

# Distinct Composite Structure and Properties of $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$ in Poly(methyl methacrylate) and Polyvinylpyrrolidone

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**ABSTRACT:** The luminescent europium complex  $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$  (phen refers to 1,10-phenanthroline) was doped in poly(methyl methacrylate) (PMMA) and polyvinylpyrrolidone (PVP), respectively. The formed composite systems with different molar ratios of C=O groups in polymers and Eu ions were characterized by X-ray diffractometry (XRD), FTIR, and photoluminescent (PL) spectroscopy and lifetime measurement. The XRD diffractograms show that the composites of PMMA/ $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$  and PVP/ $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$  have crystalline and amorphous structures, respectively, arising from different interactions between the polymers and the complex, as revealed by FTIR spectra. This leads to distinct luminescent characteristics

arising from the  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  transitions of Eu(III) ion ( $J = 0-4$ ). For the composite systems of PMMA/complex, the characteristics of the emission lines change with decreasing molar ratios of C=O/Eu and approach that of the pure complex; whereas the composite systems of PVP/complex have similar spectral features, regardless of the molar ratios, differing from that of the pure complex. The polymer matrices have a substantial influence on the structure and properties of the composites. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3524–3530, 2004

**Key words:** europium; luminescence; composites; transitions; FTIR

## INTRODUCTION

Europium complexes have attracted much attention because of the excellent luminescent properties arising from the  $4f \rightarrow 4f$  transition of Eu(III) and the antenna effect of ligands, which results in important applications in laser, phosphor, electro-optical devices, and optical communication amplifiers, for example. To prevent emission quenching suffering from concentration or vibration of coordinative  $\text{H}_2\text{O}$  molecules and to improve the processing ability of the materials, in general, the europium complexes are doped in matrices, such as polymers, silicates, and micro- or mesoporous materials, to form composites.

Two series of europium complex/polymer composites have been studied extensively. The first series can be synthesized through polymerization of europium complex monomers or reaction of polymers that contain coordinative atoms with  $\text{Eu}^{3+}$  ions or europium complexes.<sup>1–8</sup> It has been considered that such composites are homogeneous. Another series can be pre-

pared by blending europium complexes or salts with polymers simply in a solvent or mixing solvents.<sup>9–13</sup> If some kinds of supramolecular interactions (e.g., coordinate interaction exists between the complex and the polymer), homogeneous composites can be anticipated.

The spectroscopic characteristics of heterocyclic europium complexes, for example,  $\text{Eu}(\text{phen})_2\text{Cl}_3$  and  $\text{Eu}(\text{bpy})_2\text{Cl}_3$ , have been extensively studied. To our knowledge, most of the composite materials containing this kind of complexes focus on silica,<sup>14,15</sup> ORMOSIL,<sup>16</sup> and silica/polymer hybrids.<sup>17</sup> Poly(methyl methacrylate) (PMMA) and polyvinylpyrrolidone (PVP) are good matrices for incorporating europium complexes and inorganic salts. Various europium- $\beta$ -diketonates have been embedded in PMMA, and the formed composites show important applications as plastic optical-fiber lasers and amplifiers.<sup>18</sup> Some europium complexes and inorganic salts have been doped in PVP.<sup>10,19</sup> In addition, polymer optical fibers have clear technical advantages over glass fibers, such as flexibility and a large core diameter.<sup>20</sup>

The interaction between the host and the guest is essential for the structure and properties of the composites formed by blending. In this study,  $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$  were doped in PMMA and PVP separately. It was found that the composite structures

