

# Synthesis and Photoluminescence of the $\text{Eu}^{3+}$ Composite with Dibenzoylmethane and Oligoacrylic Acid

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**ABSTRACT:** An  $\text{Eu}^{3+}$ -dibenzoylmethide (DBM)-oligoacrylic acid (OAA) composite was prepared in water, ethanol, and a glycerin mixed solvent. Influence of pH value on the synthesis was also given. A composite with pH of 10.0 was most suitable for the synthesis. It was confirmed by UV-VIS, Fourier transform infrared (FTIR), excitation spectra, and conductivity measurement that DBM, the second ligand, which had low molecular weight, coordinated with  $\text{Eu}^{3+}$  in the ionomer chain, instead of dispersing in the OAA matrix. When the molar ratio of DBM- $\text{Eu}^{3+}$  was 2:1, which was found to be the best ratio to obtain the maximum intensity of fluorescence (due to the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition), the fluorescence intensity of the  $\text{Eu}^{3+}$ -DBM-OAA (emitted at 616 nm) increased logarithmically with the increase of the molar ratio of  $\text{Eu}^{3+}$ -OAA in the range of 0 to 6 : 1. Energy transfer in the composite was also discussed. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2588–2593, 1999

**Key words:** photoluminescence; oligomer;  $\text{Eu}^{3+}$ -DBM-OAA composite

## INTRODUCTION

Although considerable efforts have been expended on diverse studies of  $\text{Eu}^{3+}$ -polyelectrolyte composites because of their promising application for plastic fluorescence materials,<sup>1–3</sup> the corresponding ternary composite containing a second ligand besides polyanions has not yet been fully investigated and had been mainly observed in cases where the second ligand was dispersed in the polymer matrix. In those attempts—(1) research on the effect of low molecular weight ligands on the fluorescence properties of  $\text{Eu}^{3+}$ -polyelectrolytes<sup>4,5</sup> and (2) study of  $\text{Eu}^{3+}$ -linear and -branched polymers containing  $\beta$ -diketone

moieties in the chain<sup>6</sup>—the weak fluorescence was attributed to a structural factor. It is hoped that the introduction of the second ligand into the coordination sphere of  $\text{Eu}^{3+}$  by releasing pre-coordinated water molecules may be an efficient way to enhance fluorescence. We have initiated studies of the photoluminescent properties of  $\text{Eu}^{3+}$ -OAA and  $\text{Eu}^{3+}$ -DBM-OAA composites. This paper reports on the synthesis and properties of the  $\text{Eu}^{3+}$ -DBM-OAA composite. The energy transfer in the  $\text{Eu}^{3+}$ -DBM-OAA composite is also discussed.

## EXPERIMENTAL

### Materials

Europia ( $\text{Eu}_2\text{O}_3$ ; 99.99%) was purchased from YueLong Chemical Factory, Shanghai, People's Republic of China.  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  was prepared by

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dissolving  $\text{Eu}_2\text{O}_3$  in hydrochloric acid. Dibenzoylmethane (HDBM) and other chemicals were purchased from Beijing Chemical Factory (Beijing, People's Republic of China). Sodium dibenzoylmethide ( $\text{NaDBM}$ ) and sodium tetrakis(dibenzoylmethanato) europate ( $\text{NaEu}(\text{DBM})_4$ ) were prepared according to the literature<sup>7</sup>.

OAA ( $\overline{M}_w = 4,500$ ) was obtained from the Institute of Chemistry, Chinese Academy of Sciences. It demonstrates some of the different physical properties (e.g., solubility in ethanol) of the large  $\overline{M}_w$  members of the polymeric-homologous series. On receiving, it was neutralized to a pH of 7.0 by sodium hydroxide. A stock solution of OAA was prepared by dissolving the neutralized OAA solution in glycerin.

