectra were measured with a Bruker-400MHz nuclear magnetic resonance instrument using  $\text{CDCl}_3$  as solvent. The TG curves were recorded with a TA-SDTQ600 thermogravimetric analyzer in the temperature interval of 25-800  $^\circ\text{C}$ , under dynamic synthetic air atmosphere ( $100\text{ mL}\cdot\text{min}^{-1}$ ) and heating rate of  $10^\circ\text{C}\cdot\text{min}^{-1}$ . Fluorescence and phosphorescence spectra were recorded on a Hitachi F-4500 spectrometer. The lifetime measurements of the complexes were carried out on a SPEX 1934D spectrophotometer at room temperature.

### 2.3. Synthesis of Br-DBM

Synthetic route of Br-DBM was as follows:

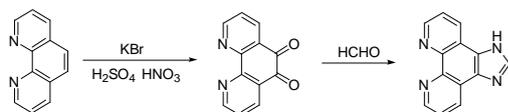


Scheme.1 Synthesis of ligand Br-DBM

$\text{NaNH}_2$  (1.56 g, 0.04 mol) was dissolved in dry benzene (80 ml) under Ar, and heated to  $65^\circ\text{C}$ , 4-bromoacetophenone (1.99 g, 0.01 mol) was added in portions. To the above stirred solution, benzoic acid ethyl ester (5.72 ml, 0.04 mol) was added dropwise, and the mixture was refluxed under Ar for 10 h at  $85^\circ\text{C}$ , then left to cool to the room temperature. The reaction mixture was added to ice water (50 ml), and the pH was adjusted to 3.5 with hydrochloric acid. The mixture was then extracted with benzene (20 ml $\times$ 3). The combined organic phase was washed with  $\text{H}_2\text{O}$ , dried over  $\text{NaSO}_4$  for 6 h and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified to afford the product 1.58 g (52.23%) as pale yellow crystals. Elemental analysis for  $\text{C}_{15}\text{H}_{11}\text{O}_2\text{Br}$  (calcd. %): C:59.39(59.17), H:3.72(3.62).  $^1\text{H}$  NMR  $\delta$ : 6.83(s, 1H), 7.35~7.37(t, 3H), 7.94~8.08(t, 4H), 8.12~8.15 (m, 2H), 16.50 (s, 1H).

### 2.4. Synthesis of IP

Synthetic route to IP was as follows:



Scheme.2 Synthesis of ligand IP

IP was prepared based on the method in [15]. Elemental analysis for  $\text{C}_{13}\text{H}_9\text{N}_4$  (calcd. %): C: 70.25(70.59), H: 3.80(3.62), N: 25.05(25.33).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 9.1(s, 4H), 8.6 (s, 1H), 8.1 (d, 2H), 3.4 (N-H).

### 2.5. Synthesis of the complexes

The complex  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  was synthesized by mixing the Eu(III) chloride with Br-DBM and IP in 1:3:1 ratio in anhydrous ethanol which was adjusted to pH 6-7 by aqua ammonia at 298 K. Then, the white-solid state complex was filtrated, washed with anhydrous ethanol and dried at  $60^\circ\text{C}$ . The complex  $\text{Eu}(\text{DBM})_3\text{IP}$  was synthesized similarly. Elemental analysis for  $\text{Eu}(\text{Br-DBM})_3\text{IP}$ (calcd.%) C: 53.65(53.83), H: 3.32(3.21), N: 4.23(4.38), Eu: 11.67(11.79);  $\text{Eu}(\text{DBM})_3\text{IP}$  (calcd.%) C: 66.54(66.73), H: 4.31(4.22), N: 5.31(5.37), Eu: 14.34(14.48);

## 3. Results and discussion

### 3.1. Elemental analysis

The results of elemental analysis indicated that the composition of the complexes conformed to  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$ .

### 3.2. IR spectra

The IR spectral of the ligands and complexes were measured in the region between 4000 and  $400\text{ cm}^{-1}$ . The main data were presented in Table 1.

