Talanta 105 (2013) 262–266

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Factors influencing the luminescence intensity of europium(III) complexes prepared via synergistic extraction

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ARTICLE INFO

Article history:
Received 7 September 2012
Received in revised form
27 November 2012
Accepted 28 November 2012
Available online 5 December 2012

Keywords:
Europium(III)
Luminescence
Synergistic extraction
Effect of beta-diketone
Phosphor
Excitation spectra

ABSTRACT

The excitation and luminescence spectra of Eu(III) extracted with pivaloyltrifluoroacetone (HA) and/or 2,2′-bipyridyl (B) into $CHCl_3$ were measured. The data were compared to those obtained in an HA/$CHCl_3$ solution into which EuA_3 or EuA_3B was dissolved. The results are summarized as follows: (1) The degree of HA influence on the luminescence intensity differs in the two systems; in the HA/$CHCl_3$-dissolved EuA_3, the intensity abruptly decreases when the HA concentration exceeds approximately 10^{-2} M, depending on EuA_3 concentration. The data measuring the size of the dominant species in the $CHCl_3$ containing EuA_3 and HA via DLS indicate that the abrupt concentration quenching is due to the formation of aggregate consisting of EuA_3 and HA. However, in the solvent-extracted sample, the luminescence intensity is not influenced by the HA concentration, even at 0.1 M HA. This difference can be explained by the difference in water content. (2) In the synergistic extraction of Eu(III) with HA and B, the intensity is not substantially influenced by HA. The effect of HA on the luminescence intensity in the B/$CHCl_3$-dissolved EuA_3 is larger than that obtained via solvent extraction. These results suggest that synergistic extraction could be an efficient method for preparing the phosphor in solution and that, when using luminescence intensity to determine Eu(III) concentration, one should be careful for the other materials, such as HA, that are involved in the solution and serve as reference materials.

1. Introduction

There is a comprehensive monograph on the chelates of trivalent lanthanides (Ln(III)) with β-diketones (HA) [1] in which it is described that Ln(III) chelates, including their adducts with Lewis bases, have previously been extensively used to separate Lns(III) via solvent extraction processes, however, the research interest has been transferred to the application for electroluminescent materials in organic light emitting diodes. The range of these applications has increased [2]. Currently, the synthesis of many new β-diketonates has been achieved [3–5], and other fundamental research [6–11] has been conducted to improve their luminescent intensity. Although the chelates sometimes exhibit quenching due to the interaction between tris(β-diketonato)Ln(III) and several materials, even the quenching can also be applied to detect the materials selectively [12,13].

Among many Ln(III) complexes involved β-diketones, several complexes formed from tris(β-diketonato)Ln(III)(LnA_3) and a strong Lewis base (B) exhibit very strong luminescence, and their intensity is often much stronger than that of the binary complex, LnA_3, especially when the Ln(III) is Eu(III) and B is a strong Lewis base such as 1,10-phenanthroline (phen) [4] or 2,2′-bipyridyl (bpy) [4,11]. The extractability of Lns(III) with HA and B is known to be markedly improved over that with HA alone due to the formation of a neutral ternary complex consisting of Ln(III), HA and B, such as LnA_3B [14–16]. Given its strong luminescence and efficient extractability, the combination of 2-thenoyltrifluoroacetone (Htta), the most popular β-diketone, and phen was used to detect a trace quantity of Eu(III) (10^{-19} g) [17]. The synergistic extraction of Eu(III) using HA and B can be an effective method for preparing a phosphor in solution because the extraction rapidly separates the materials and forms a complex; the complex can be prepared simply by shaking the two phases for a few minutes. In the solutions, very fine particles and uniform condition should be generated.

To establish a method for preparing phosphor via solvent extraction, the luminescence of the complex prepared by extraction should be similar to that of the synthesized complex. However, the luminescence intensity of EuA_3B obtained via solvent extraction—Eu(III) was extracted with HA and Schiff-base complexed with Zn(II) [18,19]—was lower than that obtained by dissolving the prepared complex. To extract Eu(III), an excess quantity of β-diketone is required compared to the Eu(III) concentration; $Eu^{3+} + 3HA_{(o)} \rightleftharpoons EuA_{3(o)} + 3H^{+}$ in which the term containing the “o” represents the organic phase. No additional β-diketone is in the solution-dissolved prepared EuA_3. Thus, the difference in luminescence intensity could be caused by the excess HA. Therefore, the aim of the present work is

