Energy Transfer Luminescence of Tb^{3+} Complexed with Oxyethylene Compounds Containing Xanthene

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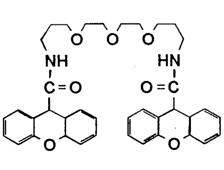
Three polyether compounds (**1-3**) which have more than two fluorescent moieties in the both terminals were synthesized, and their complexation properties with Tb^{3+} were discussed. After formation of complex with Tb^{3+}, sharp fluorescence lines were observed at visible region due to intramolecular energy transfer from xanthene chromophore to bound Tb^{3+}. The correlation between energy transfer efficiency and ligand structure for three analogous compounds were investigated.

Photophysical and photochemical features of lanthanide complexes have been of much interest as efficient luminescent materials and as labeling materials in chemical and biological applications. Crown ether derivatives,[1] 2,2'-bipyridine-containing multidentate lignds,[2,3] and other derivatives[4,5] have been reported to form complexes with lanthanide cations, and to emit luminescence in aqueous solution, organic solution, crystal, or at the air-water interface. On the other hand, the coordination chemistry of acyclic polyethylene glycols with lanthanide cations is less extensive. In this communication, three polyoxyethylene compounds having two fluorescent chromophores at both terminals have been synthesized, and structural changes before and after formation of complex with alkali or alkaline earth cations were studied by means of fluorescence spectral changes, which were evolution of excimer emission and fluorescence quenching.[6,7] In this study, xanthene[8] and benzene moieties[9] were used as efficient energy mediators, since their excited triplet energy levels are higher than the energy levels of excited Tb^{3+}.

Compound **1** was prepared from xanthene-9-carboxylic acid in the same manner as reported previously.[6] Compound **2** was synthesized by coupling of 2,2'-[oxybis(3-oxapentamethylene-oxy)]bis benzoic acid with 9-xanthene methylamine which was prepared by reduction of 9-xanthenecarbonamide with the use of B_2H_6. Their structure was confirmed by ^{1}H-NMR spectra and elemental analysis.[10] Fluorescence and excitation spectra were measured in purified acetonitrile at 25 °C. Terbium trichloride hexahydrate was used.



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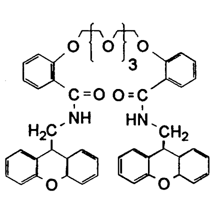

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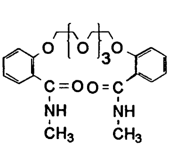

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In the absence of Tb^{3+}, **1** gave an emission of xanthene monomer around at 300 nm (Figure 1). On the other hand, **1**• Tb^{3+} indicated the disappearance of monomer emission which was caused by an increase in the intersystem crossing rate from S_1 to T_1 due to a paramagnetic ion, and luminescence having four lines which corresponded to the transition from $^5D_4$ to $^7F_6$(488 nm), $^7F_5$(543 nm), $^7F_4$(583 nm), and $^7F_3$(620 nm). This was caused by that UV light energy absorbed by xanthene moiety of **1** was transferred into visible light of Tb^{3+} emission via intramolecular energy transfer. When equimolar amount of **1** was added to Tb^{3+}, fluorescence intensity at 543 nm had about 400 times larger than that of Tb^{3+} itself.

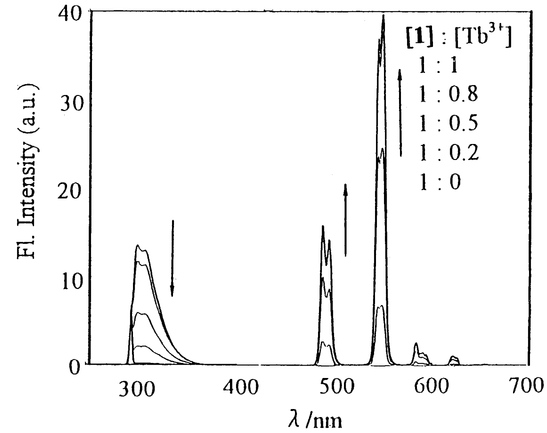

Figure 1. Fluoresence spectra of **1**•Tb^{3+} in CH_3CN at 25 °C. [**1**] = 1×10^{-5} M. Excitation wavelength : 292 nm.