For the ligand Br-DBM, the bands at  $1687\text{ cm}^{-1}$  and  $1715\text{ cm}^{-1}$  could be attributed to the keto  $\text{C}=\text{O}$ . In addition, the band at  $1586\text{ cm}^{-1}$  was assigned to the enolic  $\text{C}=\text{C}$ . The enolic  $\text{C}-\text{O}$  stretching absorption was observed at  $1275\text{ cm}^{-1}$ . These bands confirmed the presence of the keto-enol tautomer in Scheme 1.

Table 1. IR spectra data of the comp( $\text{cm}^{-1}$ ).

comp	$\nu(\text{C}=\text{O})$	$\nu(\text{C}-\text{O})$	$\nu(\text{C}=\text{C})$	$\delta(\text{C}-\text{H})$		$\nu(\text{Eu}-\text{O})$
				C)	N)	
IP				1592	722,814	
Br-DBM	1687,1715	1275	1586			
DBM	1548,1618	1216	1426			
$\text{Eu}(\text{Br-DBM})_3\text{IP}$		1213	1576	1546	726,844	418
$\text{Eu}(\text{DBM})_3\text{IP}$		1206	1412	1516	733,847	407

In the case of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$ , the bands at  $1687\text{ cm}^{-1}$  and  $1715\text{ cm}^{-1}$  disappeared; the bands at  $1586\text{ cm}^{-1}$  and  $1275\text{ cm}^{-1}$  downshifted to the low frequency; Eu-O mode

appeared at  $418\text{ cm}^{-1}$  in the complex. The above facts indicated that  $\text{Eu}^{3+}$  ion was coordinated with oxygen atoms of the first ligand Br-DBM. The band appeared around

1592  $\text{cm}^{-1}$  in IP, due to C=N, downshifted to 1546  $\text{cm}^{-1}$  in the complex, which showed that the C=N groups of the IP coordinated to the  $\text{Eu}^{3+}$  ion through nitrogen atoms. The IR spectra results of  $\text{Eu}(\text{DBM})_3\text{IP}$  was similar to that of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$ .

### 3.3. Thermal stability

The TG curves of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$  were shown in Fig. 1. The TG curves did not present any event relative to water loss in the interval 25-200 $^\circ\text{C}$ , indicating that the two new complexes were in anhydrous form. This was corroborated by IR spectroscopy and elemental analysis. For  $\text{Eu}(\text{Br-DBM})_3\text{IP}$ , there were two main weight-loss processes. The first one in the region of 325-460 $^\circ\text{C}$  was attributed to elimination and decomposition of ligand IP, and the weight-loss was 16.95% compared with the calculated value 17.18%. The second one in the region of 460-800 $^\circ\text{C}$  was attributed to elimination and decomposition of ligand Br-DBM, and the weight-loss was 13.45%, compared with the calculated value 13.66%. The thermal decomposition process of  $\text{Eu}(\text{DBM})_3\text{IP}$  was similar, two weight-loss were 21.45% and 16.62%, which were close to the calculated value 21.09% and 16.76%, respectively.

The above analysis led us to speculate the general structures of the complexes, which were shown in Fig. 2.

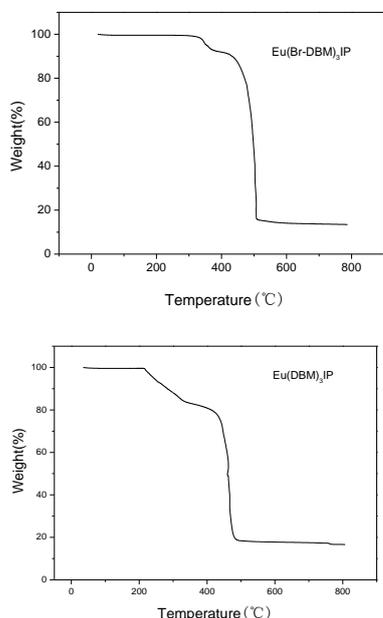


Fig. 1. TG curves of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$ .

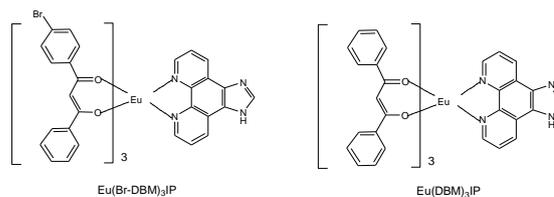


Fig. 2. The general structures of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$ .