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http://dx.doi.org/10.1016/j.talanta.2012.11.075

to compare the effect of coexisting materials such as β-diketone on the luminescence behavior of EuA_3 and the adduct of EuA_3 with B obtained by solvent extraction to that of the prepared complexes. The β-diketone, Hpta (pivaloyltrifluoroacetone, 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione, which is hereafter represented by HA) was chosen because we have already reported that the luminescence intensity of EuA_3 can be maintained for a longer period than that of $Eu(tta)_3$ [20]. The bpy (hereafter represented by B) was chosen as a simple, bidentate, and strong Lewis base. Since B forms a very stable complex with EuA_3 ($EuA_{3(o)}+B_{(o)} \rightleftharpoons EuA_3B_{(o)}$ and the stability constant β is given by $\log \beta = 5.76 \pm 0.06$ [15]), the EuA_3B complex was prepared by mixing the EuA_3 with excess B [14].

2. Experimental

2.1. Reagents

All reagents were of analytical grade. The chloroform was washed three times with deionized water to remove the C_2H_5OH stabilizer prior to use. The 2, 2′-bipyridyl was obtained from Kanto Chemical Co. The pivaloyltrifluoroacetone (98%) was purchased from Sigma-Aldrich, Germany. The europium oxide (Eu_2O_3, 99.98%) was obtained from Mitsuwa Chemicals. All reagents, except for $CHCl_3$, were used without further purification.

The chelate, EuA_3, was characterized using elemental analysis; $C_{24}H_{36}F_9EuO_9$ ($Eu(pta)_33H_2O$): Anal. Calcd. C 36.42, H 4.58; Found: C 37.00, H 4.35. The Eu(III) aqueous solution was prepared by dissolving the weighed Eu_2O_3 in a slight excess of perchloric acid. The total ionic concentration was adjusted to 0.10 M ($1\ M = 1\ mol\ dm^{-3}$) with sodium perchlorate.

2.2. Procedures

Most procedures were performed at room temperature (25 ± 2) °C. Europium(III) was extracted into $CHCl_3$ with HA and/or B in a similar manner to that described elsewhere [14,15]. The Eu(III) was back-extracted into 0.1 M perchloric acid, and the Eu(III) remaining in the aqueous phase was diluted up to 10 times with 0.1 M $HClO_4$. The concentrations were determined via ICP/OES (Seiko II SPS 3500). The hydrogen ion concentration was measured potentiometrically (Corning 445 pH meter) using 1.00×10^{-2} M perchloric acid and 0.09 M sodium perchlorate as the standard of $pC_H = 2.00$ ($pC_H = -\log[H^+]$). The excitation and luminescence spectra were recorded on a Hitachi F-4500 fluorometer. The size distributions of the Eu(III) complexes in the $CHCl_3$ solutions were measured using a dynamic light scattering technique(DLS) with a Zetasizer Nano ZS (Malvern Instruments, England) at 20.0 °C.

3. Results and discussion

The luminescence intensity of either EuA_3 or EuA_3B can be influenced by the HA and/or B concentrations, and also the Eu(III) concentration [10,11]. The intensity may also be influenced by the type of the β-diketone such as the keto-enol form. Furthermore, the intensity may be influenced by other environmental conditions and substances surrounding the complexes such as water [11,21,22]. First the manner in which the luminescence intensity of EuA_3 is influenced by HA was examined; the excitation and luminescence spectra of the $CHCl_3$-dissolved EuA_3 in the presence of HA were measured, and compared to that obtained from solvent extraction of Eu(III) with HA. Second similar experiments were performed in the presence of B to compare the effect of HA on the intensity of EuA_3 in $CHCl_3$-dissolved EuA_3 in the presence of HA and B to that obtained by solvent extraction.