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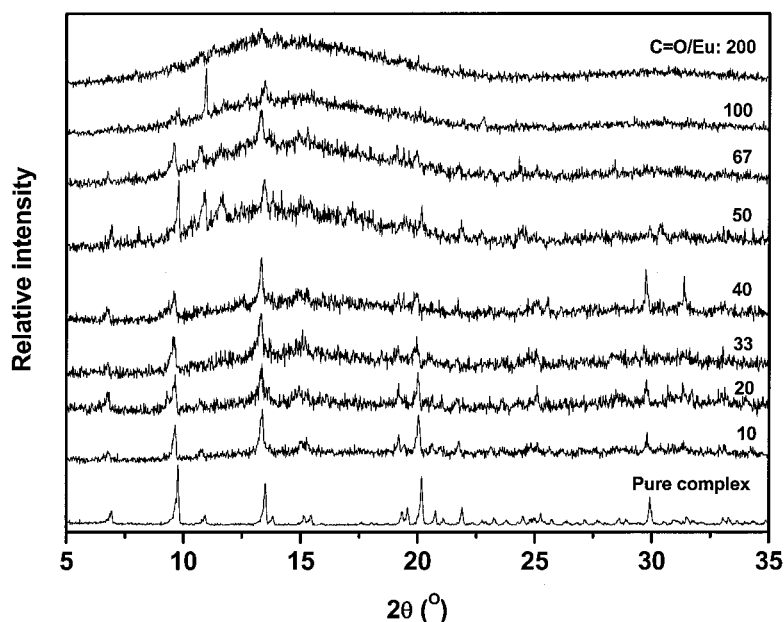


Figure 1 Powder X-ray diffractograms of the composite PMMA/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> systems.

are different because of the different intramolecular interactions between the complex and the two polymers, resulting in very different photoluminescent behaviors of the two series of composites.

## EXPERIMENTAL

### Reagents and samples

Eu<sub>2</sub>O<sub>3</sub> (99.95%), phen (99+%), PMMA ( $M_w \sim 15,000$ ), PVP ( $M_w \sim 29,000$ ), chloroform (99.8%), and ethyl alcohol were purchased from Aldrich Chemical (Milwaukee, WI). Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> was synthesized according to a method described in the literature,<sup>15</sup> and dried in a desiccator at room temperature.

### Sample preparation and characterization

Mixed systems of the complex with PMMA or PVP were prepared by dissolving the corresponding components with molar ratios of C=O/Eu of 500, 200, 125, 100, 67, 50, 40, 20, 10, and 5 into ethanol/chloroform. For the samples for photoluminescent spectroscopy, luminescent lifetime measurements were made by casting the organic solutions onto clean glass slides by the spin-coating method. Opaque or, for some, transparent thin films were formed.

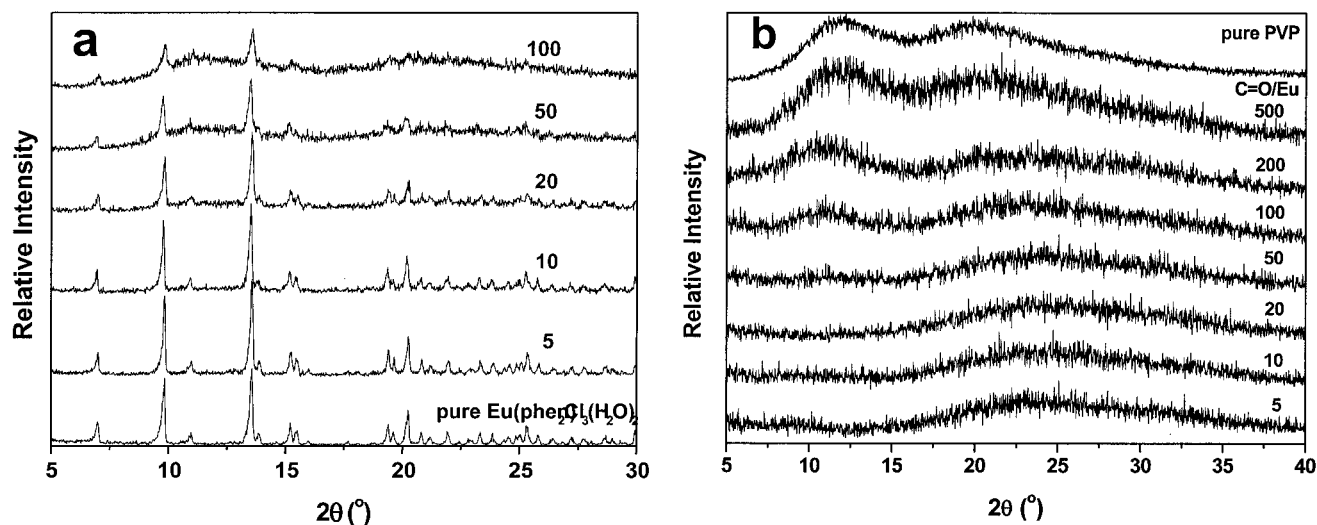
Photoluminescent spectra were obtained by use of a PC 2000 spectroscope (Ocean Optics Inc., Dunedin, FL) with the excitation at 325 nm using a He–Cd laser (LC-500; Omnichrome, Chino, CA) at room temperature. FTIR spectral work was carried out on a Nicolet Impact 410 FTIR spectroscope (Nicolet Analytical Instruments, Madison, WI) with a resolution of 2 cm<sup>-1</sup>.