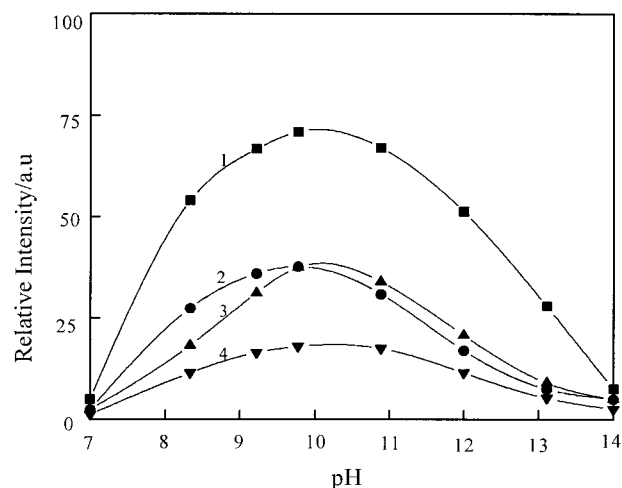
### $\text{Eu}^{3+}$ -OAA Binary Composite and $\text{Eu}^{3+}$ -DBM-OAA Ternary Composite

The  $\text{Eu}^{3+}$ -OAA binary composite was synthesized by a method similar to the one used in the literature.<sup>3</sup> The  $\text{Eu}^{3+}$ -DBM-OAA ternary composite was synthesized as follows: A mixture of  $\text{EuCl}_3$  ethanol solution, HDBM ethanol solution, and OAA glycerin solution was added into a 10-mL graduated tube, and the tube was sealed tightly. Due to the buffer ability of OAA,<sup>8</sup> the mixture reached the same pH as pristine neutralized OAA, namely 7.0. This mixture was allowed to be shaken vigorously and then kept in a thermostat at  $60^\circ\text{C}$  to accelerate the dispersing process of HDBM. The pH value of the solution was then adjusted within  $10.0 \pm 0.3$  by adding 8 M NaOH solution. Then the mixture continued to be shaken and was kept in the thermostat at  $60^\circ\text{C}$  for 36 h. The syntheses of both the binary and the ternary composites were carefully carried out to make every composite synthesized contain the same amount of OAA, i.e.,  $1.9 \times 10^{-5}$  mol in each 10 mL graduated tube, and the same solvent composition, i.e., the volume ratio of water : ethanol : glycerin = 1 : 8 : 11.

The above solutions were poured into a large amount of ethanol, and the resulting precipitate was filtered under reduced pressure and washed six times with 95% ethanol to remove glycerin and soluble ionic impurities. The white precipitate was subjected to a final drying process, at approximately  $30^\circ\text{C}$  under vacuum for 4 h.

### Measurement

All spectra were measured at room temperature. Excitation and luminescence spectra were re-



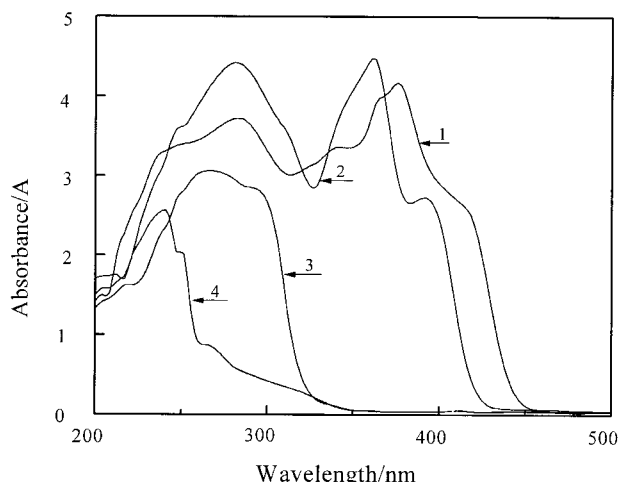
**Figure 1** Relationship between photoluminescence intensity at 616nm of the  $\text{Eu}^{3+}$ -DBM-OAA composite and pH value ( $\lambda_{\text{ex}} = 396$  nm): 1,  $\text{Eu}^{3+}$ -DBM-OAA, molar ratio of  $\text{Eu}$ -OAA = 6.0 : 1, molar ratio of DBM/ $\text{Eu} = 2$  : 1; 2,  $\text{Eu}^{3+}$ -DBM-OAA, molar ratio of  $\text{Eu}$ -OAA = 2.1 : 1, molar ratio of DBM- $\text{Eu} = 2$  : 1; 3,  $\text{Eu}^{3+}$ -DBM-OAA, molar ratio of  $\text{Eu}$ -OAA = 2.1 : 1, molar ratio of DBM- $\text{Eu} = 0.5$  : 1; 4,  $\text{Eu}^{3+}$ -DBM-OAA, molar ratio of  $\text{Eu}$ -OAA = 1.2 : 1, molar ratio of DBM- $\text{Eu} = 2$  : 1.