3.1. Effects of HA on the luminescence of the Eu(III) chelate

3.1.1. Luminescence intensity in $CHCl_3$ solution-dissolved EuA_3

Fig. 1(a) exhibits a typical luminescence intensity change at the strongest peak wavelength ($^5D_0 \rightarrow {}^7F_2$) in the HA/$CHCl_3$ solution containing 8.0×10^{-5} M EuA_3 at $\lambda_{ex} = 370$ nm as a function of the HA concentration. The intensity increases slightly as the HA concentration increases to approximately 10^{-2} M HA and then abruptly decreases as the HA concentration increases further. These results may be attributable to the interaction between EuA_3 and HA. When the HA in solution is engaged in the intensity change, the effect with HA should appear in the excitation spectra. The excitation spectra at an emission wavelength of 612 nm for each point in Fig. 1(a) are provided in Fig. 1(b). The band near 320 nm, which is attributable to A^-, not only shifts to a longer wavelength but also decreases in intensity, and a new band appears at approximately 350 nm as $[HA]_o$ increases. The variation in the spectra suggests that the HA in solution is related to the luminescence behavior of EuA_3. If the decrease in the luminescence intensity at higher HA concentrations is caused by other factors, such as saturated solubility, the change in intensity should also be observed with changes in the EuA_3 concentration.

Fig. 2 shows the luminescence intensity as a function of the Eu(III) concentration at a constant HA concentration. The open circle indicates the intensity in the absence of additional HA, i.e., in the $CHCl_3$ solution-dissolved EuA_3. The intensity increases linearly with increasing Eu(III) concentration over the entire Eu(III) concentration range studied. The typical luminescence spectrum of EuA_3 exhibits five clear bands corresponding to $^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$, and $^7F_4$ transitions. The wavelengths corresponding to these transitions are 577–581, 585–600, 610–625, 640-655, and 680–710 nm, successively. The $^5D_0 \rightarrow {}^7F_2$ electric-dipole transition is

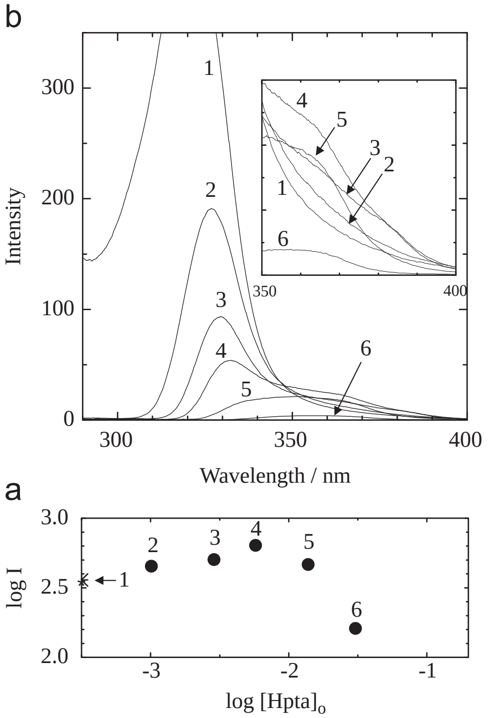

Fig. 1. (a) Effect of Hpta concentration on the luminescence intensity at the peak wavelength ($^5D_0 \rightarrow {}^7F_2$), irradiated at $\lambda_{ex} = 370$ nm and (b) the excitation spectra at $\lambda_{em} = 612$ nm in HA/$CHCl_3$ solution containing 8×10^{-5} M EuA_3. $[Hpta]_o$ = (1) 0, (2) 1×10^{-3}, (3) 3×10^{-3}, (4) 6×10^{-3}, (5) 1×10^{-2}, and (6) 3×10^{-2} M.

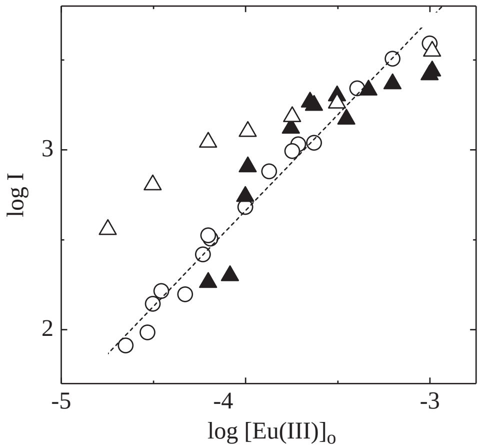

Fig. 2. Luminescence intensity at $\lambda_{ex}=370$ nm in $EuA_3/CHCl_3$ solution containing Hpta of 0 M (○), 5×10^{-3} M (Δ), and 0.02 M (▲) at the peak wavelength ($^5D_0\rightarrow{}^7F_2$) as a function of Eu(III) concentration.

