DALTON
FULL PAPER

Luminescence spectroscopy of Eu(Bis-tris)$^{3+}$ complexes in anhydrous DMF [Bis-tris = 2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol]: luminescence quenching rate constants for the $^5D_0$ state of Eu^{3+} by DMF and polyalcoholic OH groups

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Excitation and emission spectra and luminescence lifetimes of Eu^{3+} complexes obtained by dissolving anhydrous $EuCl_3$ and $EuCl_3$/2,2-bis(hydroxymethyl)-2,2′,2″-nitrilotriethanol (Bis-tris) in anhydrous dimethylformamide (DMF) and those from a Eu(Bis-tris)$_2$Cl$_3$ crystalline sample have been studied. Two distinct Eu^{3+} complexes were observed when anhydrous $EuCl_3$ was dissolved in anhydrous DMF, and one was interpreted as an outer-sphere complex of Cl^- anion. Dissolution of an excess amount of vacuum dried $NaClO_4$ or KPF_6 in anhydrous DMF resulted in longer luminescence lifetimes, presumably reducing the effects of trace amounts of water in the solvent due to competitive binding of the water in the solvent by alkali metal cations. The quenching rate constant for the $^5D_0$ state of Eu^{3+} ion by each complexed DMF molecule in solution and by each OH group in the Bis-tris from the Eu(Bis-tris)$_2$Cl$_3$ crystalline sample were 54 ± 1 and $495 \pm 5\ s^{-1}$, respectively, and these were used to interpret the plausible structures of the different Eu^{3+} complexes in the $EuCl_3$/Bis-tris/DMF solution.

1 Introduction

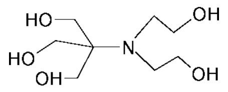
Laser-induced luminescence studies of Eu^{3+} or Tb^{3+} complexes often provide valuable structural information in solution.[1–4] It is well known that the number of Eu^{3+} complexes in solution is the same as the observed number of $^5D_0 \longleftarrow {}^7F_0$ transition bands, because the $^5D_0 \longleftarrow {}^7F_0$ transition frequency of the Eu^{3+} ion is influenced only by its chemical environment.[1,4]

Based on the large difference in luminescence quenching efficiency by inner sphere coordinated H_2O and D_2O,[5–7] Horrocks, Jr. and Sudnick have shown that measurements of the luminescence decay rate constants for the $^5D_0$ state of the Eu^{3+} ion in water and in D_2O can be used to determine the number of H_2O molecules coordinated in the inner sphere of the complex.[8] They have obtained the empirical eqn. (1), where

$$q = 1.05(k_{H_2O} - k'_{D_2O}) \qquad (1)$$

k_{H_2O} and k'_{D_2O} are the luminescence decay rate constants (in units of ms^{-1}) for the $^5D_0$ state of the Eu^{3+} ion in water and in D_2O, respectively. This equation has been applied for a variety of systems,[2,3] when the employed ligands do not have alcoholic OH groups coordinated directly to Eu^{3+} ion in aqueous solution, while modified equations applicable to ligands having alcoholic OH and amide NH groups have been reported recently.[9,10]

Recently, we have found that a commonly used buffering reagent Bis-tris binds tightly to lanthanide ions, while keeping their high reactivity for hydrolyzing phosphate esters.[11] Since the alcoholic OH groups of the Bis-tris coordinate directly to the lanthanide ions in aqueous solution, and since the magnitude of the contributions to the non-radiative decay process by OH oscillators from water and polyalcohol cannot be the same, the number of coordinated water molecules in the inner sphere of the complex is difficult to determine using eqn. (1). In this work we have studied excitation and emission spectra and luminescence lifetimes of Eu^{3+} complexes obtained by dissolving anhydrous $EuCl_3$ in DMF and a mixture of anhydrous $EuCl_3$ and vacuum dried KPF_6 in DMF, in the absence and presence of Bis-tris, and those from a Eu(Bis-tris)$_2$Cl$_3$ crystalline sample. The average non-radiative decay rate constant for the $^5D_0$ state of Eu^{3+} ion contributed by each inner-sphere complexed alcoholic OH group, and that by each solvent molecule, were used to interpret the $^5D_0 \longleftarrow {}^7F_0$ excitation spectra observed from 1 : 1 and 1 : 2 mixtures of $EuCl_3$ and Bis-tris in DMF.



