Energy-Transfer Luminescence of Eu^{3+} and Tb^{3+} Complexed with Hexakis(4-carboxylatophenoxy)cyclotriphosphazene

Tomoyuki Itaya, Yutaka Sasaki, Teiichi Tanigaki, Akira Matsumoto,† and Kenzo Inoue*
Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790
†Laboratory of Chemistry, Faculty of Education, Ehime University, Matsuyama 790

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Hexakis(4-carboxylatophenoxy)cyclotriphosphazene, **1**, forms a stable 1:2 **1** - lanthanide ion (Eu^{3+} and Tb^{3+}) complex. The fluorescence behavior and structure of the complexes have been discussed.

A considerable effort has been devoted to the preparation of a stable lanthanide ion complex with strong luminescence. Host molecules such as 2,2'-bipyridine-based cryptands[1] and calixarene derivatives[2,3] are known to form inclusion complexes with Eu^{3+} and Tb^{3+} ions that display strong luminesence.

Cyclic phosphazenes have attracted much interest since unique properties and functionalities are attainable through the introduction of organic groups into P-Cl group in hexachlorocyclotriphosphazene. A number of cyclophosphazene derivatives have been synthesized and their functionalities have been reported.[4] However, to our knowledge, no studies have been reported on the formation of lanthanide - cyclotriphosphazene complexes and their fluorescence behavior. In phenoxycyclotriphosphazene, the O-P-O and P-O-C angles have been reported to be 97.2 and 123.2 °, respectively.[5] This suggests that three carboxylato groups in hexakis(4-carboxylatophenoxy)cyclotriphosphazene (**1** in Scheme 1) could be located on both sides of almost planar phosphazene ring and act as a host of trivalent lanthanide ions. Here, we report on the utility of **1** as a host molecule for Eu^{3+} and Tb^{3+}, and the fluorescence behavior of the complexes of **1** with the ions in aqueous solution.

The complex can be easily isolated from the mixture of Eu^{3+} and sodium salt of hexakis(4-carboxyphenoxy)cyclotriphosphazene in water.[6,7] While the FT-IR spectrum of **1** exhibits a C=O stretching band of carboxylato group at 1560 cm^{-1}, the absorption in the complexes disappears completely and shift to the lower wavelength by 32 cm^{-1}, indicating that all carboxylato groups take part in the complex formation. The elemental analysis and complexometric titration of the complex showed the formation of a 1:2 **1**-Eu^{3+} complex.[8] Similarly, **1** binds with Tb^{3+} ions to form a 1 : 2 complex. Thus, a stable complex can be obtained from **1** and lanthanide ions, suggesting that a coordination through the carboxylatophenoxy units attached to the same phosphazene ring contribute to the formation of complexes.[9]

Figure 1 shows typical absorption, excitation, and emission spectra of Eu^{3+} in the presence of **1** in a dilute aqueous solution.[10] The absorption spectrum of **1** exhibited a red shift by the addition of lanthanide ion to a solution of **1**. The characteristic luminescence of Eu^{3+} ion complexed with **1** was observed under the excitation of 396 nm, but not for the Eu^{3+} alone under the same conditions. This indicates that a part of coordinated water molecules, which serve as effective quencher of the emission, are eliminated from Eu^{3+} by the complexation. As expected, in the continuous variation plot, the strongest intensity was obtained at [metal ion]/[**1**] =2. Similar results were obtained for **1**-Tb^{3+} complexes.

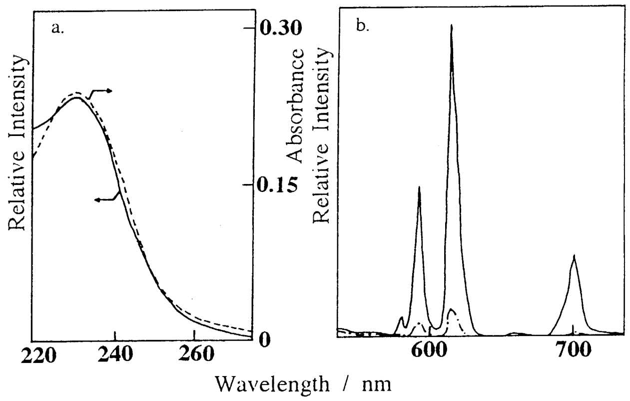


Figure 1. **a**. Absorption (- - - -) and corrected excitation (——) spectra of the complex of **1** with Eu^{3+} in aqueous solution. **b**. Emission spectra of the complex of **1** with Eu^{3+} obtained under the direct excitation of Eu^{3+} (— - —) and the excitation of carboxylatophenoxy unit (——). $[\mathbf{1}] = 8.16 \times 10^{-6}$ mol dm^{-3}, $[Eu^{3+}] = 1.83 \times 10^{-6}$ mol dm^{-3}.