hypersensitive, while $^5D_0\rightarrow{}^7F_1$ is a magnetic-dipole-allowed transition, and it is not significantly influenced by the local structure environment. The luminescence intensity ratio, $I(^5D_0\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_1)$, is reportedly an effective method for interpreting the symmetry of the Eu^{3+} site, i.e., a higher intensity ratio leads to a lower symmetry [1,7]. The intensity ratio ($I(^5D_0\rightarrow{}^7F_2)/I(^5D_0\rightarrow{}^7F_1)$) in Fig. 2 (open circle) does not change over the range suggesting that the Eu(III) adopts a similar form; the species will likely exist as a monomer but not as a dimer. The open and closed triangles in Fig. 2 indicate the correlation between the intensity and the EuA_3 concentration at 5×10^{-3} M HA and 0.02 M HA, respectively. The intensity at a particular $[EuA_3]_o$ appears to be independent of $[HA]_o$ at higher EuA_3 concentrations, however, at lower $[EuA_3]_o$ ($<10^{-4}$ M), the intensity at 5×10^{-3} M HA is higher than that in the absence of additional HA, while the intensity at 0.02 M HA is lower. These observations may be related to the two types of reactions that function differently—EuA_3 forming a complex with HA and the complex interacting with EuA_3 to form a dimer:

$$EuA_{3(o)}+HA_{(o)}\rightleftharpoons EuA_3HA_{(o)} \tag{1}$$

$$EuA_3HA_{(o)}+EuA_{3(o)}\rightleftharpoons (EuA_3)_2HA_{(o)} \tag{2}$$

The luminescence of the EuA_3HA complex should be stronger than that of EuA_3, but the luminescence of the dimer should fade more smoothly than that of the monomer. It is reported that the Ln(III) β-diketonates exhibit significant concentration quenching due to the dimerizations [22]. However, the change in slope is too abrupt to be explained by quenching with dimerization alone. Tris(β-diketonato)Eu(III)) can reportedly form an aggregate in $CHCl_3$ [23]. The smaller increase in the intensity of 0.02 M and 0.06 M HA solutions over the 2×10^{-4} M EuA_3 solution could most likely be explained by aggregation between EuA_3 and HA. To confirm the formation of the aggregate, the size of the dominant species in the $CHCl_3$ containing EuA_3 and/or 0.06 M HA was measured via DLS. The data indicated that in $CHCl_3$ containing 8×10^{-5} M EuA_3 and 0.06 M HA, the species distribute over a narrow size range (89 ± 15 nm). However, in a $CHCl_3$ solution at 8×10^{-5} M EuA_3 or 0.06 M HA alone, the size was not determined within the limits of detection (the data indicated a size <0.6 nm). These results led to the conclusion that due to the formation of EuA_3 aggregates involved HA molecules, the luminescence intensity abruptly decreased at higher HA concentrations as indicated in Fig. 1(a).

In the next step, the extraction of the Eu(III) with HA and its luminescence behavior was examined to compare the luminescence change with that in a $CHCl_3$ solution containing HA and EuA_3.

3.1.2. Extraction of Eu(III) with HA and the luminescence of the extracted species

The distribution ratio of Eu(III) (D, denoted as the total concentration ratio of Eu(III) in the organic and the aqueous phases) was measured as a function of pC_H between 0.10 M $NaClO_4$ and $CHCl_3$ containing a constant HA concentration [15]. The plot of $\log D$ vs. pC_H yielded a straight line with a slope of three. The extraction constant $\log K_{ex30}$ (see Eq. (5)) was reported to be −10.48. In the present work, the distribution ratio of Eu(III) was measured as a function of the HA concentration between pC_H 3.0 and 4.6. The constant obtained from the data analysis is consistent with the reported value. When EuA_3 is extracted together with the self-adduct in the extraction of Eu(III) with HA, the distribution ratio of Eu(III) can be represented as follows;

$$D=\frac{[EuA_3]_o+[EuA_3HA]_o}{[Eu^{3+}]} \tag{3}$$

By introducing the extraction constant for EuA_3, K_{ex30}, and the formation constant, β, represented by Eq. (6), Eq. (3) can be rewritten as follows:

$$D=K_{ex30}([HA]_o/[H^+])^3(1+\beta[HA]_o) \tag{4}$$

in which

$$K_{ex30}=[EuA_3]_o[H^+]^3[Eu^{3+}]^{-1}[HA]_o^{-3} \tag{5}$$

and

$$\beta=[EuA_3HA]_o[EuA_3]_o^{-1}[HA]_o^{-1} \tag{6}$$

When $\log D([H^+]/[HA]_o)^3$ was plotted as a function of log $[HA]_o$, no large change in the distribution ratio was observed, although the distribution ratio, D, was measured till higher $[HA]_o$ range (≤ 0.4 M). By analyzing the mass balance of the relevant species, the formation constant, β, 1.5 was obtained. Since the EuA_3HA complex is unstable, the complex formation does not appear to be the important factor in the decrease in luminescence intensity demonstrated in Fig. 1(a), or at least for the results obtained in solvent extraction. At the next step, the effect of HA on the intensity obtained through solvent extraction was compared to that in the $CHCl_3$ solution-dissolved EuA_3.