corded on a Hitachi 850 fluorescence spectrophotometer. The excitation source was a 150W xenon lamp. The band pass for the excitation and the emission was set at 5nm. A long-wavelength pass filter, with a maximum and uniform transmittance (more than 95%) above 290 nm, was placed in front of the emission monochromator in order to reduce the scatter of the incident beam into the emission monochromator. Solutions were placed in a 1-cm path-length quartz cell for fluorescence measurements. All spectra were blankly subtracted. The UV-VIS spectra were recorded on a Shimadzu double-beam spectrometer, model UV-250. Conductivity measurement was run at room temperature using a DDS-11A conductivity meter. Infrared spectra of the composites were measured using a Nicolet 7199B FTIR spectrometer in the range of  $4,000$ – $400$   $\text{cm}^{-1}$ . Raman spectra of the composites were recorded on a 910 FT-Raman spectrometer in the range of  $3,600$ – $100$   $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

### Influence of pH on the Formation of the $\text{Eu}^{3+}$ -DBM-OAA Composite

Figure 1 shows the highest intensity of photoluminescence of the ternary composite, at 616 nm,



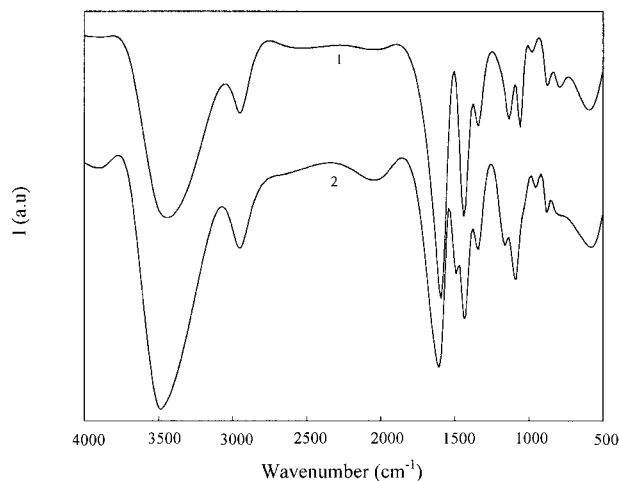
**Figure 2** UV-VIS spectra of  $\text{Eu}^{3+}$ -DBM-OAA composite,  $\text{Eu}^{3+}$ -OAA composite,  $\text{NaEu}(\text{DBM})_4$ , and pristine neutralized OAA: 1,  $\text{NaEu}(\text{DBM})_4$ ; 2,  $\text{Eu}^{3+}$ -DBM-OAA, molar ratio of DBM-Eu = 2 : 1; 3,  $\text{Eu}^{3+}$ -OAA; 4, OAA (pH = 7.0). For 1–3 systems, the Eu content is the same ( $4 \times 10^{-3} \text{ mol L}^{-1}$ ).

