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# Energy-Transfer Luminescence of Lanthanide Ions Complexed with Water-Soluble Calix[n]arenes

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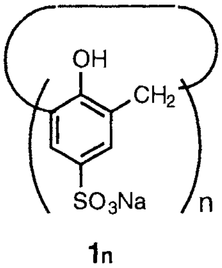
It was shown that $Tb^{3+}$ ion complexed with water-soluble calix[n]arenes becomes strongly fluorescent on the basis of energy-transfer luminescence ($\Phi$=0.02-0.20).

The luminescence properties of lanthanide ions have been of much recent endeavor because of their potential use as probes and labels for a variety of chemical and biological applications. It has already been shown that certain calix[4]arene derivatives are useful as potential ligands for energy-transfer luminescence of $Tb^{3+}$ because $Tb^{3+}$ is efficiently shielded from solvent molecules through encapsulation into the calix[4]arene and the benzene rings have the lowest excited-state sufficiently high for the energy-transfer to $Tb^{3+}$.1-3) For biological applications it is a prerequisite that these luminescent complexes are water-soluble. Previously, we exploited a new class of water-soluble calix[n]arenes with the *p*-sulfonate group.4,5) The calix[4]arenes specially designed in the past for energy-transfer luminescence in an aqueous system1,2) have ionophoric groups such as amides or pyridine-*N*-oxides for efficient encapsulation of $Tb^{3+}$, so that we considered that simple water-soluble calix[n]arenes (**1**$_n$) would not be useful for this purpose. Through the screening test of **1**$_n$ as a coloration reagent for transition and rare-earth metal cations,6,7) however, we unexpectedly found that **1**$_n$·$Tb^{3+}$ complexes show the strongly fluorescent nature even in water. We here studies the stoichiometries, quantum yields, and energy-transfer mechanisms of the **1**$_n$·$Tb^{3+}$ complexes. To the best of our knowledge, this is a rare example for energy-transfer luminescence in an aqueous system.

The fluorescence intensity of the **1**$_n$·$Tb^{3+}$ complexes is pH-dependent. The maximal intensity was observed at pH 12.5 for **1**$_4$, 13.0 for **1**$_6$, and 10.8 for **1**$_8$. The emission spectra at these pH's are illustrated in Fig. 1. It is seen from Fig. 1 that the spectra have four structures which correspond to the transition from $^5D_4$ to $^7F_6$ (488 nm), $^7F_5$ (543 nm), $^7F_4$ (583 nm), and $^7F_3$ (620 nm) in $Tb^{3+}$. The slight difference in the spectral pattern reflects the structural difference in the **1**$_n$·$Tb^{3+}$ complexes (*vide post*).