In the extraction of Eu(III) with HA, the quantity of Eu(III) extracted changes with small changes in the pC_H and HA concentration. Accordingly, controlling of the concentration of Eu(III) extracted is difficult. Hence, the intensity at a single concentration of Eu(III) extracted into the organic phase cannot be given as a function of HA concentration, as shown in Fig. 1. The luminescence intensity at 612 nm was normalized to the Eu(III) concentration; the intensity was divided by the concentration of Eu(III). As described in Section 3.1.1, since the intensity depends on the EuA_3 concentration, the normalization was performed for a narrow EuA_3 concentration range; the EuA_3 concentration range was $(1.2-3.1)\times10^{-5}$ M (closed symbols) and $(0.8-1.9)\times10^{-4}$ M (open symbols). The intensity normalized to the concentration of EuA_3 obtained via extraction into $CHCl_3$ is given in Fig. 3(a) as a function of HA concentration at $\lambda_{em}=612$ nm and $\lambda_{ex}=370$ nm (circles). The intensity does not change with increasing HA concentration. It suggests that in solvent extraction, the complexation between EuA_3 and HA including aggregation is unimportant when compared with that in the $CHCl_3$ solutions-dissolved EuA_3. When Eu(III) was extracted into the $HA/CHCl_3$ solution, the luminescence intensity increased linearly with an increasing concentration of extracted Eu(III) and the slope did

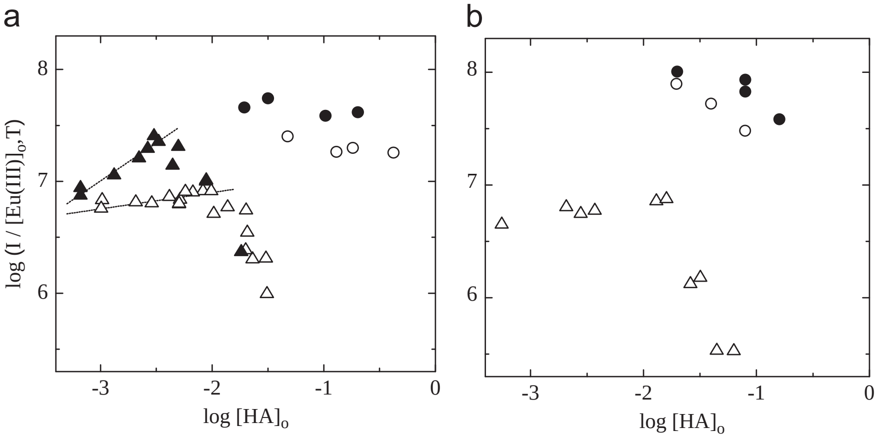

Fig. 3. Luminescence intensity at λ_{ex}=370 nm as a function of HA concentration. Organic phase: (a) HA/$CHCl_3$ and (b) HA/CCl_4 in solutions-dissolved EuA_3 (triangles), and in solutions obtained by solvent extraction of Eu(III) with HA (circles). $[Eu(III)]_o=(1.2-3.1)\times10^{-5}$ M (closed symbols), $(0.8-1.9)\times10^{-4}$ M (open symbols). Luminescence intensity is normalized to the Eu(III) concentration.