The KBr pellets for FTIR spectra were made by mixing KBr powder with the composites or with the physical mixtures. Decay curves were obtained by monitoring the 612–614 nm emission by using a 300-MHz digital oscilloscope (LeCroy 9310, Geneva, Switzerland) and triple-grating monochromator (Spectra Pro-750 ARC, Actron Research Corp., MA) under the excitation at 355 nm dye laser (Spectron SL 4000B/G, Spectron Laser Systems, Warwickshire, UK) at room temperature. Powder or film XRD patterns were obtained on a Philips (The Netherlands) X'Pert MPD/PW3040 X-ray diffractometer with Cu–K<sub>α</sub> irradiation.

## RESULTS AND DISCUSSION

### X-ray diffraction

Figure 1 shows the powder XRD diffractograms of PMMA/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> composites with various molar ratios, together with that of the pure complex. Several features should be noticed: (1) all the composites, including the sample with C=O/Eu molar ratio of 200, give sharp diffraction peaks, indicating the crystalline structure; (2) the composites with different compositions show different features. The samples, with C=O/Eu molar ratios < 50, give similar XRD patterns to that of the pure complex, whereas some new peaks appear in the XRD patterns of the samples with higher molar ratios, indicating different crystalline structures were formed; (3) although the XRD patterns of the samples with lower molar ratios are similar to that of the pure complex, the positions of the corresponding XRD peaks shift slightly. These results suggest that the composites with different molar ratios



**Figure 2** X-ray diffractograms of PVP/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> physical mixture powders (a) and composite thin films (b).

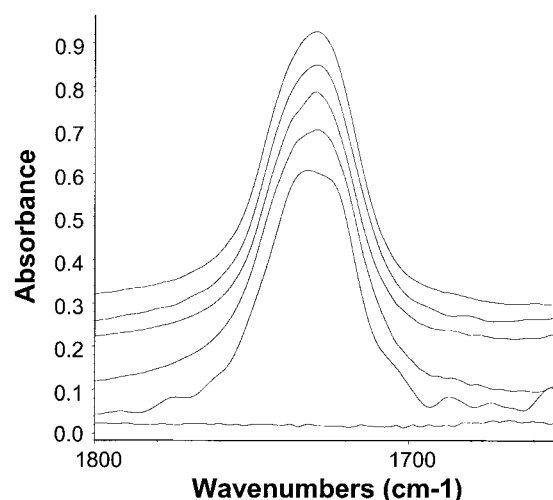
have different structures, attributed to the interaction between the host and the guest.

Figure 2 shows the powder XRD diffractograms of PVP/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> physical mixtures and the corresponding composite thin films. As can be seen from Figure 2(a), the physically mixed powders give the same XRD peaks as those of the pure complex. However, no XRD peak can be found in the diffractograms of the composite films, even for the sample with a C=O/Eu molar ratio of 5, as shown in Figure 2(b). These results indicate that amorphous composites are formed where the europium complex molecules thoroughly dispersed into the host, perhaps because of the stronger supramolecular interactions between the components. Another noteworthy feature is the variation of the diffraction halos of the composites. PVP gives two XRD halos at 2θ angles of 11.9 and 19.9°, respectively, as shown in Figure 2(b). The sample with the molar ratio of 500 gives a similar XRD pattern to that of pure PVP. With decreasing molar ratios, the XRD pattern changes. Two XRD halos, appearing in the diffractograms of the samples with the molar ratios of 200 and 100, shift to lower and higher 2θ regions with respect to the corresponding ones in the pattern of the pure PVP, respectively. The first XRD halo disappears gradually with further decreases in molar ratio. These results indicate structural change with the compositions of the systems.