**1n**

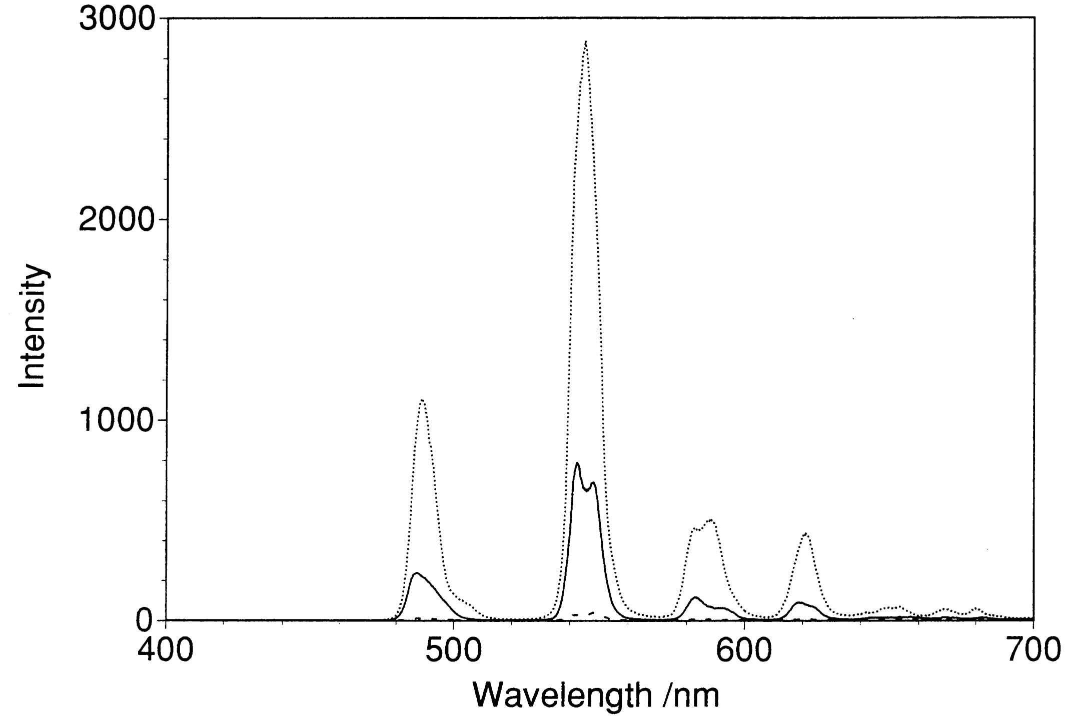


Fig. 1. Emission spectra of $1_n$·$Tb^{3+}$ complexes: 25 °C, $[Tb^{3+}]=5.20x10^{-7}$ mol $dm^{-3}$, $[1_4]=4.80x10^{-6}$ mol $dm^{-3}$, excitation at 260 nm for $1_4$ (——); $[Tb^{3+}]=1.56x10^{-6}$ mol $dm^{-3}$, $[1_6]=4.80x10^{-6}$ mol $dm^{-3}$, excitation at 260 nm for $1_6$ (- - - -); $[Tb^{3+}]=1.56x10^{-5}$ mol $dm^{-3}$, $[1_8]=1.60x10^{-6}$ mol $dm^{-3}$, excitation at 255 nm for $1_8$ (·······). The spectra were corrected for the sensitivity.

Absorption and excitation spectra are illustrated in Fig. 2. Both spectra are similar to each other, indicating that fluorescence arises from the energy-transfer from the chromophoric benzene rings to bound $Tb^{3+}$. From a continuous variation method we estimated the stoichiometry of the $1_n$·$Tb^{3+}$ complexes to be 2:1 ($1_n/Tb^{3+}$) for $1_4$ and 1:1 for $1_6$ and $1_8$.

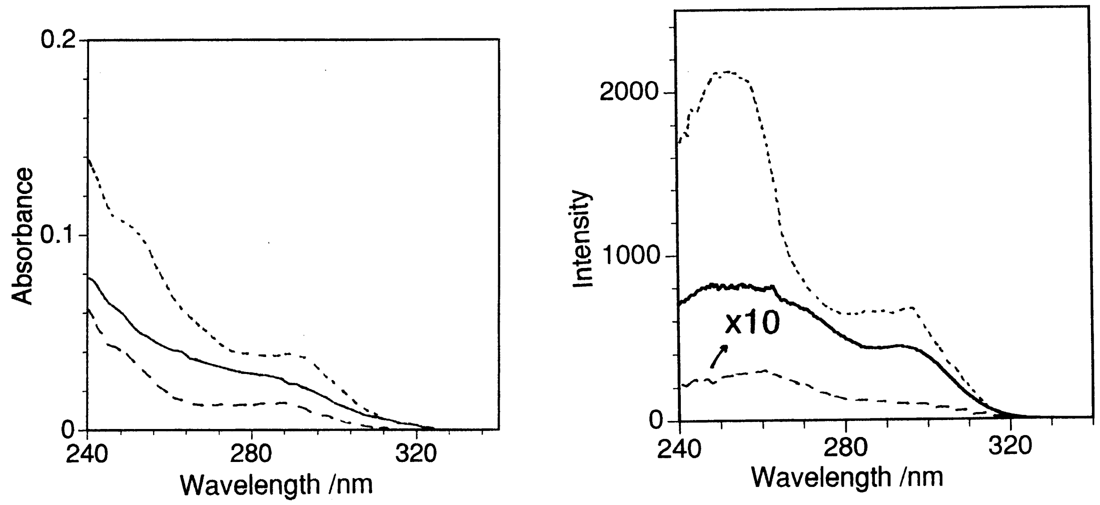


Fig. 2. Absorption and excitation spectra of complexes: 25 °C, emission 543 nm for $1_4$ (——), 548 nm for $1_6$ (- - - - - -), and 545 nm for $1_8$ (·······). The concentrations were recorded in a caption to Fig. 1. The excitation spectra were corrected for the sensitivity.

