Eu^{3+} Ion as Luminescent Probe: Eu^{3+} Sites in Eu(PBI)$_3$ · phen and [Eu(PBI)$_3$ · C$_2$H$_5$OH · H$_2$O] · H$_2$O Complexes*

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Abstract   The luminescence of Eu^{3+} in Eu(PBI)$_3$phen and [Eu(PBI)$_3$ · C$_2$H$_5$OH · H$_2$O] · H$_2$O (PBI: 3-phenyl-4-benzoyl isoxazate, phen: 1,10-phenanthroline) is reported. It is shown that the Eu^{3+} ions in Eu(PBI)$_3$phen are positioned on the two sites and the various lines are assigned to each site. However, Eu^{3+} ions occupy a single site in [Eu(PBI)$_3$ · C$_2$H$_5$OH · H$_2$O] · H$_2$O and the crystal field splittings of the $^7F_{1\sim4}$ levels are much larger than those in Eu(PBI)$_3$phen.

Keywords: Luminescence spectra, Europium, Complex

The unique spectroscopic properties of the trivalent lanthanide ions make them ideal candidates as probes in various fields of science[1]. In particular, the Eu^{3+} ion displays intense luminescence from a long-lived excited state $^5D_0$ so that high-resolution, laser-excited excitation and emission spectra of Eu^{3+} complexes yield abundant structural and chemical information. In the previous work, we have analyzed the number and local symmetry of the metal ion sites in several β-diketonate and carboxylate complexes[2~5] and shown that the sensitivity of this luminescene method is able to resolve structural differences overseen by X-ray diffraction analysis. The Eu^{3+} probe is especially sensitive to small differences in the metal-ion environments. The crystal structures of Eu(PBI)$_3$phen and [Eu(PBI)$_3$ · C$_2$H$_5$OH · H$_2$O] · H$_2$O were determined[6,7]. In this work we present a luminescence study of the two complexes to show how the photophysical properties of the complexes can contribute to a deeper understanding of the detailed structure of the two complexes.

1 Experimental

Eu(PBI)$_3$phen and [Eu(PBI)$_3$ · C$_2$H$_5$OH · H$_2$O] · H$_2$O were synthesized by reference to [6,7]. Excitation and luminescence spectra were observed at 77 K on finely powdered microcrystalline samples.

The spectrometer and experimental techniques have been previously described[2,4].

2 Results and Discussion

The survey luminescence spectrum of $Eu(PBI)_3phen$ complex obtained with $\lambda_{exc} =$ 337. 1 nm contains transitions originating almost exclusively from the $^5D_0$ level, along with vibronic transitions as shown in Fig. 1. Ofelt[8] has shown that for the configuration f^n with even n electric dipole transitions between a $J = 0$ level and odd-J level are not strongly induced by the crystal field. Thus the transitions $^5D_0 \rightarrow ^7F_1$, $^7F_3$ and $^7F_5$ are expected to be weaker than the transitions $^5D_0 \rightarrow ^7F_2$, $^7F_4$ and $^7F_6$. These expectations are in agreement with our experimental observations in which transitions observed to ^7F_J levels with $J = 0 \sim 4$, with $^5D_0 \rightarrow ^7F_2$ the most instense. The number of components of $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions reveals the presence of more than one different metal ion environments. The weak and forbidden transition $^5D_0 \rightarrow ^7F_0$ is composed of a band with a shoulder centred at 17230 cm^{-1}, indicating probably the presence of two Eu^{3+} sites. A more sensitive way of studying this transition is to record its excitation spectrum of the intense hypersensitive $^5D_0 \rightarrow ^7F_2$ transition emission. At 77 K two components of $^7F_0 \rightarrow ^5D_0$ transition were observed at 580. 47 nm and 580. 32 nm as seen in Fig. 2. To confirm the above consideration, selective excitations of different Eu^{3+} sites to their specific $^5D_0$ levels were performed and gave rise to the luminescence spectra as shown in Fig. 3. These spectra are typical of low symmetry species, as indicated by the number of components of each $^5D_0 \rightarrow ^7F_J$ transition and by the relative intensity of $^5D_0 \rightarrow ^7F_J$ with $J = 0 \sim 4$ transitions (Fig. 1). Tables 1 and 2 summarize the results of the two Eu^{3+} sites in $Eu(PBI)_3phen$.