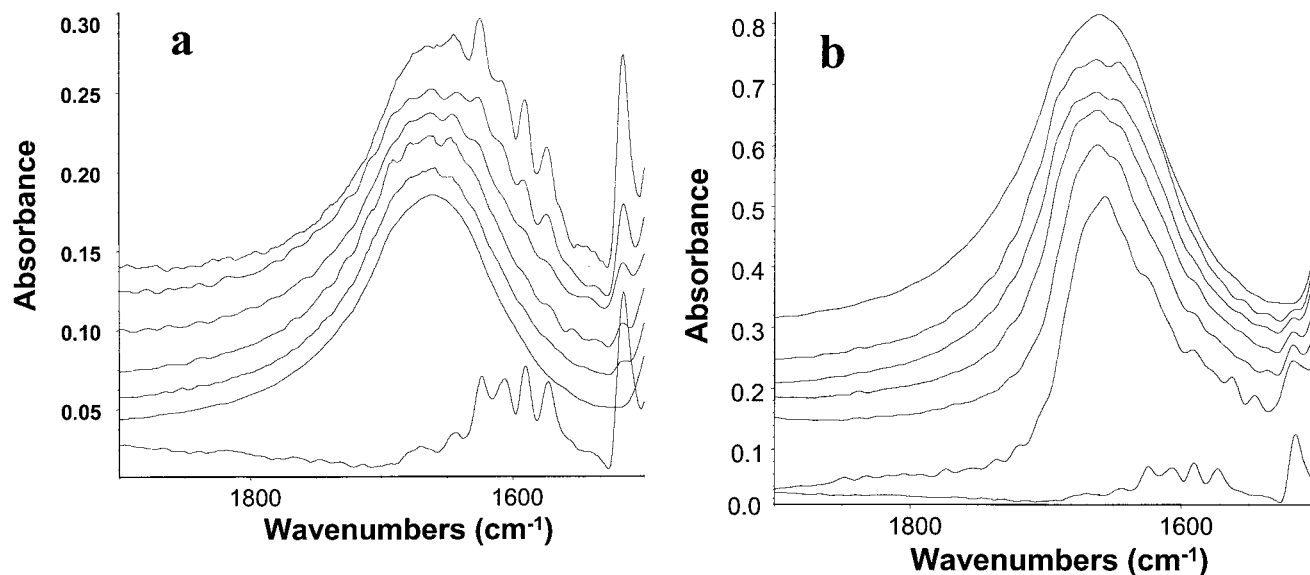
#### FTIR spectra

The composites of PMMA/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and PVP/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> were investigated by using FTIR spectra, as shown in Figures 3–5. As can be seen from Figure 3, no absorption can be observed in the 1800–1600 cm<sup>-1</sup> region for the complex, and one peak

appears at 1729 cm<sup>-1</sup> in the spectrum of pure PMMA that corresponds to C=O stretching vibration. The C=O stretching band also appears at 1729 cm<sup>-1</sup>, for the composite system with the C=O/Eu molar ratio of 125. However, two peaks can be observed at 1729 and 1740; 1728 and 1738; and 1724 and 1735 cm<sup>-1</sup> in the FTIR spectra of the composites with the molar ratios of 40, 20, and 10, respectively, and the relative intensities change with decreasing molar ratios. The shift of the C=O stretching band to a lower frequency can be attributed to H-bonding or coordination to metal ions. In general, the formation of H-bonds causes a more apparent shift of about 20–30 cm<sup>-1</sup>,<sup>21,22</sup> whereas the coordination effect results in a several



**Figure 3** FTIR spectra of PMMA and PMMA/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> composite systems with molar ratios of C=O/Eu of 125, 40, 20, and 10 and pure complex (from top to bottom).