Bis-tris

2 Experimental method

(a) Reagents and sample preparation

Bis-tris (98%) was purchased from Aldrich Chemical Co. and dried at 60 °C under vacuum (1×10^{-5} Torr) for 3 hours before adding to the Eu^{3+} solution in DMF. Anhydrous $EuCl_3$ (Aldrich, 99.99%) and DMF (Aldrich, 99.8%, water < 0.005%) were used as purchased. All the solutions were prepared in a glove box filled with dry nitrogen, and sample solutions transferred to an air-tight quartz cell for excitation and emission spectra and luminescence lifetime measurements. The Eu(Bis-tris)$_2$Cl$_3$ crystalline sample was prepared from an equimolar mixture of anhydrous $EuCl_3$ and Bis-tris in methanol.[11]

(b) Excitation and emission spectra and luminescence lifetime measurement

A Nd-YAG-DYE laser (Quantel YG681-TDL 60) operating at 10 Hz was used as the excitation light source. The band width of the dye laser was ≈0.06 cm^{-1} and the pulse width 8 ns. The pulse energy of the laser was kept constant at 1.8–2.0 mJ per

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pulse to avoid sample decomposition. The excitation laser pulse was passed through a 1 cm quartz cell containing the sample solution. The europium(III) $^5D_0 \longleftarrow {}^7F_0$ excitation spectra were obtained by monitoring the luminescence from the $^5D_0 \longrightarrow {}^7F_2$ transition centered at about 614–616 nm, while scanning the laser wavelength in the 578.0–581.0 nm region. The excitation laser frequency was monitored using a Fizeau wavelength meter (New Focus 7711). To obtain luminescence spectra, the laser wavelength was fixed at an appropriate position and the monochromator scanned in the 581–720 nm region. The luminescence signal was collected at 90° from the laser beam direction using a 0.5 m monochromator (Spex 500M) equipped with a cooled photomultiplier tube (Hammamatsu R928). The signal from the latter was amplified using a current amplifier (Keithly 428), then fed into a digital oscilloscope (Tektronix TDS 520) for digitization and signal averaging. The output from the digital oscilloscope after signal averaging from 300 laser shots was transferred to a laboratory computer for signal processing and analysis. The excitation and emission spectra were deconvoluted using the Lorentzian–Gaussian product function[12,13] (2) where Y_{max} is the maximum intensity,

$$Y = Y_{max}\exp\{-0.5[(X-\mu)/\sigma]^2\}/\{1+[(X-\mu)/\sigma]^2\} \quad (2)$$

X is the wavelength, μ the wavelength of the peak maximum, and 2σ the full width at half-maximum (FWHM).

To measure the luminescence lifetimes of various species in solution, the luminescence *vs.* time profiles were obtained by monitoring the luminescence intensity at 616 nm, while the excitation laser wavelengths were set at appropriate positions. The profiles were analyzed by single or double exponential decay fits to obtain the luminescence lifetimes.

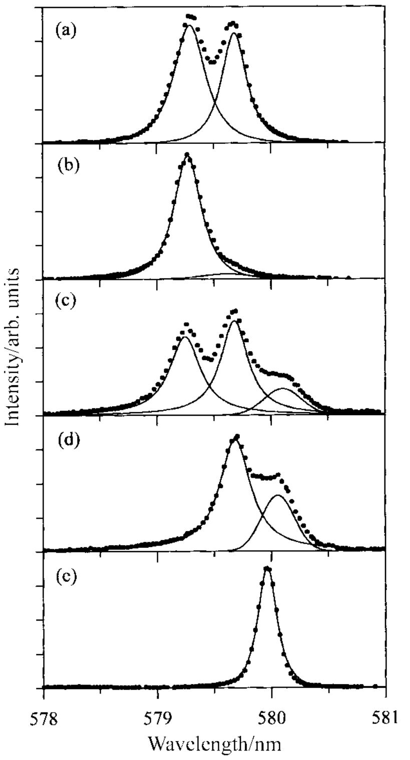

Fig. 1 Excitation spectra of the $^5D_0 \longleftarrow {}^7F_0$ transition of Eu^{3+} complexes obtained on dissolving 0.010 M $EuCl_3$ in anhydrous DMF. (a) $EuCl_3$ in DMF; (b) 0.050 M KPF_6 added to (a); (c) 0.010 M Bis-tris added to (b); (d) 0.020 M Bis-tris added to (b); (e) Eu(Bis-tris)$_2$-Cl_3(crystal).

