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Energy-Transfer Luminescence of Lanthanide Ions Encapsulated in Calix[4]arenes. Correlation between the Energy Level of Sensitizers and the Quantum Yield

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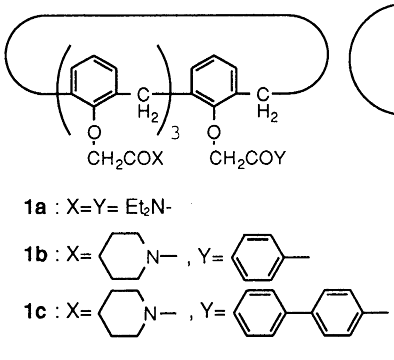
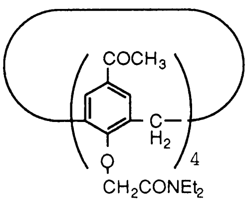
It was shown that the Tb^{3+} and Eu^{3+} complexes of 5,11,17,23-tetraacetyl-25,26,27,28-tetrakis(*N*,*N*-diethylaminocarbonylmethoxy)calix[4]arene give the high luminescence quantum yields (Φ=0.164 for Tb^{3+} and 0.017 for Eu^{3+}). The mechanistic investigations established that the high quantum yields are due to the energy level suitable to the energy-transfer and the presence of the carbonyl groups which mediate the intersystem crossing.

The luminescence properties of lanthanide ions (Ln^{3+}) have been of much recent attention because of their potential applications to probes and labels for a variety of chemical and biological systems. The past studies teach us that to design such an efficient emitting system from Ln^{3+} it must satisfy two prerequisites: that is, (i) desolvation of Ln^{3+} through encapsulation in the ligand and (ii) efficient energy-transfer from a sensitizer to concerned Ln^{3+}.1) It has been shown that amide derivatives of calix[4]arenes satisfy prerequisite (i) through encapsulation of Ln^{3+} in the ionophoric cavity.1,2) In the Tb^{3+} complexes which emit green light prerequisite (ii) is potentially satisfied by energy-transfer from benzene groups combined in the calix[4]arene ring because they usually give Φ=0.1-0.3.1,2) In contrast, the Φ values for the Eu^{3+} complexes which emit red light are generally low (*ca.* 10^{-4}) because of inefficient energy-transfer and/or possible energy-transfer to the C=O-to-Eu^{3+} charge-transfer band.1-3) We previously found that **1b** and **1c** which have respectively a benzoyl group and a biphenylcarbonyl group as an intramolecular sensitizer give the somewhat improved Φ (0.060-0.061) for Eu^{3+}.1) The results imply that energy-transfer to Eu^{3+} can take place, although partially, from these sensitizer groups but the mechanistic view why the energy-transfer is allowed was not investigated in detail.





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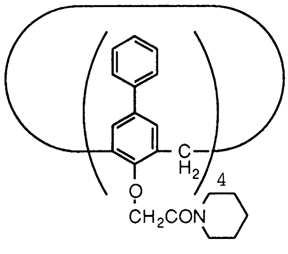

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To obtain an insight into a possible correlation between the emission efficiency and the sensitizer structure we synthesized calix[4]arene derivatives **2** and **3**. In comparison to **1a**, compound **2** is useful to examine the role of the cabonyl group and compound **3** is useful to examine the energy-transfer efficiency from the expanded conjugation system without the carbonyl group. In comparison to **1b** and **1c**, one can discuss the influence of the spatial distance between the sensitizer and Ln^{3+}. We found that the carbonyl group plays an important role in the intersystem crossing and sensitizer should be appeared in the close proximity of Ln^{3+}.

Compound **2** was synthesized from the reaction of 5,11,17,23-tetraacetylcalix[4]arene-25,26,27,28-tetrol⁴⁾ and *N,N*-diethylchloroacetamide in the presence of K_2CO_3: mp 229-230 °C, yield 27%. Compound **3** was synthesized from the reaction of 5,11,17,23-tetraphenylcalix[4]arene-25,26,27,28-tetrol⁵⁾ and bromoacetopiperidine in the presence of Na_2CO_3: mp 230-236 °C, yield 30%. The structures were identified by IR and ^1H NMR spectral evidence and elemental analysis. ^1H NMR spectroscopy supported that these compounds are immobilized to a cone conformation.