**Figure 4** (a) FTIR spectra of PVP/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> physical mixtures with C=O/Eu of 100, 50, 20, 10, and 5, pure PVP, and pure complex (from top to bottom); (b) FTIR spectra of PVP composite systems with C=O/Eu of 100, 50, 20, 10, and 5 and pure complex (from top to bottom).

cm<sup>-1</sup> shift only.<sup>23,24</sup> Based on the experimental and the literature results we can conclude that some C=O groups coordinate to Eu<sup>3+</sup> ions in the composite systems.

Figure 4 shows the FTIR spectra of the physical mixtures and composites of PVP/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> with various molar ratios in the 1500–1900 cm<sup>-1</sup> region. For the physical mixtures, the curves can be regarded as overlap of the spectrum of pure PVP and that of pure complex with different molar ratios, respectively, as shown in Figure 4(a). The IR spectra of the composites show new features compared to those of the physical mixtures. First, the vibration band of C=O, appearing at about 1660 cm<sup>-1</sup> in the spectrum of pure PVP, shifts to a lower wavenumber in the spectra of the composites, and the width of the band decreases with decreasing molar ratios. This indicates the coordination of C=O groups to Eu<sup>3+</sup> ions, similar to that of the C=O group in PVP to Co<sup>2+</sup>, Ni<sup>2+</sup>,<sup>25</sup> or Ag<sup>+</sup> ions,<sup>26,27</sup> and the dissociation of the aggregated PVP chains.<sup>28</sup> Second, the relative intensities of the vibration bands of the complex in the spectra of the composites become much weaker than those of the corresponding mixtures, as can be seen from Figure 4(a) and (b). Third, the vibration band at 1516 cm<sup>-1</sup>, of the pure complex, shifts to 1519 cm<sup>-1</sup> when the composites are formed. These results indicate stronger interaction between the complex and PVP.

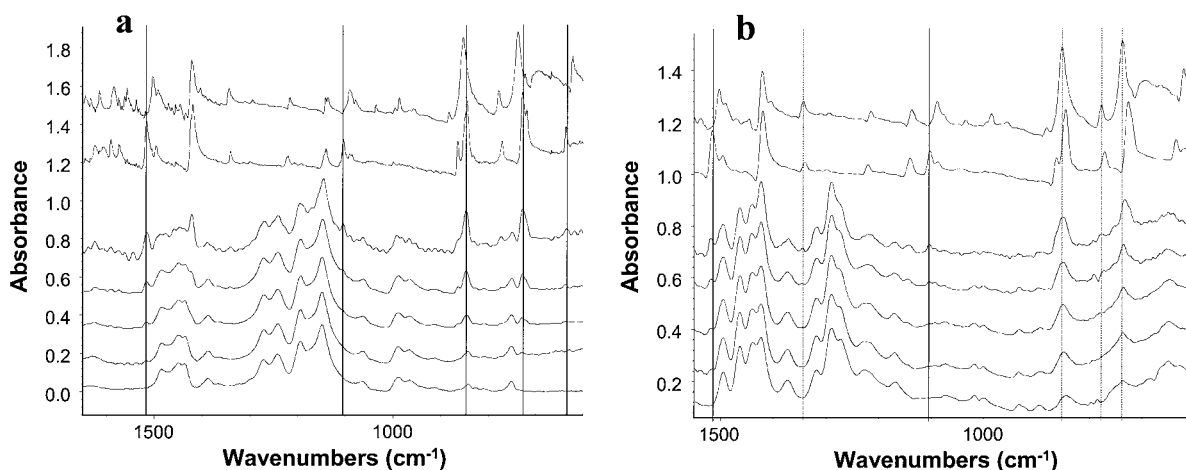
Figure 5 shows the FTIR spectra of the two series of composites in the lower-wavenumber regions. As pointed out by the lines in Figure 5(a), the absorption peaks at 1516, 1104, 864, 728, and 637 cm<sup>-1</sup>, in the spectrum of the pure complex, also appear in the spectra of