was obtained when pH was adjusted to 10.0. As reported in the literature,<sup>9</sup> at a pH of 7.0, the acid residue in polyacrylic acid (PAA)'s anion chain is about 30 mol % due to the weak acidity of PAA. It's known that a hydrogen bond exists between COOH groups of interchain and intrachain in OAA.<sup>9</sup> Moreover, HDBM may also form hydrogen bonds with these COOH groups. At a pH of 7.0, some of the HDBM molecules may undergo deprotonation to form enol anions. To maintain a pH value of 7.0, OAA, a buffer substance, must undergo protonation. When more OAA was protonated, the effective charge of the chain was reduced and the electrostatic attraction between the chain and the  $\text{Eu}^{3+}$  ions was reduced, too; hence loose structure may come into being and the multidentate coordinate sphere was vitiated. This may provide an insight into the phenomenon of very low fluorescence intensity observed at a pH of 7.0 due to failure of the formation of the ternary composite. When pH value is adjusted to 10.0, it is believed that both OAA and DBM become more deprotonated, they together rap around the positively charged  $\text{Eu}^{3+}$  ion owing to polymer (oligomer) cooperative effect,<sup>10</sup> and the composite is formed. It was known that, upon the formation of metallocene polymer or oligomer composite, multimembered rings would be involved in chelation.<sup>11</sup> In the  $\text{Eu}^{3+}$ -DBM-OAA composite, it's probable that DBM may replace pre-coordinated water to form five-membered coordination rings.

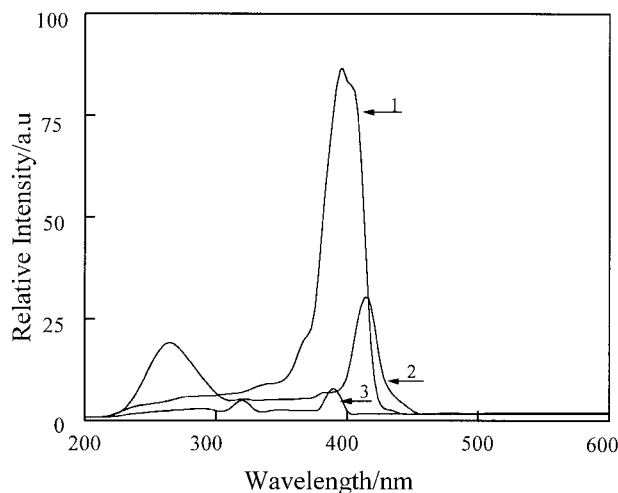
### Evidence for the Formation of the $\text{Eu}^{3+}$ -DBM-OAA Ternary Composite

The UV-VIS absorption spectrum of the  $\text{Eu}^{3+}$ -DBM-OAA composite is shown in Figure 2 in contrast with the spectra of  $\text{NaEu}(\text{DBM})_4$ ,  $\text{Eu}^{3+}$ -OAA, and pristine neutralized OAA. The spectrum of the  $\text{Eu}^{3+}$ -DBM-OAA composite is different from the three compared, and a peak with a shoulder at 362 nm arising from  $n \rightarrow \pi^*$  transition of DBM shows a blue shift compared with that of  $\text{NaEu}(\text{DBM})_4$ . This blue shift of the band can be accounted for by the carbonyl group of OAA in the  $\text{Eu}^{3+}$ -DBM-OAA to contribute fewer electrons to the coordination bond than those in  $\text{NaEu}(\text{DBM})_4$ . This means that both OAA and DBM took part in the formation of the composite, not OAA alone or DBM alone.