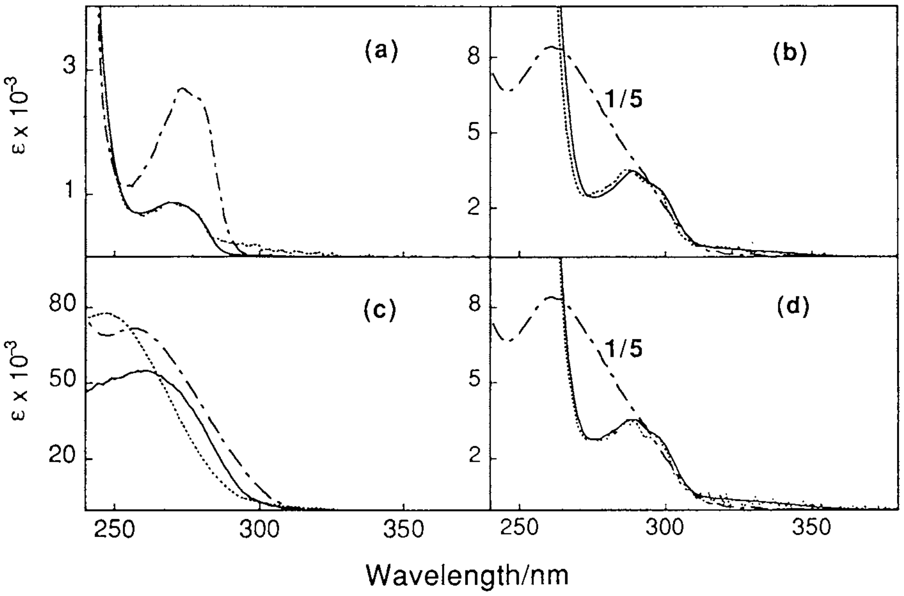

Fig. 1. Absorption (----) and excitation (——) spectra of four complexes: acetonitrile, 25 °C, emission 542 nm for Tb^{3+} complexes and 614 nm for the Eu^{3+} complexes: (a) **1a** (1×10^{-5} mol dm^{-3}) + $TbCl_3 \cdot 6H_2O$ (5×10^{-5} mol dm^{-3}); (b) **2** (1×10^{-5} mol dm^{-3}) + $TbCl_3 \cdot 6H_2O$ (5×10^{-5} mol dm^{-3}); (c) **3** (1×10^{-5} mol dm^{-3}) + $TbCl_3 \cdot 6H_2O$ (5×10^{-5} mol dm^{-3}); (d) **2** (1×10^{-5} mol dm^{-3}) + $EuCl_3 \cdot 6H_2O$ (5×10^{-5} mol dm^{-3}). (– – –) inserted into each spectrum shows the absorption spectra of free ligands.

We first estimated the stoichiometry of the Tb^{3+} complexes and **2**•Eu^{3+} complex at 25 °C in acetonitrile by a continuous variation method. $TbCl_3 \cdot 6H_2O$ and $EuCl_3 \cdot 6H_2O$ were used for this purpose. To choose the wavelength for ordinate we measured the emission spectra of the complexes. They displayed three to five structures. Of them, we chose the strongest peak at 542 nm for Tb^{3+} and 614 nm for Eu^{3+}. For **1a**•Eu^{3+} and **3**•Eu^{3+} complexes the stoichiometry of these complexes were confirmed by isosbestic points of absorption spectra of **1a** and **3** with successive additions of $EuCl_3 \cdot 6H_2O$ because the luminescence intensity of **1a**•Eu^{3+} and **3**•Eu^{3+} complexes were very small, and the luminescence of free Eu^{3+} present in excess could not be removed completely. These isosbestic points were observed at 289 nm for the **1a**•Eu^{3+} complex, at 236, 260, and 307 nm for the **3**•Eu^{3+} complex. They were shown that **1a**, **2**, and **3** all form a 1:1 complex. We then plotted the emission intensity against the metal concentration while the ligand concentration was maintained constant. It was shown that the emission intensity reaches a plateau above [Ln^{3+}] > [calix[4]arene]. We thus determined the measurement conditions as [Ln^{3+}]/[calix[4]arene]=5.0. Absorption spectra for free calix[4]arenes and absorption and excitation spectra for Tb^{3+} complexes and a **2**•Eu^{3+} complex are illustrated in Fig. 1. In the absorption spectra for **1** and **3** (Fig. 1a and c) a slight blue shift and a significant intensity change occurred upon complexation with Ln^{3+}. These changes are attributed to the decrease in the electron density of the OCH_2 groups interacting with Ln^{3+}. Compound **2** has push (R-O-) and pull (CH_3CO-) substituents within a molecule. The interaction with Ln^{3+} suppresses the electron-donating ability of the push (R-O-) substituents. This change is reflected as a difference between free **2** and **2**•Ln^{3+} complexes (Fig. 1b and d). In these complexes, both spectra are similar to each other, indicating that fluorescence arises from energy-transfer from the chromophores in calix[4]arenes to bound Ln^{3+}.6) In **3** the fluorescence emission from the biphenyl groups also appears at this wavelength region (330 nm).