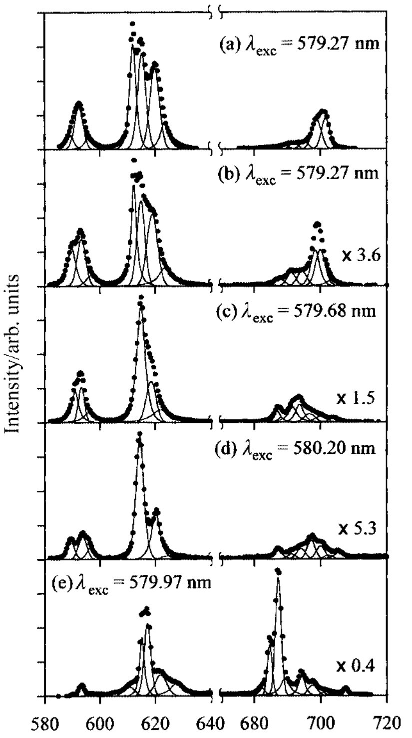

Fig. 2 Luminescence spectra of $^5D_0 \longrightarrow {}^7F_J$ (J = 1, 2 or 4) transitions of various Eu^{3+} complexes: (a) $[Eu(DMF)_x]^{3+}$, (b)–(d) $[Eu(Bis\text{-}tris)(DMF)_m]^{3+}$, and (e) Eu(Bis-tris)$_2Cl_3$(crystal). The excitation wavelengths as well as the magnification factors are shown.

3 Results

(a) Excitation and emission spectra

The excitation spectrum for the $^5D_0 \longleftarrow {}^7F_0$ transition of Eu^{3+} complexes obtained on dissolving 0.010 M anhydrous $EuCl_3$ in anhydrous DMF is shown in Fig. 1(a). It shows apparently two peaks centered at 579.27 and 579.68 nm, respectively, with comparable intensities. When vacuum dried KPF_6 was added to give a 0.050 M solution, however, the 579.68 nm band intensity decreased dramatically as shown in Fig. 1(b), and a small amount of white precipitate, presumably KCl, was formed. Fig. 1(c) shows a typical excitation spectrum observed from dissolving equimolar amounts (0.010 M) of anhydrous $EuCl_3$ and Bis-tris in anhydrous DMF in the presence of 0.050 M KPF_6. Comparing with Fig. 1(a), there appeared a new band centered at 580.11 nm and the relative intensity of the 579.27 nm band decreased while that at 579.68 increased. The spectrum could be fitted reasonably well using three Lorentzian–Gaussian type peaks centered at 579.27, 579.68 and 580.11 nm, respectively. The shape of the excitation spectrum suggests that some of the solvent molecules are replaced by OH's of the Bis-tris ligand in accord with the large formation constant for the Eu(Bis-tris)$^{3+}$ complex in aqueous solution,[11] although the stabilities of the Eu(Bis-tris)$^{3+}$ complexes might be slightly different in the DMF solvent. When the concentration of Bis-tris was increased to twice that of $EuCl_3$ the 579.27 nm band disappeared completely as seen in Fig. 1(d). A typical excitation spectrum from the Eu(Bis-tris)$_2$Cl$_3$ crystalline sample is shown in Fig. 1(e), and there appears only one band centered at about 580.0 nm.

We have also investigated the shapes of the luminescence spectra. Fig. 2(a) shows a typical luminescence spectrum obtained from excitation of $Eu(DMF)_n{}^{3+}$ complexes at 579.27 nm, and the shape of the spectrum from excitation at 579.68 nm was the same. On the other hand, the shapes of the spectra obtained upon dissolving equimolar amounts of anhydrous $EuCl_3$ and Bis-tris in DMF were different as shown in Fig. 2(b)–(d), when different bands were excited. The spectrum from the Eu(Bis-tris)$_2$Cl$_3$ crystalline sample is also shown in Fig. 2(e) for comparison purposes. All luminescence spectra in Fig. 2