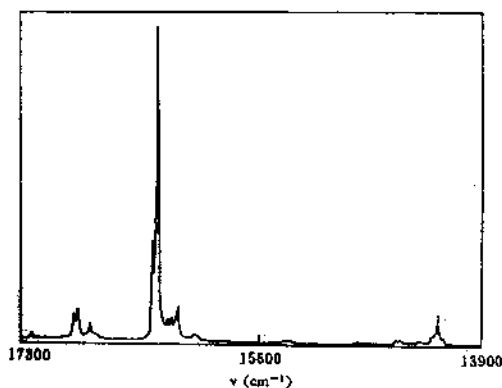**Fig. 1** Eu^{3+} emission spectrum of $^5D_0 \rightarrow ^7F_J (J = 0 \sim 4)$ transitions in $Eu(PBI)_3phen$ (77 K)
$\lambda_{ex} = 337. 1$ nm
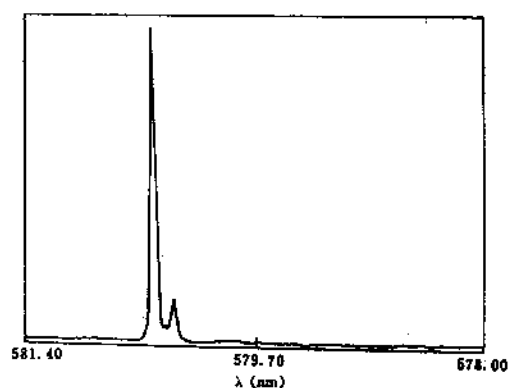
Fig. 2 Excitation spectrum of $^7F_0 \rightarrow ^5D_0$ transition of $Eu(PBI)_3 \cdot phen$ (77 K)
$\lambda_{em} = 592. 07$ nm

The complex $[Eu(PBI)_3 \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$ displays rather intense Eu^{3+} luminescence obtained by non-selective excitation at 337. 1 nm and the transitions originating from the $^5D_0$ level possess a maximum number of $2J + 1$ components. This may be explained by the Eu^{3+} site having a low local symmetry, which leads to a relatively intense $^5D_0 \rightarrow ^7F_0$ transition and a very strong hypersensitive $^5D_0 \rightarrow ^7F_2$ transition.