not change over the $[Eu(III)]_o$ range studied, which differs from the results shown in Fig. 2 (the data are not provided). Fig. 3 also demonstrates the variation in intensity obtained for the solution-dissolved EuA_3 (triangles) with regards to the $[HA]_o$. The intensity obtained via solvent extraction is almost independent of the $[HA]_o$, despite using higher HA concentration ($>10^{-2}$ M), while the intensity in the HA/$CHCl_3$ solution-dissolved EuA_3 abruptly decreases similar to that shown in Fig. 1(a). What is the difference between the HA/$CHCl_3$ used in the solvent extraction and the HA/$CHCl_3$-dissolved EuA_3? The only difference should be in their water content. In the solvent extraction, since water molecules contact the $CHCl_3$, they can always attack the HA and EuA_3, and prevent both interaction between EuA_3 and HA and aggregation. In contrast, in dry solvents, there are not enough water molecules to prevent such occurrences. To examine whether water molecules are involved in the formation of aggregates, CCl_4, in which the water solubility is lower than that in $CHCl_3$ (the water solubility=$(7.2\pm0.2)\times10^{-2}$ M in $CHCl_3$ and $(8.5\pm0.3)\times10^{-3}$ M in CCl_4 [24]) was used, and the data were compared. The results are also shown in Fig. 3. As shown in Fig. 3(b), the use of CCl_4 caused a larger decrease in the luminescence intensity. Several reports indicating that the formation of dimers or the aggregation of Ln(III) β-diketonates is related to water molecules (the dimer can be formed with bridging water molecules) can be found in the literature [21–23,25]. For example, it was reported [21,22] when water was added into toluene solutions of LnL_3 where L describes fluorinated β-diketonate ions, significant enhancement of the luminescence intensity was observed. The phenomena were explained as follows [21–23]; poorly luminescent dimers dissociate with water molecules to give monomers, and the luminescence intensity of Ln(III) could be enhanced; indicating the effect of additional water molecules on the luminescence intensity of tris(β-diketonato)Ln(III).

Another example of the involvement of water molecules in the complexation of tris(β-diketonato)Lns(III) [26,27] is the formation of outer-sphere complexes between the Ln(III) β-diketonates and the Lewis bases; hydrogen bonding is formed between the Lewis base and the hydrogen atoms of the water molecules coordinated to the Ln(III). Although further discussion will be required, when HA molecules via water molecules coordinated to Eu(III) could form outer-sphere complexes with EuA_3 chelate, the luminescence intensity of EuA_3 can be sensitized with the presence of HA (see Fig. 1), however, the effect of HA is too weak to change the distribution ratio of Eu(III). Accordingly, the results obtained in the present work suggest that the luminescence intensity can be influenced by the co-existing materials such as HA and water molecules, even when the influence does not appear in the extraction data.

3.2. Effect of HA on the luminescence intensity in the presence of B

Since B forms a stable complex with EuA_3, the interaction of HA with EuA_3B should be much smaller than that with EuA_3. Fig. 4 shows typical examples of the luminescence intensity (Fig. 4(a)) as a function of the HA concentration in a $CHCl_3$ solution containing 1.0×10^{-5} M EuA_3, 2.6×10^{-3} M B and HA together with their excitation spectra (Fig. 4(b)). The intensity in the $CHCl_3$ solutions in the absence of additional HA is ~240 (represented by asterisk in Fig. 4(a)), however, in the presence of 1×10^{-2} M HA the intensity reaches 3500, while in 8×10^{-5} M EuA_3 without extra HA and B, it is nearly 360 (asterisk in Fig. 1(a)) and only 600 in a 1×10^{-2} M HA/$CHCl_3$ solution as shown in Fig. 1(a). As seen by comparing Fig. 1 to Fig. 4, the effect of HA on the intensity is larger for EuA_3B than for EuA_3. This result can be explained as follows: EuA_3 keeps three water molecules, but EuA_3B removes all the water molecules [14,15]. As already described, EuA_3 can form an outer-sphere complex with HA through the H atom in the water molecules that are coordinated with the EuA_3. Since the basicity of N in EuA_3B is strong, B can coordinate with or attract HA in solution despite a lack of water molecule. The complex shows a band around 360–370 nm as seen in Fig. 4(b). Thus, the effect of HA on the luminescence of EuA_3B is larger than that of EuA_3. Due to the strong bonding between B and Eu(III) and the large molecular volume, the ternary complex, EuA_3B, does not form aggregates in the solution. Therefore, unlike the intensities of the EuA_3 provided in Fig. 1(a) or Fig. 3, no abrupt decrease is observed.