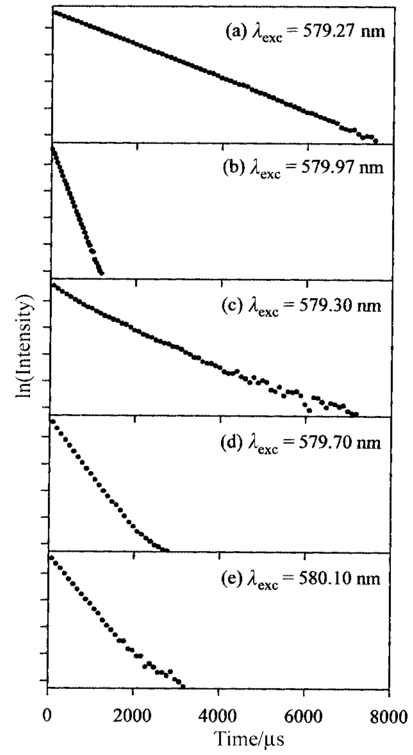

Fig. 3 Luminescence decay profiles monitored at the $^5D_0 \longrightarrow {}^7F_2$ transition from various Eu^{3+} complexes: (a) $[Eu(DMF)_x]^{3+}$, (b) $Eu(Bis\text{-}tris)_2Cl_3$(crystal), and (c)–(e) $[Eu(Bis\text{-}tris)(DMF)_m]^{3+}$. To avoid congestion one point from every five data points was plotted. The excitation wavelengths are shown.

show that the intensity of the $^5D_0 \longrightarrow {}^7F_2$ transition is stronger than that of the $^5D_0 \longrightarrow {}^7F_1$ transition, which suggests that these Eu^{3+} complexes have no inversion center.[4,14]

(b) Luminescence lifetime measurements

Typical luminescence *vs.* time profiles observed in this work are shown in Fig. 3. When only anhydrous $EuCl_3$ (0.010 M) was dissolved in DMF the time profiles showed a good single exponential decay, and the observed lifetime was 1480 ± 10 μs for both 579.27 and 579.68 nm bands. When KPF_6 was added to the $EuCl_3$/DMF solution ($[KPF_6] = 0.050$ M) the profiles also showed a good single exponential decay, Fig. 3(a), and the luminescence lifetime was increased to 1580 ± 10 μs. Interestingly, the luminescence lifetimes of the $^5D_0$ state of Eu^{3+} complexes observed from both $EuCl_3$/DMF and $EuCl_3/KPF_6$/DMF solutions did not show excitation wavelength dependence in spite of the appearance of two distinct bands in the excitation spectrum. The time profiles observed from the $Eu(Bis\text{-}tris)_2Cl_3$ crystal also showed single exponential decay as shown in Fig. 3(b), and luminescence lifetime was 239 ± 2 μs.

When equimolar amounts of anhydrous $EuCl_3$ and Bis-tris were dissolved in anhydrous DMF that contains 0.050 M KPF_6, however, the luminescence time profiles showed double exponential decay behavior. When the 579.27 nm band was excited at 579.30 nm a slow component with 1540 ± 60 μs lifetime was dominant, while a fast component with 415 ± 20 and 420 ± 20 μs lifetimes, respectively, was dominant when the excitation wavelengths were set at 579.70 and 580.10 nm, respectively, as plotted in Fig. 3(c)–(e). Although the excitation frequencies for the 579.27 and 579.68 nm bands were virtually the same as those without the Bis-tris ligand, the luminescence lifetimes were substantially decreased. The reduced luminescence lifetimes in the presence of Bis-tris indicate that some of the solvent molecules are obviously replaced by the OH groups of the added Bis-tris ligand. When the concentration of Bis-tris was increased to twice that of $EuCl_3$ the time profiles from 579.70 and 580.10 nm excitation showed apparent single exponential decay with 430 ± 5 and 520 ± 5 μs lifetimes, respectively. All the luminescence lifetimes measured in this work are shown in Table 1.

Table 1 Luminescence lifetimes for different Eu^{3+} complexes obtained on dissolving 0.010 M $EuCl_3$ in anhydrous DMF containing 0.050 M KPF_6

	$[Eu^{3+}]:[L]^a$	λ_{exc}/nm	τ/μs
DMF solution	1 : 0	579.27	1580 ± 10; 1480 ± 10^b
		579.68	1580 ± 10; 1480 ± 10^b
	1 : 1	579.30	550 ± 30 (f); 1540 ± 60 (s)
		579.70	415 ± 20 (f); 1100 ± 50 (s)
		580.10	420 ± 20 (f); 800 ± 50 (s)
			520 ± 5 (single exponential)
	1 : 2	579.70	430 ± 5 (single exponential)
		580.10	520 ± 5 (single exponential)
Crystal	1 : 2	579.96	239 ± 2

^{a} Bis-tris. ^{b} Without KPF_6.