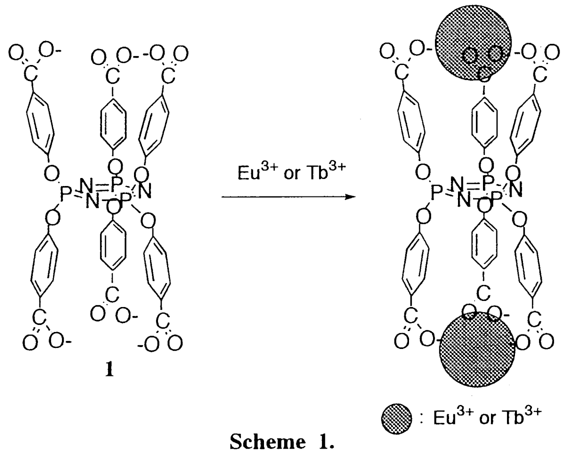
It is highly interest whereabouts lanthanide ions are located. As described above, there is a possibility to form a pocket composed of the carboxylatophenoxy groups on one side of the phosphazene ring and to encapsulate metal ions. When carboxylatophenoxy units were excited at 260 nm, the emission of the Eu^{3+} complex was remarkably enhanced compared to that excited at 396 nm. The excitation spectra of the Eu^{3+} and Tb^{3+} complexes were nearly identical with each other, which are similar to the absorption spectra of the complexes, suggesting the occurrence of efficient energy transfer from the carboxylatophenoxy units to the bound metal ions. Table 1 showed the luminescence lifetimes[11] and quantum yields of the Eu^{3+}- and Tb^{3+}- complexes. For both complexes monoexponential luminescence decay curves were observed, showing that the emission occurs from only ion bound to **1**. The emission quantum yields are significantly high. These values are comparable to those reported for complexes of ionophoric calixarens with lanthanide ions, where only one water molecule is coordinated to the metal ion in the complex.[2] Horrocks and Sudnick[12] have shown that the number of coordinated water molecules to the metal ion in the complex is given by the equation, the number of water molecules = $q(\tau(H_2O)^{-1} - \tau(D_2O)^{-1})$, where q = 1.05 for Eu^{3+} and 4.2 for

Table 1. Luminescence lifetimes and quantum yields of the complexes of **1** with Eu^{3+} and Tb^{3+}[a]

	Lifetime / ms[b]		Quantum yield[c]
	τ (H_2O)	τ (D_2O)	ϕ (H_2O)
Eu^{3+}-complex	0.18	1.4	0.01
Tb^{3+}-complex	0.50	1.6	0.3

[a] [**1**] = 2.50×10^{-6} mol dm^{-3}, [Eu^{3+}] = [Tb^{3+}] = 5.00×10^{-6} mol dm^{-3}, λ_{ex} = 260 nm.
[b] Measued in correspondence with the most intense emission band (620 nm for Eu^{3+} and 545 nm for Tb^{3+}). Experimental error ±10%.
[c] Evaluated by the method described by Haas and Stein,[13] using $[Ru(Bpy)_3]^{2+}$ as a standard (ϕ = 0.028 in aerated solution).[14] Experimental error ±30%.

Tb^{3+}. The number calculated are 5.1 and 5.6 for Eu^{3+}- and Tb^{3+}- complexes, respectively, suggesting that only 4 -5 water molecules are expelled.[12] The emission quantum yields, nevertheless, are high as described above. This might be due to the occurrence of energy transfer with high efficiency from ligands to metal ions, i. e., the lanthanide ions are not located on carboxylate units but in proximity to benzene ring, although details remain unclear at the present time (Scheme 1).



Scheme 1.

Thus, **1** forms a stable 1:2 complex with Eu^{3+} and Tb^{3+}. It is noteworthy that the quantum yields are high, which is probably due to the efficient energy transfer from ligand to metal ions, in spite of insufficient shielding effect. On the basis of these results, the preparation of new host molecules for lanthanide ions utilizing cyclotriphosphazene are currently underway.

References and Notes

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6 **1**: Anal. Found: C, 42.03; H, 2.39; N, 3.48%. Calcd for $C_{42}H_{24}N_3O_{18}P_3Na_6 \cdot 5.5H_2O$: C, 42.44; H, 2.97; N,3.54%. IR(KBr) 1560, 1410, 1220-1160 cm^{-1}. ^1H NMR(270 MHz, D_2O) 7.68 (12H, d, J = 8.5 Hz), 6.79 (12H, d, J = 8.0 Hz).

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8 Found: C, 36.86; H, 2.76; N, 3.46; Eu, 22.07%. Calcd for $C_{42}H_{24}N_3O_{18}P_3Eu_2 \cdot 6H_2O$: C, 36.98; H, 2.64; N, 3.08; Eu, 22.29%. Found: C, 35.16; H, 2.73; N, 3.02; Tb, 21.91%. Calcd for $C_{42}H_{24}N_3O_{18}P_3Tb_2 \cdot 8H_2O$: C,35.69; H, 2.85; N, 2.97; Tb, 22.48%. The content of lanthanide metals were determined by ethylenediaminetetraacetic acid titrations using xylenol orange as an indicator.[15]

9 In the mixture of sodium benzoate and Eu^{3+}, the emission of the ions was not observed, indicating that benzoate anions do not form the complex with Eu^{3+}.

10 Absorption spectra were measured with a Shimadzu UV-260 spectrophotometer. Excitation and emission spectra were measured with a Shimadzu RF-5000 spectrofluorometer.

11 Lifetime measurements were carried out using a modified UNISOKU FSS-400 spectrometer equipped with a Hamamatsu R2949 phototube and a transient memory (KAWASAKI TMR-80). The samples were excited by the UV light of 260 nm selected through Toshiba interference filter from a pulsed lamp (UNISOKU TSP-601-12). The resulting emission was detected at 620 nm for Eu^{3+} and 545 nm for Tb^{3+}.

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