To determine stoichiometry of complexes and complex formation constants several consentration of Tb^{3+} was added to 1×10^{-5} M of **1**, and the emission intensity of Tb^{3+} was observed. It was shown that the emission intensity (at 543 nm) was gradually saturated with increase of concentration of Tb^{3+} and reached an asymptotic value above $[Tb^{3+}]$ / [**1**] = 1 showing a 1:1 complex at this point. A bending point was also observed at $[Tb^{3+}]$ / [**1**] = 0.5 showing a 1 : 2 complex formation. Thus, on the assumption that **1** forms a 1 : 2 complex ($[Tb^{3+}]$: [**1**]) at low concentration of Tb^{3+} and a 1 : 1 complex at high concentration of Tb^{3+}, complex formation constants were evaluated by means of non-linear least square curve fitting method,[6] and were listed in Table 1.

Table 1. Complex formation constants, molar extinction coefficients at 284 nm, and relative quantum yields in CH_3CN at 25 °C

L	$\log K_1$	$\log K_2$	ε	ε•Φ_{rel}	Φ_{rel}
1	6.59	4.17	6400	6400	1.00
2	7.21	4.97	18800	3948	0.21
3	4.05	-	4200	3570	0.85

$$K_1 = \frac{[L\cdot Tb^{3+}]}{[L][Tb^{3+}]} \qquad K_2 = \frac{[L_2\cdot Tb^{3+}]}{[L\cdot Tb^{3+}][L]}$$

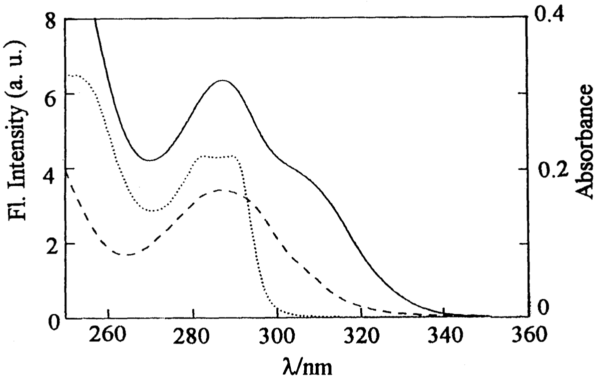

Figure 2. Excitation spectrum of **2** • Tb^{3+}(solid line), absorption spectra of **1**•Tb^{3+}(dotted line) and **3**•Tb^{3+} (broken line) in CH_3CN at 25 °C. Monitored wavelengh : 543 nm. $[\mathbf{1}] = [\mathbf{2}] = [\mathbf{3}] = [Tb^{3+}] = 1\times10^{-5}$ M.

A relationship between the emission efficiency and the sensitizer structure was investigated by using analogous compounds (**2** and **3**). The complex formation constants, molar extinction coefficients at 284nm, and relative quantum yields ($\Phi = 1$ for **1**) of these compounds are summarized in Table 1. Complex formation constants and molar extinction coefficients of **2** which contained two benzene rings in the polyether chain of **1** were the largest in all the compounds, whereas its quantum yield was the lowest. On the other hand, compound **3**, which has only benzene moieties in the molecule, had high quantum yield in spite of its lower molar extinction coefficient than that of **2**. To clarify this phenomenon, excitation spectrum of **2** • Tb^{3+} (monitored at 543 nm) and absorption spectra of **1** and **3** in the presence of Tb^{3+} were measured (Figure 2). The shape of excitation spectrum of **2**•Tb^{3+} resembled to that of absorption spectrum of **3**•Tb^{3+} more than that of **1**•Tb^{3+}. This result indicated that benzene chromophore of **2** dominated over the energy transfer to bound Tb^{3+}, and the efficiency from xanthene to Tb^{3+} decreased.

This reason was explained in terms of energy level difference in benzene and xanthene, and the distance between the sensitizers and Tb^{3+}. **2** and **3** themselves showed broad emission spectra around at 340 nm due to n-π* transition derived from phenolic ether derivative. However, **2** did not gave the emission of xanthene monomer around at 300 nm which was observed in fluorescence spectrum of **1**. This observation indicated that excitation energy of S_1 level of xanthene transferred into n-π* excited energy level of benzene moiety. As a result, excited energy of singlet xanthene transferred indirectly into Tb^{3+} via n-π* energy level of phenolic ether derivative. This multistep energy transfer would cause the lowest quantum yield of **2**.