4 Discussion

(a) Eu^{3+} complexes in $EuCl_3$/DMF and $EuCl_3/KPF_6$/DMF solutions

The apparent two peaks appearing in the excitation spectrum upon dissolving only anhydrous $EuCl_3$ in DMF, Fig. 1(a), strongly suggest that two types of complexes exist in the solution. If we assume that the two bands separated by ≈12 cm^{-1} in Fig. 1(a) were due to the different coordination environments in the inner sphere, the ground states of the Eu^{3+} complexes in this work would correspond to one of the equilibrium pair given by eqns. (3) and (4), since there are only two types of ligands in the solution.

$$[Eu(DMF)_x]^{3+} + DMF \rightleftharpoons [Eu(DMF)_{x+1}]^{3+} \qquad (3)$$

$$[Eu(DMF)_x]^{3+} + yCl^- \rightleftharpoons [EuCl_y(DMF)_{x-y}]^{(3-y)+} + yDMF \qquad (4)$$

Recently, Frey and Horrocks, Jr. have reported nephelauxetic parameters for various types of Eu^{3+} complexes.[15] Using the nephelauxetic parameters reported by them, the energy separation between the two species in eqn. (3) corresponds to 8.5 cm^{-1} for $x = 8$, which is much smaller than that observed in Fig. 1(a). On the other hand, since the differences in the nephelauxetic parameters between amide oxygen and Cl^- ion are 5.5 and 5.9 cm^{-1} for 9- and 8-coordination, respectively, the energy separation between the two species in eqn. (4) corresponds to 11–11.8 cm^{-1} when two Cl^- ions bind to Eu^{3+} ion in its inner sphere. This is fortuitously consistent with the observed value. However, the luminescence lifetimes as well as the shapes of the luminescence spectra should be different from each other when two species have different inner-sphere coordination environments.[16,17] Effectively the same luminescence lifetimes as well as the same shapes of luminescence spectra in the 585–715 nm region regardless of the excitation wavelength strongly suggest that the inner-sphere coordination numbers as well as the chemical environments should be the same for the two complexes.

As shown in Fig. 1(b), the 579.68 nm band intensity decreased dramatically when KPF_6 was added to the solution. To obtain additional information, we have also investigated the shapes of excitation spectra and variation of the luminescence lifetimes of the Eu^{3+} complexes on adding an excess amount (0.050 M) of vacuum dried NaCl and $NaClO_4$ to the $EuCl_3$ solution. When excess of NaCl was added, although NaCl did not dissolve well in dry DMF, the relative intensity of the 579.68 nm band increased slightly but the luminescence lifetimes did not change. On the other hand, when excess (0.050 M) of $NaClO_4$ was added, the intensity of the 579.27 nm band increased and that of the 579.68 nm band decreased substantially. Also, the luminescence lifetimes increased to 1580 ± 10 μs in the presence of $NaClO_4$. It was also observed that the intensity and luminescence lifetime of the 579.68 nm band decreased substantially on addition of a small amount of water to the $EuCl_3$ solution. All these results suggest that the intensity of the 579.68 nm band is clearly affected by the types of anions and the amount of water in the solution. Thus, it seems more reasonable that its origin in Fig. 1(a) and (b) is ascribed to Eu^{3+} complexes with loosely bound Cl^- ion(s), *i.e.* outer-sphere Cl^- complexes,[18] which can be destroyed by an excess amount of PF_6^-, ClO_4^- or water. The spectral red shift of the $^5D_0 \longrightarrow {}^7F_0$ transition caused by outer-sphere complexed anions has also been reported by Bünzli *et al.*[19] They have shown that europium perchlorate in anhydrous acetonitrile solution forms inner- and outer-sphere complexes with ClO_4^- anion, and the $^5D_0 \longrightarrow {}^7F_0$ transition for the latter appears at longer wavelength, which is in accord with our interpretation for the origin of the 579.68 nm band.

The dominant band centered at 579.27 nm in Fig. 1(b) suggests that one type of Eu^{3+} complex is dominant in the solution containing 0.050 M KPF_6. The luminescence lifetime measured in this work (1.58 ± 0.01 ms) is slightly longer than that (1.44–1.47 ms) reported by Bünzli and Yersin.[14] The latter is in good agreement with our value (1.48 ± 0.01 ms) observed from a $EuCl_3$ solution without KPF_6. In fact, the anhydrous DMF solvent contains about 0.005% (≈0.0026 M) of water. Since K^+ ions are expected to compete with Eu^{3+} ions for their coordination to water molecules in the solution, the effect of trace amounts of water in the solution on non-radiative deexcitation of the europium(III) $^5D_0$ state seems to be reduced by the addition of KPF_6, that results in a longer lifetime for the $^5D_0$ state in $EuCl_3/KPF_6$/DMF solution.