### 3.4. Fluorescence spectra

The fluorescence spectra of the complexes were measured at 298 K in solid state ( $\lambda_{\text{ex}}$ : 275 nm). In Fig. 3,  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$  displayed four characteristic emission bands of  $\text{Eu}^{3+}$  ion, which were assigned to the  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  ( $J=1, 2, 3, 4$ ) transitions. The fluorescence data of the complexes were shown in Table 2. The  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition is a typical electric dipole transition and strongly varies with the local symmetry of  $\text{Eu}^{3+}$  ions, while the  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition corresponds to a partly allowed magnetic dipole transition. In addition, among these transitions, the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition showed the strongest emission, suggesting the chemical environment around  $\text{Eu}^{3+}$  ion was in low symmetry.

Compared with the fluorescence intensity of the complexes in Table 2,  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  was obviously stronger. To explain the difference of the fluorescence intensity, the lowest triplet state of the ligands were given next.

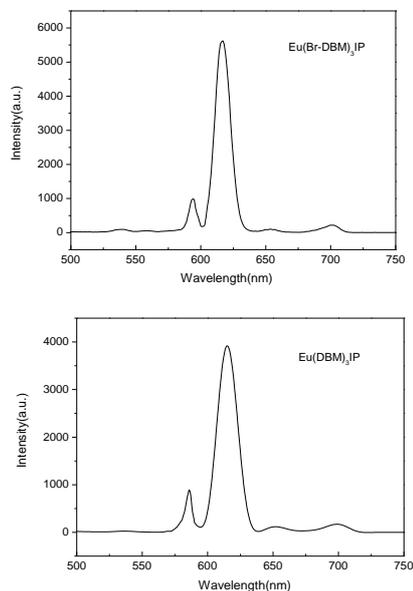


Fig. 3. Fluorescence spectra of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$ .

Table 2. The fluorescence data of the complexes.

complexes	Assignment(nm)				PI <sup>a</sup> (a.u.)
	$^5\text{D}_0 \rightarrow ^7\text{F}_1$	$^5\text{D}_0 \rightarrow ^7\text{F}_2$	$^5\text{D}_0 \rightarrow ^7\text{F}_3$	$^5\text{D}_0 \rightarrow ^7\text{F}_4$	
$\text{Eu}(\text{Br-DBM})_3\text{IP}$	594	617	654	702	5624
$\text{Eu}(\text{DBM})_3\text{IP}$	586	615	652	698	3919

<sup>a</sup>PI: peak intensity

### 3.5. Triplet state of the ligand and energy transfer

The phosphorescence spectra of Gd-(Br-DBM) was measured at 77 K ( $\lambda_{\text{ex}}$ : 275 nm) [16]. Gd complex was selected as the model complex for the determination of the triplet state energy of the ligand owing to their high phosphorescence-fluorescence ratios. In Fig. 4, taken the reciprocal of the shortest emission wavelength at 493 nm, the lowest triplet state energy level of Br-DBM was confirmed at 20284  $\text{cm}^{-1}$ . The lowest triplet state energy level of DBM was determined at 20520  $\text{cm}^{-1}$  as the reference [17].

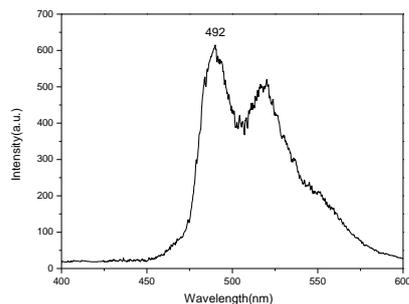


Fig. 4. Phosphorescence spectra of Gd-(Br-DBM).

From the fluorescence spectra of the complexes, it was clearly observed that the fluorescence intensity of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  was much stronger than that of  $\text{Eu}(\text{DBM})_3\text{IP}$ . According to the intramolecular energy transfer mechanism [18], the fluorescence intensities are influenced by the intramolecular energy transfer efficiency between the ligand and the rare earth ion, which depends on the Dexter electron exchange from the lowest triplet level of ligand to the excited energy level of rare earth ion [19], the rate constant of energy transfer  $K_{\text{ET}}$  is:

$$K_{\text{ET}} = KJ \exp(-2R_{\text{DA}}/L)$$

Where  $K$  is a constant,  $R_{\text{DA}}$  is intermolecular distance between energy donor and energy acceptor,  $L$  is van der Waals radius, both  $R_{\text{DA}}$  and  $L$  are considered to be constant for intramolecular energy transfer, so:

$$K_{\text{ET}} = CJ = C \int F_{\text{D}}(E) \cdot E_{\text{A}}(E) dE$$

Where  $F_{\text{D}}(E)$  is the luminescence spectrum of energy donor (ligand) and  $E_{\text{A}}(E)$  is the absorption spectrum of energy acceptor ( $\text{Re}^{3+}$  ion) separately. The integral of spectra overlap in this equation represents the energy difference between the lowest triplet state energy level of ligand and the excited energy level of rare earth ion. So  $K_{\text{ET}}$  consists with the energy difference matching between the lowest triplet state energy level of ligand and the excited energy level of rare earth ion. Thus, the energy difference is neither too large nor too small, and can be assumed that there existed an optimal value [20].

Based on the above analysis, the energy difference

$\Delta E(\text{T}_1\text{-Eu}^{3+})$  between the lowest triplet state energy level  $\text{T}_1$  of IP (28000  $\text{cm}^{-1}$ ) and the excited energy level of  $\text{Eu}^{3+}$  ( ${}^5\text{D}_0$ , 17260  $\text{cm}^{-1}$ ) was 10740  $\text{cm}^{-1}$ , and this energy difference was too large to sensitize  $\text{Eu}^{3+}$  ion. So, it could be concluded that the energy transfer was mainly from the first ligand to  $\text{Eu}^{3+}$  ion.

In  $\text{Eu}(\text{Br-DBM})_3\text{IP}$ , the energy difference  $\Delta E'(\text{T}_1\text{-Eu}^{3+})$  between the lowest triplet state energy level  $\text{T}_1$  of Br-DBM (20284  $\text{cm}^{-1}$ ) and the excited energy level of  $\text{Eu}^{3+}$  ( ${}^5\text{D}_0$ , 17260  $\text{cm}^{-1}$ ) was 3024  $\text{cm}^{-1}$ . Compared with the energy difference  $\Delta E'(\text{T}_1\text{-Eu}^{3+})$ , the energy difference between the lowest triplet state energy level  $\text{T}_1$  of DBM (20520  $\text{cm}^{-1}$ ) and the excited energy level of  $\text{Eu}^{3+}$  ( ${}^5\text{D}_0$ , 17260  $\text{cm}^{-1}$ ) became larger, which was 3260  $\text{cm}^{-1}$  in  $\text{Eu}(\text{DBM})_3\text{IP}$ , and this larger energy difference was unfavorable for the energy transfer. Thus,  $\text{Eu}(\text{DBM})_3\text{IP}$  showed lower luminescence intensity

### 3.6. Fluorescence quantum efficiency and life time

The luminescence decay curves of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$  were presented at 298 K. In Fig. 5, the curves fit first-order exponential decay law, which revealed that only one symmetry site was occupied by the  $\text{Eu}^{3+}$  ions.

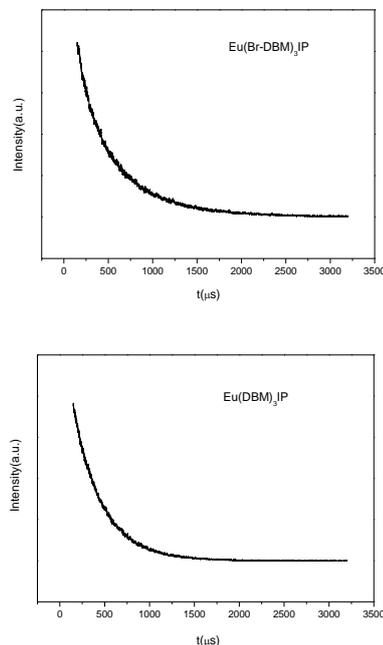


Fig. 5. Luminescence decay curves of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$ .