The  $\text{Eu}^{3+}$ -DBM-OAA composite and the  $\text{Eu}^{3+}$ -OAA composite were both investigated by measuring the FTIR and Raman spectra. The IR spectra are shown in Figure 3. The spectrum of the  $\text{Eu}^{3+}$ -OAA composite has a strong absorption at  $\sim 3,500 \text{ cm}^{-1}$ , which is the diagnostic vibration of the OH group in the  $\text{Eu}^{3+}$ -OAA composite, while in the  $\text{Eu}^{3+}$ -DBM-OAA ternary composite, this absorption decreased considerably in intensity, meaning the coordinated water in the  $\text{Eu}^{3+}$ -OAA composite was replaced by DBM. This means that upon the formation of the  $\text{Eu}^{3+}$ -DBM-OAA composite, the pre-coordinated water molecule, which was reported as many as 3–4 in



**Figure 3** FTIR spectra of the  $\text{Eu}^{3+}$ -DBM-OAA composite (molar ratio of Eu-OAA = 2.1 : 1, molar ratio of DBM-Eu<sup>3+</sup> = 2 : 1) and the  $\text{Eu}^{3+}$ -OAA composite (molar ratio of Eu<sup>3+</sup>-OAA = 2.1 : 1): 1,  $\text{Eu}^{3+}$ -DBM-OAA; 2,  $\text{Eu}^{3+}$ -OAA.



**Figure 4** Excitation spectra: 1,  $\text{Eu}^{3+}$ -DBM-OAA composite (molar ratio of DBM- $\text{Eu}^{3+}$  = 2 : 1, molar ratio of  $\text{Eu}$ -OAA = 2.1 : 1)— $\text{Eu}^{3+}$ :  $4 \times 10^{-3} \text{ mol L}^{-1}$ ; 2,  $\text{NaEu}(\text{DBM})_4$ ; 3,  $\text{Eu}^{3+}$ -OAA composite. For all the systems,  $\lambda_{\text{em}} = 616 \text{ nm}$ , the Eu content is the same.

the similar system,<sup>12</sup> was further expelled. The peaks at around  $1,570 \text{ cm}^{-1}$  and  $1,400 \text{ cm}^{-1}$  are assigned to  $\nu_{\text{as}}\text{COO}$  and  $\nu_{\text{s}}\text{COO}$ , respectively. Compared with  $\nu_{\text{as}}\text{COO}$  and  $\nu_{\text{s}}\text{COO}$  for the  $\text{Eu}^{3+}$ -OAA composite, the former for the  $\text{Eu}^{3+}$ -DBM-OAA is slightly red-shifted and the latter is slightly blue-shifted. This means the coordination sphere of the  $\text{Eu}^{3+}$ -DBM-OAA composite is different from that of the  $\text{Eu}^{3+}$ -OAA composite because coordination of the  $\text{Eu}^{3+}$  ion for DBM is preferred to that for  $\text{H}_2\text{O}$ . In addition, we compared the FT-Raman spectra ( $3,600\text{--}100 \text{ cm}^{-1}$ ) of the  $\text{Eu}^{3+}$ -OAA composite and the  $\text{Eu}^{3+}$ -DBM-OAA composite—a new vibrational peak at ( $600 \text{ cm}^{-1}$ ) appeared in the  $\text{Eu}^{3+}$ -DBM-OAA composite, which may be attributed to DBM's presence in the coordination sphere.

The molar conductance data of the  $\text{Eu}^{3+}$ , DBM, and OAA mixture before reaction and the  $\text{Eu}^{3+}$ -DBM-OAA composite are  $2.75 \times 10^2$  and  $1.75 \times 10^2 \mu\Omega^{-1} \text{ cm}^{-1}$ , respectively. The formation is explained by the incorporation of OAA and DBM with the  $\text{Eu}^{3+}$  ion, making the chain less mobile, which renders it hard to contribute to macroscopic conductivity.<sup>13</sup>