Bünzli and Yersin have also reported that on dissolving anhydrous $Eu(ClO_4)_3$ in anhydrous DMF the Eu^{3+} ion coordinates eight solvent molecules based on the analysis of the $^5D_0 \longrightarrow {}^7F_J$ emission spectrum following $^5L_6 \longleftarrow {}^7F_0$ excitation at 393 nm.[14] Since their luminescence lifetime matches very well with ours without KPF_6, the 579.27 nm band in Fig. 1(a) and (b) is thought to be due to the $[Eu(DMF)_8]^{3+}$ species. Using the measured luminescence lifetime (1.58 ± 0.01 ms) for the Eu^{3+} complex from $EuCl_3/KPF_6$/DMF in this work as well as the true radiative lifetime of about 5000 μs for Eu^{3+} ion,[7] each DMF molecule contributes 54 ± 1 s^{-1} to the non-radiative decay rate constant of the Eu^{3+} ion.

(b) Non-radiative decay rate constant for the europium(III) $^5D_0$ state involving an alcoholic OH group

The non-radiative decay rate constant involving an alcoholic OH group coordinated directly to Eu^{3+} ion can be obtained from the luminescence lifetime observed from the Eu(Bis-tris)$_2$Cl$_3$ crystalline sample. The Eu^{3+} ion in the Eu(Bis-tris)$_2$Cl$_3$ crystal is known to coordinate 8 OH groups and 2 N atoms as shown by X-ray crystallography.[11] As listed in Table 1, the luminescence lifetime observed from the crystalline Eu(Bis-tris)$_2$Cl$_3$ sample was 239 ± 2 μs. Using the true radiative lifetime of the Eu^{3+} ion of about 5000 μs,[7] each OH group coordinated directly to the Eu^{3+} ion contributes to the non-radiative decay rate about 495 ± 5 s^{-1} for the $^5D_0$ state, assuming that the contribution from the skeletal N–C vibrations to the non-radiative decay rate is much smaller than that of OH.[20]

Horrocks, Jr. and co-workers investigated luminescence lifetimes of Eu^{3+} complexes in MeOH.[21] When $EuCl_3$ was dissolved in MeOH and MeOD, respectively, they observed luminescence decay rate constants of 4.08 and 0.69 ms^{-1}, respectively. They have determined that 7.1 ± 0.5 MeOH molecules coordinate to Eu^{3+} ion using eqn. (5) based on the

$$m = 2.1(\tau^{-1}{}_{\mathrm{MeOH}} - \tau^{-1}{}_{\mathrm{MeOD}}) \qquad (5)$$

assumption that MeOH behaves like half a water molecule. Then the average luminescence quenching rate constant involving an alcoholic OH group corresponds to 485 s^{-1}, which is in accord with our value obtained from the crystalline Eu(Bis-tris)$_2$Cl$_3$ sample.

(c) Eu^{3+} complexes from 1 : 1 and 1 : 2 mixtures of $EuCl_3$ and Bis-tris in DMF

The non-radiative decay rate constants for the europium(III) $^5D_0$ state contributed by each DMF molecule and that by an OH group of the Bis-tris discussed above provide a useful clue for the interpretation of the excitation spectra shown in Fig. 1(c). The luminescence *vs.* time profiles from the 579.27 nm band excitation in the 1 : 1 mixture of $EuCl_3$ and Bis-tris showed a fast decay component having 550 ± 30 μs lifetime for the initial short period, but a slow component showing 1540 ± 60 μs lifetime was dominant as shown in Fig. 3(c). Since the peak position is almost identical to that in Fig. 1(b), and since the lifetime of the dominant slow component is comparable to that of $[Eu(DMF)_8]^{3+}$, it seems that the major portion for this band is contributed by unchanged $[Eu(DMF)_8]^{3+}$. However, the appearance of the minor fast component having 550 ± 30 μs lifetime suggests that a minor portion for this band is contributed by complexes having two or three solvated DMF molecules replaced by OH groups of the Bis-tris ligand molecule.