As another reason, it should be considered that the rate of triplet-triplet energy transfer from triplet state depends on the distance between donor and acceptor. When **2** complexes with Tb^{3+}, benzenes which are bound to oxyethylene moiety can locate near Tb^{3+} and transfer the excitation energy to Tb^{3+} efficiently. On the other hand, xanthene is squeezed out and is far from Tb^{3+} and can not transfer excitation energy efficiently. This caused the lowest quantum yield of **2**•Tb^{3+}. In the case of **3**•Tb^{3+}, benzene chromophore could transfer excitation energy into Tb^{3+} efficiently because of short distance between Tb^{3+} and benzenes, which caused high quantum yield.

As shown in Table 1, **1** and **2** both of which contained xanthene moieties had about 1000 times higher complex formation constants than those of **3**. This result shows that interaction between both terminal xanthene moieties contributes greatly to stabilization of the complex like a dimer formation.

References and Notes

1 M. Sowinska, M.-T. LeBris, and B. Valeur, *J. Photochem. Photobiol.*, **60**, 383 (1991).

2 V. Balzani, E. B. Hmans, J.-M. Lehn, N. Sabbatani, R. Terodeand, and R. Ziessel, *Helv. Chim. Acta.*, **73**, 2083 (1990).

3 V. Alexander, *Chem. Rev.*, **95**, 273 (1995).

4 N. Sato, I. Yoshida, and S. Shinkai, *Chem. Lett.*, **1993**, 1261.

5 N. Sato, M. Goto, S. Matsumoto, and S. Shinkai, *Tetrahedron. Lett.*, **34**, 4847 (1993).

6 Y. Kakizawa, T. Akita, and H. Nakamura, *Chem. Lett.*, **1993**, 1671.

7 R. Tahara, K. Hasebe, and H. Nakamura, *Chem. Lett.*, **1995**, 753.

8 M. B. Ryzhikov, A. N. Rodinov, and A. N.Stepanov, *Zh. Fiz. Khim.*, **63**, 2515 (1989).

9 T. V.-Dinh, E. L. Yen, and, J. D. Winefordner, *Anal. Chem.*, **48**, 1186 (1976).

10 *N,N'*-(4,7,10-trioxatridecane-1,13-diyl)bis(xanthene-9-carbonamide) (**1**) :Yield 40.5%, white crystal, mp 185-187 °C, ^{1}H-NMR($CDCl_3$, 400MHz) δ = 1.55 -1.61 (4H, m), 3.21 (4H, q), 3.30 (4H, t), 3.35 (4H, d), 3.43 (4H, d), 4.85 (2H, s), 5.86 (2H, t), 7.06 - 7.12 (8H, m), 7.28 (4H, t), 7.37 (4H, d). Found: C, 71.22; H, 6.50; N, 4.38%. Calcd for $C_{38}H_{40}N_2O_7$: C, 71.69; H, 6.33; N, 4.40%.
2,2-oxybis(3-oxapentamethyleneoxy)bis[*N*-(xanthene-9-methylene-benzamide] (**2**): Yield 15.6%, oil, ^{1}H-NMR ($CDCl_3$, 400MHz) δ = 3.15 - 3.19 (4H, m), 3.22 - 3.26 (4H, m), 3.35 - 3.38 (4H, m), 3.50 -3.55 (4H, m), 3.99 - 4.03 (4H, m), 4.35 (2H, t), 6.85 (2H, d), 7.05 - 7.15 (8H, m), 7.20 - 7.38 (10H, m), 7.45 (2H, t), 8.22 (2H, d), 8.35 (2H, t). Found: C, 67.99; H, 6.02; N, 3.15%. Calcd for $C_{50}H_{48}N_2O_9$•7/2H_2O: C, 67.94; H, 6.27; N, 3.17%.
2,2-oxybis(3-oxapentamethyleneoxy)bis[*N*-methylbenzamide] (**3**):Yield 30.5%, oil, ^{1}H-NMR ($CDCl_3$, 400MHz) δ = 3.68 -3.75 (8H, m), 3.92 - 3.95 (4H, m), 4.39 - 4.42 (4H, m), 5.52 (6H, d), 7.05 (d, 2H), 7.12 (t, 2H), 7.52 (t, 2H), 8.15 (d, 2H). Found: C, 58.25; H, 7.38; N, 5.42%. Calcd for $C_{24}H_{32}N_2O_7$•2H_2O: C, 58.06; H, 7.31; N, 5.64%.