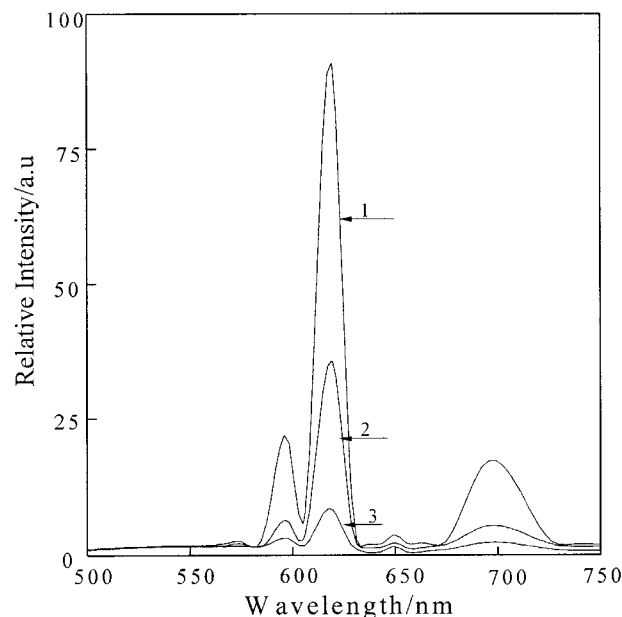
#### Photoluminescence of the $\text{Eu}^{3+}$ -DBM-OAA Composite and Its Energy Transfer Process

The excitation spectrum of the  $\text{Eu}^{3+}$ -DBM-OAA composite as shown in Figure 4 is different from

that of  $\text{NaEu}(\text{DBM})_4$ . The highest peak of the  $\text{Eu}^{3+}$ -DBM-OAA composite is blue-shifted to 395 nm compared with the corresponding band of  $\text{NaEu}(\text{DBM})_4$ . The  $\text{Eu}^{3+}$ -OAA composite produces two small peaks: one at 320 nm and the other at 390 nm. The latter mostly corresponds to  ${}^7\text{F}_{0,1} \rightarrow {}^5\text{L}_6$  of  $\text{Eu}^{3+}$ . The highest peak of the  $\text{Eu}^{3+}$ -DBM-OAA composite centered at 395 nm covers the region of 300–425 nm, indicating that OAA is involved in the ternary composite. All these may help to confirm that both OAA and DBM are present in the coordination sphere, which may let the  $\text{Eu}^{3+}$ -DBM-OAA composite be efficiently excited by UV light. The sharp band emission of the  $\text{Eu}^{3+}$ -DBM-OAA composite was observed, as shown in Figure 5. The spectra were composed of 594 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ ), 616 nm (the maximum emission peak,  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ ), 650 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_3$ ), and 695 nm ( ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ ). When the fluorescence intensities of the ternary composite (molar ratio of  $\text{Eu}^{3+}$ -OAA = 2.1 : 1) are compared with those of the  $\text{Eu}^{3+}$ -OAA binary composite and other systems that contain the same Eu concentration, we found that the fluorescence intensities are in the following order:

Ternary composite >  $\text{NaEu}(\text{DBM})_4$

    >> Binary composite



**Figure 5** Photoluminescence spectra of the  $\text{Eu}^{3+}$  composites: 1,  $\text{Eu}^{3+}$ -DBM-OAA (molar ratio of DBM- $\text{Eu}^{3+}$  = 2 : 1)  $\text{Eu}^{3+}$ :  $4 \times 10^{-3} \text{ mol L}^{-1}$ ; 2,  $\text{NaEu}(\text{DBM})_4$ ; 3,  $\text{Eu}^{3+}$ -OAA (molar ratio of  $\text{Eu}^{3+}$ -OAA = 2.1 : 1). For all the systems, excited at 396 nm, Eu content is the same.