the composites of PMMA/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>. However, not only do the absorption peaks at 1516 and 1104 cm<sup>-1</sup>, in the spectrum of the pure complex, appear in the spectra of the composites of PVP/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>, as marked by the base lines, but also the peaks at 1344, 852, 778, and 738 cm<sup>-1</sup> in the spectrum of phen appear in the spectra of the composites, as inferred by the dashed lines, meaning dissociation of some complex molecules. In other words, the coordinate bonds of phen to Eu<sup>3+</sup> ions are kept in the PMMA/complex composites, whereas some coordination bonds of phen to Eu<sup>3+</sup> are broken in the PVP/complex composites as a result of the stronger coordinate interaction between C=O groups and Eu<sup>3+</sup> ions. This results in different composite structures, as shown by the XRD results, and leads to different luminescent properties, as shown below.

### Photoluminescent behavior

Figure 6 shows the emission spectra of the composites and the pure complex under laser excitation of 325 nm at room temperature. Five emission bands appear in these spectra, corresponding to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0,1,2,3,4</sub> transitions, respectively.

It may be observed from Figure 6(a), four emission peaks appear at 611.7, 614.9, 617.9, and 621.9 nm in the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition band and two emission peaks appear at 590.9 and 595.3 nm in the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> transition band for the pure complex. The PMMA/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> composites, with different molar ratios of C=O/Eu, show different luminescent characteristics. The profiles of the emission bands are similar to one another for the samples with molar ratios of



**Figure 5** (a) FTIR spectra of phen,  $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$ , PMMA/complex with  $\text{C}=\text{O}/\text{Eu}$  of 10, 20, 40, and 125 and PMMA (from top to bottom); (b) FTIR spectra of phen,  $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$ , PVP/complex with  $\text{C}=\text{O}/\text{Eu}$  of 10, 20, 50, and 100 and PVP (from top to bottom).

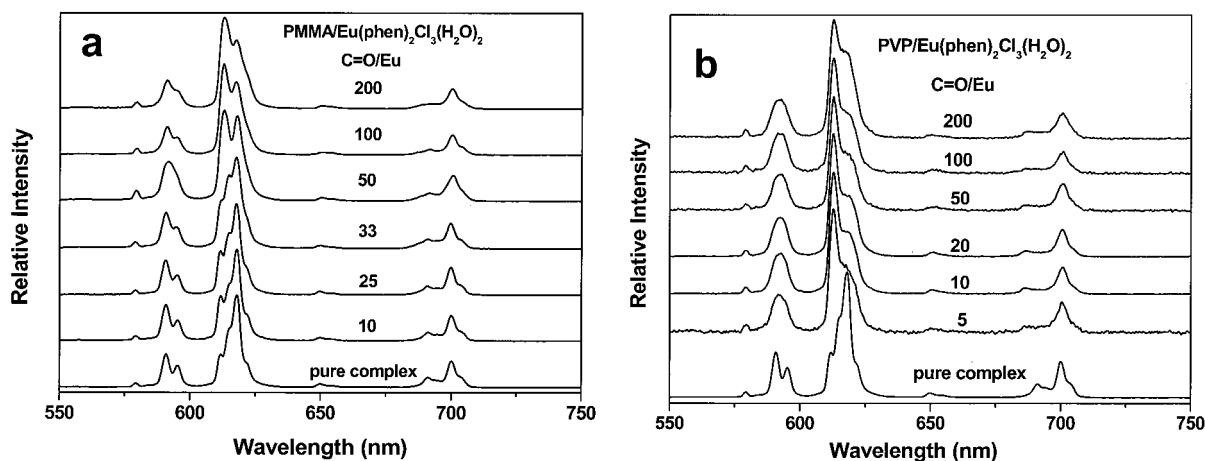
$\text{C}=\text{O}/\text{Eu}$  of 33, 25, and 10, and similar to those of the pure complex. However, the relative intensities of the emission peaks in the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition band change with the molar ratios. All three samples with molar ratios of  $\text{C}=\text{O}/\text{Eu}$  of 200, 100, and 50 show two emission peaks, centering at 612.8 and 617.5–617.9 nm in the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition bands, respectively, which clearly differ from those of the samples with the lower molar ratios. In addition, the relative intensities of the two peaks change with the molar ratios.