In order to determine the number of chemically different metal ion environments

in $[Eu(PBI)_3 \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$, we have examined the excitation spectrum in the region of $^7F_0 \rightarrow ^5D_0$ transition. The excitation spectra of three single bands monitored at 588. 75 nm, 596. 48 nm and 616. 71 nm are presented in Fig. 4, which shows that the peak positions of different excitation spectra are almost the same centered at 579. 47 nm, 579. 39 nm and 579. 35 nm respectively. The Eu^{3+} ion emission bands in the region of $^5D_0 \rightarrow ^7F_J$ transitions from the complex for excitation with 579. 50 nm, 579. 30 nm and 337. 1 nm are very similar to each other. Fig. 5 gives $^5D_0 \rightarrow ^7F_2$ emission bands. $2J+1$ components for $^5D_0 \rightarrow ^7F_1$, and $^7F_2$ transitions were observed. The above observations indicate the presence of a single distinct emitting centre of Eu^{3+} that resides in a low-symmetry environment[9].
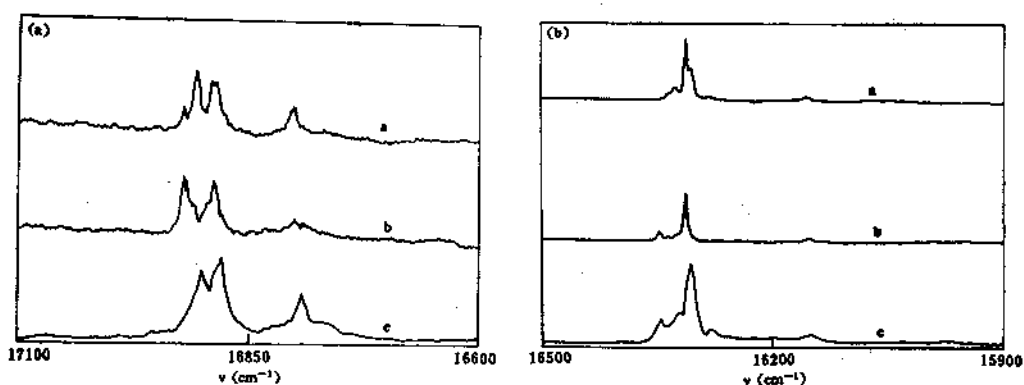

Fig. 3 $^5D_0 \rightarrow ^7F_1$, $^7F_2$ transition emission spectra of Eu(PBI)$_3$phen (77 K)

a, $\lambda_{ex}=580. 47$ nm; b. $\lambda_{ex}=580. 32$ nm, c. $\lambda_{ex}=337. 1$ nm

Table 1   Emission data of Eu^{3+} site I in Eu(PBI)$_3$phen (77 K, $E_{ex}=17227$ cm^{-1})

λ (nm)	E(cm^{-1})	ΔE(cm^{-1})	Raman (cm^{-1})	Assignment	λ (nm)	E(cm^{-1})	ΔE(cm^{-1})	Raman (cm^{-1})	Assignment
580. 47	17227	0		$^5D_0 \rightarrow ^7F_0$	612. 71	16321	906	910	Vibr * *
590. 98	16921	306		site I *	613. 08	16311	916		$^5D_0 \rightarrow ^7F_2$
591. 51	16906	321		$^5D_0 \rightarrow ^7F_1$	613. 35	16304	923		$^5D_0 \rightarrow ^7F_2$
592. 21	16886	341		$^5D_0 \rightarrow ^7F_1$	614. 21	16281	946		$^5D_0 \rightarrow ^7F_2$
595. 27	16799	428		$^5D_0 \rightarrow ^7F_1$	617. 44	16196	1031	1029	Vibr * *
612. 03	16339	888		site I *	619. 20	16150	1077		$^5D_0 \rightarrow ^7F_2$
612. 48	16327	900		$^5D_0 \rightarrow ^7F_2$					

* site I : Eu^{3+} site I emission; * * Vibr, Vibronic transition

Table 2   Emission data of Eu^{3+} site II in Eu(PBI)$_3$phen (77K, $E_{ex}=17232$ cm^{-1})

λ (nm)	E(cm^{-1})	ΔE(cm^{-1})	Raman (cm^{-1})	Assignment	λ (nm)	E(cm^{-1})	ΔE(cm^{-1})	Raman (cm^{-1})	Assignment
580. 32	17232	0		$^5D_0 \rightarrow ^7F_0$	612. 59	16324	908		$^5D_0 \rightarrow ^7F_2$
591. 05	16919	313		$^5D_0 \rightarrow ^7F_1$	612. 67	16322	910	910	Vibr * *
591. 37	16910	322		site I *	613. 05	16312	920		$^5D_0 \rightarrow ^7F_2$
592. 10	16889	343		$^5D_0 \rightarrow ^7F_1$	616. 18	16229	1003	1003	Vibr * *
595. 24	16800	432		$^5D_0 \rightarrow ^7F_1$	617. 21	16202	1030	1029	Vibr * *
611. 73	16347	885		$^5D_0 \rightarrow ^7F_2$	619. 12	16152	1080		$^5D_0 \rightarrow ^7F_2$
612. 11	16337	895		$^5D_0 \rightarrow ^7F_2$					