We plotted the fluorescence intensity at 543 nm for $\mathbf{1_4}$ and $\mathbf{1_6}$ against $[\mathbf{1_n}]/[Tb^{3+}]$ while the $Tb^{3+}$ concentration was maintained constant. A plateau was obtained at $[\mathbf{1_n}]/[Tb^{3+}]=10$ for $\mathbf{1_4}$ and 3 for $\mathbf{1_6}$, where their quantum yields were determined with respect to an aquo ion of $Tb^{3+}$ ($\Phi=0.08$ for 308 nm excitation). On the other hand, the $\mathbf{1_8}\cdot Tb^{3+}$ complex did not give a stable plateau but the fluorescence intensity decreased at the high $\mathbf{1_8}$ concentration via a maximal value. We thus made a plot of the fluorescence intensity versus $[Tb^{3+}]/[\mathbf{1_8}]$ while the $\mathbf{1_8}$ concentration was maintained constant. We obtained a stable plateau at $[Tb^{3+}]/[\mathbf{1_8}]>9$, where we determined the quantum yield (Table 1).

Table 1. Luminescence quantum yields of $\mathbf{1n}\cdot Tb^{3+}$ complexes in water at 25 °C

| $\mathbf{1_n}$ (conc./mol $dm^{-3}$) | $Tb^{3+}$ /mol $dm^{-3}$ | Ex /nm | $\Phi$ |
|---|---|---|---|
| $\mathbf{1_4}$ ($4.80 \times 10^{-6}$) | $5.21 \times 10^{-7}$ | 260 | 0.13 |
| $\mathbf{1_4}$ ($4.80 \times 10^{-6}$) | $5.21 \times 10^{-7}$ | 295 | 0.13 |
| $\mathbf{1_6}$ ($4.80 \times 10^{-6}$) | $1.56 \times 10^{-6}$ | 260 | 0.02 |
| $\mathbf{1_8}$ ($1.60 \times 10^{-6}$) | $1.56 \times 10^{-5}$ | 255 | 0.20 |

Examination of Table 1 reveals that the quantum yields for $\mathbf{1_4}$ and $\mathbf{1_8}$ are very high as comparable with those obtained from ionophoric calix[4]arenes in acetonitrile ($\Phi=0.16$-$0.27$).1-3) Since the energy-transfer mechanism should be similar (*i.e.*, from phenol to $Tb^{3+}$),8) the difference in the quantum yields would be ascribed to the difference in the metal encapsulation ability. As demonstrated from the stoichiometry, $Tb^{3+}$ ion in the $\mathbf{1_4}\cdot Tb^{3+}$ complex is sandwiched by two $\mathbf{1_4}$ molecules. The number of phenolic oxygen around $Tb^{3+}$ ion is therefore eight and water molecules can hardly find the remaining coordination site. In contrast, $\mathbf{1_6}$ forms a 1:1 complex and the number of phenolic oxygen is only six. This situation allows the coordination of water molecules, resulting in fluorescence quenching by the coordinated water molecules.9) To explain the high quantum yield for the $\mathbf{1_8}\cdot Tb^{3+}$ complex, we now presume the formation of a 2:2 complex which is capable of encapsulating $Tb^{3+}$ ions (although the detail is still a matter of discussion) because (i) the plot of the fluorescent intensity versus $[\mathbf{1_8}]/[Tb^{3+}]$ does not satisfy the equilibrium-shift equation for a 1:1 complex, (ii) the plot based on the equation $K=[(\mathbf{1_8})_2\cdot(Tb^{3+})_2]/[\mathbf{1_8}]^2[Tb^{3+}]^2$ gives a good linear relationship, and (iii) the coordination of eight phenolic oxygens in $\mathbf{1_8}$ is structurally difficult.

In conclusion, the present paper shows that water-soluble calix[n]arenes $\mathbf{1_n}$ serve as a useful ligand for energy-transfer luminescence in an aqueous system.

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8) The energy transfer occurs from the excited state ($^3\pi\pi^*$) in the benzene moiety to the excited state ($^5D_3$ or $^5D_4$) in $Tb^{3+}$ and the emission occurs from the $^5D_4$ level. The phosphorescence emission from $^3\pi\pi^*$ is partially overlapped with the absorption band of $Tb^{3+}$. The details of the energy-transfer mechanism have been discussed in Refs. 1 and 3.

9) The preliminary results for the measurement of fluorescence life time indicate that in $D_2O$ $\Phi$ for the **14**·$Tb^{3+}$ complex is scarcely increased whereas that for the **16**·$Tb^{3+}$ complex is significantly increased. This supports the view that the **16**·$Tb^{3+}$ complex is partly hydrated.

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