The fluorescence intensity of the ternary composite (molar ratio of  $\text{Eu}^{3+}$ -OAA = 2.1 : 1) is nearly 12 times as high as the binary composite (molar ratio of  $\text{Eu}^{3+}$ -OAA = 2.1 : 1). Literature<sup>6</sup> has reported that  $\text{Eu}^{3+}$ -tetrakis(dibenzoylmethide) has the highest intensity among  $\text{Eu}^{3+}$ -tetrakis-, tris-, and bis(dibenzoylmethide) groups and also has a higher intensity than other  $\text{Eu}^{3+}$ -polymer composites that contain  $\beta$ -diketone moieties in the polymer chain. So the ternary composite we synthesized has the highest fluorescence among those systems. The plot representing the 616-nm band intensity of the  $\text{Eu}^{3+}$ -DBM-OAA composite at 616 nm against the molar ratio of  $\text{Eu}^{3+}$ -OAA shows that fluorescence intensity increases logarithmically with the increasing of the molar ratio of  $\text{Eu}^{3+}$ -OAA in the range of 0 to 6 : 1 when the molar ratio of DBM to  $\text{Eu}^{3+}$  is 2 : 1. Suppose the molar ratio of  $\text{Eu}^{3+}$ -OAA is  $x$  and fluorescence intensity is  $y$ , then an empirical formula is obtained:

$$y = 5.521 \ln x + 1.983$$

The increased photoluminescence is due to the following:

1. The introduction of DBM into the coordination sphere of the  $\text{Eu}^{3+}$  ion by releasing pre-coordinated water molecules enhances photoluminescence, as has been commonly proposed in literature.<sup>14</sup>
2. The introduction of DBM, which is an excellent light-harvesting center, into the coordination sphere may result in a more asymmetric coordination geometry than that in the  $\text{Eu}^{3+}$ -OAA binary composite. The formation of a unique asymmetric environment surrounding the  $\text{Eu}^{3+}$  ion leads to increased transition probability, and the fluorescence of the  $\text{Eu}^{3+}$  ion is greatly enhanced.<sup>15</sup>
3. The DBM may act as both the energy donor and acceptor involved in the energy transfer process. In the  $\text{Eu}^{3+}$ -DBM-OAA composite, two energy transfer processes may exist simultaneously. One is the nonselective excitation energy absorbed by DBM, whose triplet state ( $20,300 \text{ cm}^{-1}$ ) matches the  $^5\text{D}_0$  level ( $\text{Eu}^{3+(16)}$ ). When the energy is transferred to the  $^5\text{D}_0$  energy level ( $\sim 17,240 \text{ cm}^{-1}$ ) of the  $\text{Eu}^{3+}$  ions, photons are emitted when the ions deactivate from

the  $^5\text{D}_0$  level to  $^7\text{F}_{J(J=0-6)}$ , which can account for the bands observed. The other is the excitation energy first absorbed by OAA, then transferred to DBM in the coordination sphere, and finally to the  $\text{Eu}^{3+}$  ion, as similarly described about a  $\text{Eu}^{3+}$  ternary system reported in the literature.<sup>17</sup> The latter energy-transfer mechanism is confirmed by the presence of DBM considerably reducing the fluorescence intensity of the ligand OAA in the  $\text{Eu}$ -DBM-OAA composite, indicating energy transfer from OAA to DBM. Thus, a high efficiency of intramolecular energy transfer and a higher intensity of fluorescence are obtained.

## CONCLUSIONS

A novel, intense photoluminescence ternary composite,  $\text{Eu}^{3+}$ -DBM-OAA was synthesized when the pH value of the solution was adjusted to 10.0. Evidence accumulated from UV-VIS, FTIR, excitation spectra, and conductivity measurement confirm that coordination bonds formed between  $\text{Eu}^{3+}$  and DBM, and between  $\text{Eu}^{3+}$  and OAA in the  $\text{Eu}^{3+}$ -DBM-OAA composite. The second ligand, DBM, which acts as light-harvesting center, is involved in the highly efficient energy-transfer process. When the molar ratio of DBM to  $\text{Eu}^{3+}$  is 2 : 1, the fluorescence intensity of the  $\text{Eu}^{3+}$ -DBM-OAA composite increases logarithmically with the rising of the molar ratio of  $\text{Eu}^{3+}$ -OAA in the range of 0 to 6 : 1.

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