In addition, the emission spectra present broadened bands from the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of  $\text{Eu}(\text{III})$  ion attributed to the inhomogeneous broadening of the transitions, suggesting that these systems show the existence of more than one kind of  $\text{Eu}(\text{III})$  sites.

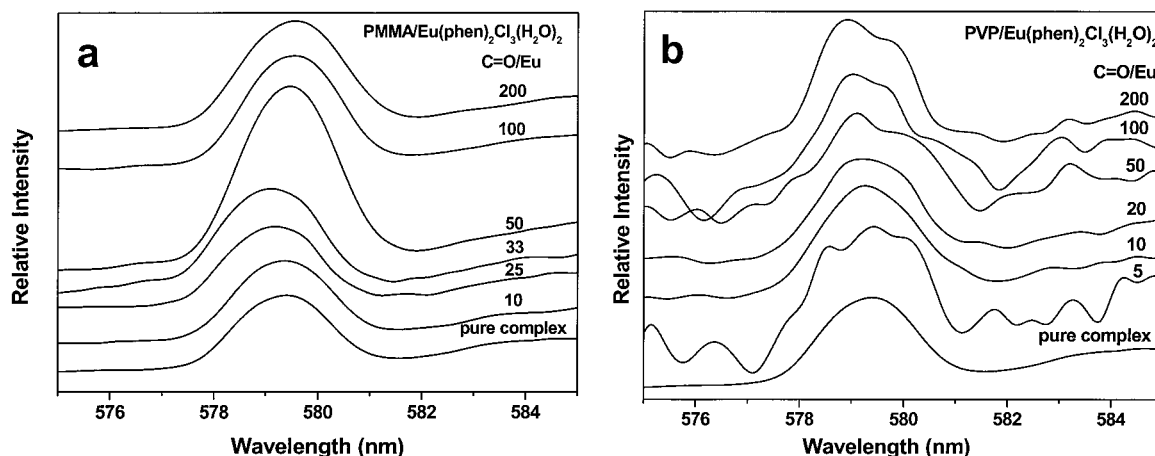
It is well known that the so-called “hypersensitive”  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition is very sensitive to the first coordination sphere around  $\text{Eu}^{3+}$  ions. It can be concluded, from these results, that  $\text{Eu}^{3+}$  ions occupy dif-

ferent microenvironments around them in these composites.

Jin et al.<sup>14</sup> studied the doped systems of europium complex with phen in silica. They found that two kinds of point group symmetries (i.e., hydrated  $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$  and anhydrous  $\text{Eu}(\text{phen})_2\text{Cl}_3$ ) show distinct luminescent features: the hydrated one gives an intense  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  peak at 620 nm, and the anhydrous one gives an intense peak at 615 nm and a weak one at 622 nm. As can be seen from Figure 6(a), for the composite systems of  $\text{Eu}/\text{phen}$  complex in PMMA with lower  $\text{C}=\text{O}/\text{Eu}$  molar ratios ( $<50$ ) and the pure complex, one intense peak at 617.7–617.8 and three weaker peaks at 611.7–611.8, 614.8–614.9, and 622 nm appear, respectively, which means that  $\text{Eu}(\text{phen})_2\text{Cl}_3(\text{H}_2\text{O})_2$  is the main component of the formed composites. For the composite systems, with higher molar ratios of  $\text{C}=\text{O}/\text{Eu}$  ( $\geq 50$ ), two peaks can be observed at 612 and 618 nm in the emission spectra,



**Figure 6** Emission spectra of  $\text{Eu}(\text{III})$  in the composite systems ( $\lambda_{\text{ex}}$ : 325 nm).



**Figure 7**  ${}^5D_0 \rightarrow {}^7F_0$  transition bands of Eu(III) in the composite systems: (a) PMMA/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> and (b) PVP/Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> ( $\lambda_{\text{ex}}$ : 355 nm).

and the relative intensity of  $I_{618}/I_{612}$  increases with decreasing molar ratio of C=O/Eu from 200 to 50. These two peaks should correspond to different species, anhydrous and hydrated, according to their positions and studies reported in the literature.<sup>14</sup> The variation of the relative intensity of these two peaks indicates the change of the relative weightings of these species.