In Table 3 the lifetime ( $\tau$ ) of the emitting state  ${}^5\text{D}_0$ , nonradiative ( $A_{\text{nrad}}$ ), radiative ( $A_{\text{rad}}$ ) and tot-radiative rates ( $A_{\text{tot}}$ ) can be related through the following equation:

$$A_{\text{tot}} = \frac{1}{\tau} = A_{\text{rad}} + A_{\text{nrad}}$$

$A_{rad}$  can also be obtained by summing over the radiative rates  $A_{0J}$  for each  ${}^5D_0 \rightarrow {}^7F_J$  ( $J=1, 2, 4$ ) transitions of  $\text{Eu}^{3+}$  ion:

$$A_{rad} = \sum A_{0J} = A_{01} + A_{02} + A_{04}$$

$A_{0J}$  can be calculated according to the equation:

$$A_{0J} = A_{01} \left( \frac{I_{0J}}{I_{01}} \right) \left( \frac{v_{01}}{v_{0J}} \right)$$

Where  $I_{01}$  and  $I_{0J}$  are the integrated intensities of the  ${}^5D_0 \rightarrow {}^7F_1$  and  ${}^5D_0 \rightarrow {}^7F_J$  transitions ( $J=2, 4$ ),  $v_{01}$  and  $v_{0J}$  are the respective energy barriers of these transitions. The magnetic dipole allowed  ${}^5D_0 \rightarrow {}^7F_1$  transition which is not influenced by the chemical environment was taken as the reference [21], the coefficient of spontaneous emission  $A_{01}$  is given by the expression  $A_{01} = 0.31 \times 10^{-11} (n)^3 (v_{01})^3$ , and its value is estimated to be  $50 \text{ S}^{-1}$  [22].

The quantum efficiencies ( $\eta$ ) of the emitting  ${}^5D_0$  level can be obtained from the following equation:

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}}$$

Table 3. Luminescence properties data of the complexes.

	$\tau/\mu\text{s}$	$A_{rad}/\text{S}^{-1}$	$A_{nrad}/\text{S}^{-1}$	$A_{tot}/\text{S}^{-1}$	$\eta/\%$
$\text{Eu}(\text{Br-DBM})_3\text{IP}$	456	613	1579	2192	28
$\text{Eu}(\text{DBM})_3\text{IP}$	405	592	1875	2467	24

As shown in Table 3, the quantum efficiencies ( $\eta$ ) of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  was higher than that of  $\text{Eu}(\text{DBM})_3\text{IP}$ , which indicated the energy transfer efficiency from Br-DBM to  $\text{Eu}^{3+}$  ion was higher. The energy transfer efficiency depends on two processes: one is the intersystem crossing from excited single state of the ligand changes to the triplet state (ISC,  $S_1 \rightarrow T_1$ ), the other is the intramolecular energy transfers from the triplet state of the ligand to the excited energy level of  $\text{Eu}^{3+}$  ion ( $T_1 \rightarrow {}^5D_0$ ). In the  $\text{Eu}(\text{Br-DBM})_3\text{IP}$ , the heavy atom (Br) effect improved the ISC process, and  $T_1$  of Br-DBM was closer to the  ${}^5D_0$  of  $\text{Eu}^{3+}$  ion. So, both of the factors made  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  present higher quantum efficiency.

#### 4. Conclusions

In this paper, two novel complexes of Eu (III) with Br-DBM, DBM and IP have been synthesized. The compositions of the complexes were  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$ . Fluorescence and phosphorescence spectra confirmed that the luminescence intensity was influenced by the energy difference between the lowest triplet level of the first ligand and the  ${}^5D_0$  level of  $\text{Eu}^{3+}$  ion, and energy difference was well matched in  $\text{Eu}(\text{Br-DBM})_3\text{IP}$ . So,  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  exhibited much higher emission than  $\text{Eu}(\text{DBM})_3\text{IP}$ . In addition, the luminescence decay curve

of the complexes fit a single-exponential decay law and the quantum efficiencies of  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  and  $\text{Eu}(\text{DBM})_3\text{IP}$  were 28% and 24%, respectively. Further investigation showed that the quantum efficiency was influenced by the heavy atom effect and the energy difference between the triplet state of ligand and the  ${}^5D_0$  of  $\text{Eu}^{3+}$  ion. Therefore,  $\text{Eu}(\text{Br-DBM})_3\text{IP}$  was an excellent red-emitter which would be considered as a promising material for photoluminescent applications.

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\*Corresponding author: changpingwei@hotmail.com