When the 579.68 nm band was excited in the 1 : 1 mixture of $EuCl_3$ and Bis-tris a fast component with 415 ± 20 μs lifetime was dominant, but a weak slow component with 1100 ± 50 μs lifetime was also observed. Although it is difficult to interpret the nature of the slow component, the lifetime of the fast component is in accord with an [Eu(Bis-tris)(DMF)$_4$]$^{3+}$ complex, where four DMF molecules are replaced by the same number of OH groups from one Bis-tris ligand. (Note that a maximum of 4 OH's among the 5 OH groups in a Bis-tris ligand can coordinate to Eu^{3+} because of the geometrical constraints.) The single exponential lifetime for the 579.68 nm band observed from a 1 : 2 mixture of $EuCl_3$ and Bis-tris is also in accord with the [Eu(Bis-tris)(DMF)$_4$]$^{3+}$ complex, even though the peak position overlaps coincidentally with the one for the proposed outer-sphere complex, *i.e.* $[Eu(DMF)_8]^{3+}Cl^-$.

When the 580.11 nm band of a 1 : 1 mixture of $EuCl_3$ and Bis-tris was excited at 580.10 nm a fast component with 420 ± 20 μs lifetime was dominant, but a weak slow component with 800 ± 50 μs lifetime was also observed. When only the early time data points of the 580.11 nm band excitation were analyzed using a single exponential function the apparent lifetime was 520 ± 5 μs. Since the peak separation between the 579.68 and 580.11 nm bands in Fig. 1(c) is almost identical to that between the 579.27 and 579.68 nm bands, the origin of the 580.11 nm band appears to be related to an Eu^{3+} complex in which two Bis-tris molecules are involved. This is supported by the substantial increase of the 580.11 nm band intensity as well as the complete disappearance of the 579.27 nm band when the concentration of Bis-tris was increased to twice that of $EuCl_3$. However, the peak position and luminescence lifetime of the 580.11 nm band do not agree with those of the Eu(Bis-tris)$_2$Cl$_3$ crystalline sample. The observed lifetime (520 ± 5 μs) of the 1 : 2 complex in the solution is too long to correspond to the same type of the complex as that in the crystalline state. In other words, the results imply that not all the 8 OH's from two Bis-tris molecules coordinate to an Eu^{3+} ion in solution. The apparent single exponential decay with the longer effective lifetime for the 580.11 nm band in the 1 : 2 mixture seems to reflect an average lifetime of two or more different kinds of species involved in a fast ligand exchange reaction.[22] A very fast exchange reaction between the coordinated OH groups and uncoordinated OH groups that are accessible geometrically could be an example. Although it is very difficult to interpret the origin of the 580.11 nm band, it seems that this band appears from the influence of Cl^- anions, considering that the peak separation between the 579.68 and 580.11 nm bands in Fig. 1(c) is almost identical to that between 579.27 and 579.68 nm bands in Fig. 1(a).

5 Conclusion

In this work we have investigated excitation and emission spectra and luminescence lifetimes of Eu^{3+} complexes obtained upon dissolving anhydrous $EuCl_3$ and $EuCl_3$/Bis-tris in anhydrous DMF as well as those from the Eu(Bis-tris)$_2$Cl$_3$ crystalline sample. It was observed that the intensity of the 579.68 nm peak for pure $EuCl_3$ solution decreased dramatically and the luminescence lifetime of the Eu^{3+} complex was lengthened by dissolution of an appropriate amount of vacuum dried $NaClO_4$ or KPF_6 in DMF. Based on the efficient decrease of the 579.68 nm band by dissolution of $NaClO_4$ or KPF_6, the 579.68 nm band from pure $EuCl_3$ solution was interpreted as due to an outer-sphere complex of Cl^- anion. Also, the observed lengthening of luminescence lifetime in the presence of $NaClO_4$ or KPF_6 was ascribed to the reduced effects of trace amounts of water in the solvent. The quenching rate constants for the $^5D_0$ state of Eu^{3+} ion by each complexed DMF molecule in solution and that by each OH group in the Bis-tris from the Eu(Bis-tris)$_2$Cl$_3$ crystalline sample were 54 ± 1 and $495 \pm 5\ s^{-1}$, respectively. Although only three apparent excitation bands were observed from a 1 : 1 mixture of $EuCl_3$ and Bis-tris in DMF, luminescence lifetimes indicated that at least five different species were present in the solution.

Acknowledgements

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