The luminescent decay curves of the  ${}^5D_0$  level of Eu<sup>3+</sup> ions in these systems were investigated, and can be fitted by bi- or triexponential functions, indicating that more than one species must exist in these samples. It is possible that anhydrous, monohydrated, and hydrated complexes exist in the samples whose relative amounts changed with the molar ratios, the first two species coming from the hydrated complex by replacing either two or one coordinate water molecule with the C=O group of PMMA. The interactions between C=O groups and lanthanide ions are predominant in the solid doped systems, for example, in the composite systems of Nd<sup>3+</sup>/PMMA,<sup>29</sup> EuL<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> in polyimide (L: pyridine carboxylic acid),<sup>10</sup> and in the ureasil containing Eu(CF<sub>3</sub>SO<sub>3</sub>)<sub>3</sub>.<sup>30</sup>

The  ${}^5D_0 \rightarrow {}^7F_0$  transition can supply much information about the coordination sphere around Eu<sup>3+</sup> ions because of two factors. First, both the ground ( ${}^7F_0$ ) and excited ( ${}^5D_0$ ) states are nondegenerate. The transition between these two levels gives one peak for one species. Second, the energy of the  ${}^5D_0 \rightarrow {}^7F_0$  or  ${}^7F_0 \rightarrow {}^5D_0$  transitions is related to the first coordination sphere around Eu<sup>3+</sup> ions, according to the nephelauxetic effect.<sup>30–33</sup> Figure 7 shows the enlarged emission spectra of the composites. The  ${}^5D_0 \rightarrow {}^7F_0$  transition band shifts with the molar ratios, indicating the change of the first coordination spheres. Apparent variation can be found between the emission bands of the samples with molar ratios of 50 and 33, indicating that the microenvironments around Eu<sup>3+</sup> ions clearly

changed. This is consistent with  ${}^5D_0 \rightarrow {}^7F_2$  emission bands shown in Figure 6(a) and the XRD patterns shown in Figure 1.

The doped systems in PVP show very different emission behaviors from those in PMMA, as shown in Figure 6(b) and Figure 7(b). Only one  ${}^5D_0 \rightarrow {}^7F_1$  transition peak appears, centering at about 592 nm, and one  ${}^5D_0 \rightarrow {}^7F_2$  transition peak and a shoulder appear at 612.6 and about 619 nm, respectively, in the emission spectra of the composites. These spectra are similar to one another, regardless of the molar ratios, but differ greatly from that of the pure complex, suggesting that the Eu<sup>3+</sup> ions occupy similar microenvironments in the doped systems, which are different from that in Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>. It can be seen from Figure 7(b) that the  ${}^5D_0 \rightarrow {}^7F_0$  emission bands shift to the blue region with increasing molar ratios of C=O/Eu, and more peaks appear for the samples with higher molar ratios. These results mean that the first coordination sphere around Eu<sup>3+</sup> ions changes with composition according to the nephelauxetic effect and more than one site symmetry exists in these systems. The broadened emission bands also suggest that these systems have an amorphous phase, as shown by XRD patterns, and have more than one kind of Eu sites.

## CONCLUSIONS

Europium complex Eu(phen)<sub>2</sub>Cl<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub> can be doped into polymer matrices to form composite systems because of the interactions between the components. The composites with PMMA and PVP have different structures, resulting from different interactions between the guest and the hosts, leading to different luminescent characteristics. The nature of the polymers has a substantial effect on the structure and properties of the formed hybrids. The luminescent property can be

tuned by choosing an appropriate matrix together with changing the compositions.

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