As similar as the results obtained in the solvent extraction of Eu(III) with HA alone, controlling the concentration of Eu(III) extracted with HA and B into $CHCl_3$ is difficult. Fig. 5 shows the variation in the intensity with the HA concentration when the Eu(III) was extracted with 2.6×10^{-3} M B and HA together with that for the HA/$CHCl_3$ solution containing 1×10^{-5} M EuA_3 and 2.6×10^{-3} M B. The effect of HA on the luminescence intensity obtained via solvent extraction is smaller than that obtained in the B/$CHCl_3$ solution-dissolved EuA_3. This is one of the advantages for using a synergistic extraction to prepare phosphor, because careful control of the experimental conditions, at least the β-diketone concentration, is unnecessary. The intensity obtained via solvent extraction is slightly weaker than that in the solution-dissolved EuA_3B. In the solvent extraction, since water is always

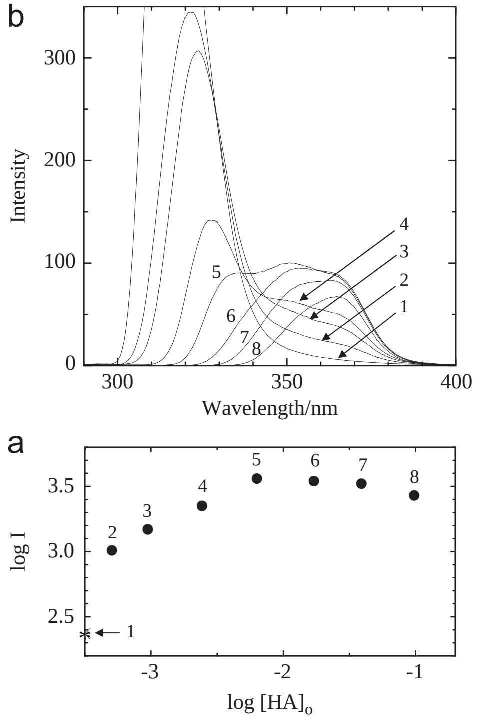

Fig. 4. Effect of HA concentration on the luminescence of Eu(III). (a) the luminescence intensity at the peak wavelength ($^5D_0 \rightarrow {}^7F_2$) at λ_{ex}=370 nm, (b) the excitation spectra in HA/$CHCl_3$ solution containing 2.6×10^{-3} M B and 1×10^{-5} M EuA_3 (λ_{em}=612 nm). $[Hpta]_o$=(1) 0, (2) 5×10^{-4}, (3) 1×10^{-3}, (4) 2×10^{-3}, (5) 6×10^{-3}, (6) 2×10^{-2}, (7) 4×10^{-2}, and (8) 0.1 M.

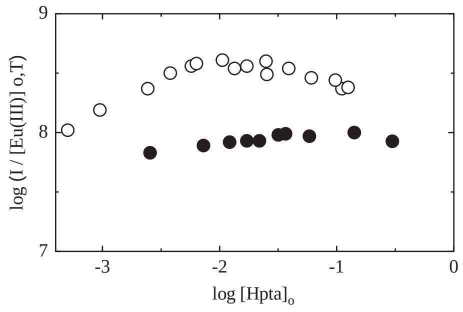

Fig. 5. Luminescence intensity as a function of the HA concentration. ○ in HA/$CHCl_3$ containing 2.6×10^{-3} M B and 1×10^{-5} M EuA_3. ● in $CHCl_3$ extracted Eu(III) $(0.5-1.6) \times 10^{-5}$ M with HA and 2.6×10^{-3} M B. Luminescence intensity is normalized for Eu(III) concentration.

in contact with HA, B and Eu(III) species and interacts with them, the interaction of HA to EuA_3B could be obstructed.

4. Conclusion

In the extraction of Eu(III) with HA from 2×10^{-2} M to 0.4 M into $CHCl_3$, the dominant extracted species was EuA_3. The luminescence intensity in the $CHCl_3$ was not influenced by the HA. However, the luminescence intensity in HA/$CHCl_3$ into which synthesized EuA_3 was dissolved abruptly decreased when the HA concentration reached approximately 10^{-2} M. In an extraction in which water molecules contact and interact with all relevant species, the water molecules obstruct the interaction between the HA and EuA_3 or HA and EuA_3B, however, in dry solvents, the HA interacts with EuA_3 via water molecules coordinated to EuA_3 to form aggregates. The results in the present work suggest that the luminescence intensity can be influenced with coexisting materials. Furthermore, the luminescence intensity in 2,2′-bipyridyl (B)/$CHCl_3$ solution-dissolved EuA_3 is more largely influenced by the HA, compared to that in the $CHCl_3$ extracted Eu(III) with HA and B. The use of the synergistic extraction of Eu(III) should provide an efficient method for preparing a phosphor in solution.

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