* site I : emission of Eu^{3+} site I ; * * * Vibr; Vibronic transition

The central Eu^{3+} ion in $Eu(PBI)_3phen$ is bonded to six oxygen atoms from three PBI groups and to two nitrogen atoms from phen[6]. However, the Eu^{3+} ion in $[Eu(PBI)_3 \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$ is not only bonded to the three PBI groups but also to two oxygen atoms from C_2H_5OH and H_2O molecules[7]. The crystal field splittings of $^7F_1$ (243 cm^{-1}) and $^7F_2$(330 cm^{-1}) observed in $[Eu(PBI)_3 \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$ are larger than those of $^7F_1$(107 cm^{-1} for site I, and 119 cm^{-1} for site II) and of $^7F_2$(177 cm^{-1} for site I, and 195 cm^{-1} for site II) in $Eu(PBI)_3phen$, since the intrinsic ligand non-equivalence, i. e. , environment as well as metal-ligand bond distance, logically provides a more distortion of bicapped trigonal prism for $[Eu(PBI)_3 \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$ relative to a square antiprism for $Eu(PBI)_3$ phen[6,7], and there exists larger crystal field effect in the former.
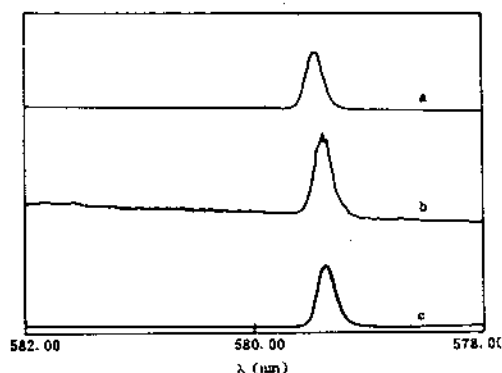

Fig. 4   Excitation spectrum of $^7F_0 \rightarrow ^5D_0$ transition of $[Eu(PBI)_3 \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$ (77 K)
a. $\lambda_{em} = 588.75$ nm, b. $\lambda_{em} = 596.48$ nm, c. $\lambda_{em} = 616.71$ nm
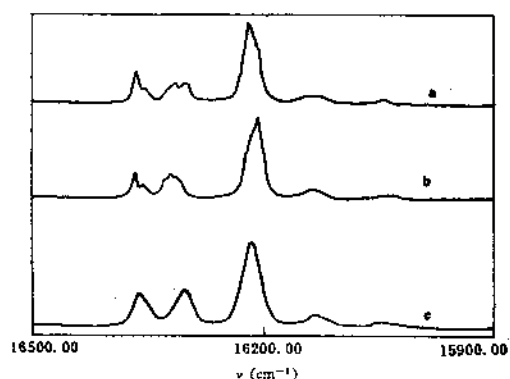
Fig. 5 $^5F_0 \rightarrow ^7F_2$ transition emission spectra of $[Eu(PBI)_3 \cdot C_2H_5OH \cdot H_2O] \cdot H_2O$ (77 K)
a. $\lambda_{exc} = 579.50$ nm, b. $\lambda_{exc} = 579.30$ nm, c. $\lambda_{exc} = 337.1$ nm

The two Eu^{3+} sites occur in the complex $Eu(PBI)_3phen$. The interpretation of the emission spectra is not straight forward since Eu (PBI)$_3$phen is a mononuclear molecule[6]. Nevertheless, a careful analysis of thermal parameters of non-hydrogen atoms in the complex reflects disordered oscillation of the phenyl group in PBI ligand at room temperature and provides the two slightly different environments at 77K, resulting in the two sites.

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