Table 1. Lifetimes and quantum yields of the luminescence of Tb^{3+} and Eu^{3+} complexes in acetonitrile at 25 °C

	Tb^{3+}		Eu^{3+}	
Ligand	τ/ms a)	Φ (λex/nm)	τ/ms a)	Φ (λex/nm)
1a	1.07	0.128 (270)	—	< 0.001 (285)
2	1.11	0.164 (289)	1.17	0.017 (288)
3	0.76	0.072 (300)	—	< 0.001 (300)

a)Measured in correspondence with the most intense emission band (542 nm for Tb^{3+} complexes and 614 nm for Eu^{3+} complex).

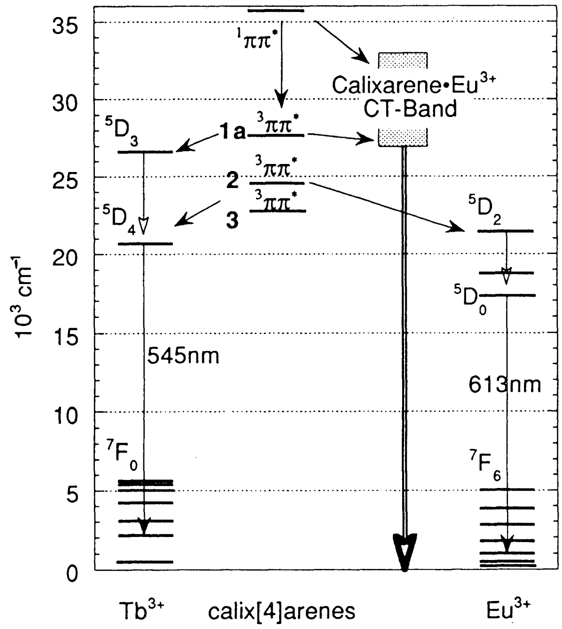

Fig. 2. Schematic energy level diagram for the Tb^{3+}, Eu^{3+}, and calix[4]arenes.

The Φ values were determined by using aquo ions of Tb^{3+} (Φ=0.08 for 370 nm excitation)7) or Eu^{3+} (Φ=0.0073 for 394 nm excitation)8) as standards. Under these measurement conditions the emission intensity was not affected by free Ln^{3+} present in excess. The results and luminescence lifetimes (τ) of complexes are summarized in Table 1.

Comparison of the **2** complexes with the **1a** complexes reveals that the Φ for the **2**•Tb^{3+} complex is only slightly higher than that for the **1a**•Tb^{3+} complex whereas the Φ for the **2**•Eu^{3+} complex is incomparably higher than that for the **1a**•Eu^{3+} complex. The difference indicates the importance of the carbonyl group in the energy-transfer to Eu^{3+}. The similar trend is also seen between the **2** and **3** complexes but the Φ for the **2**•Tb^{3+} complex is higher by more than 2-fold than that for the **3**•Tb^{3+} complex. To obtain a further insight into the energy-transfer mechanism we measured the phosphorescence spectra of the three calix[4]arenes at 77 K in dichloromethane:methanol=1:1 v/v. The spectral study established that the triplet energy levels are 27500 cm^{-1} (τ=1.2 s) for **1a**, 24400 cm^{-1} (τ=200 ms) for **2**, and 22600 cm^{-1} (τ=1.9 s) for **3**. Taking these energy levels into account,[1,2,9] we can now propose an energy-transfer diagram as in Fig. 2. The triplet energy levels of **1a**, **2**, and **3** are high enough to transfer the energy to the Tb^{3+} ion levels. The high Φ for **2** in comparison to those of **1a** and **3** is attributed to the contribution of the carbonyl groups facilitating the intersystem crossing. The Φ for **3** is unexpectedly low. Probably, this energy-transfer is energetically-unfavorable because (i) the distance between the energy donors (biphenyl groups) and Tb^{3+} is longer than others and (ii) a particular deactivation process presents in **3** because of the shorter lifetime and the observation of fluorescence of biphenyl groups. On the other hand, energy-transfer to Eu^{3+} is complicated by the presence of the ligand-to-metal charge-transfer band at 300-370 nm (33300-27000 cm^{-1})[1,2,9] and the Φ values are generally low. In **1a** both the singlet level and the triplet level can be deactivated by the charge-transfer band and one can only observe weak emission from the charge-transfer band. In **3**, the Φ is low again. This is attributed to the emission from the singlet level and the long distance from the chromophore to Eu^{3+} although the triplet level is not deactivated by the charge-transfer band. In fact, one can observe fluorescence from the biphenyl groups. In **2**, in contrast, the carbonyl groups facilitate the intersystem crossing and the triplet state is not deactivated by the charge-transfer band. Thus, energy-transfer can take place efficiently from the triplet level to the ^5D levels. This is why **2** gives the higher Φ values (0.017).

In conclusion, the present paper shows that the high luminescence quantum yields of Tb^{3+} or Eu^{3+} encapsulated in calix[4]arenes are attained by skillfully choosing the triplet energy level of calix[4]arenes against the excitation level of Tb^{3+} or Eu^{3+} ion and introducing the carbonyl groups facilitating the intersystem crossing. Taking these structural requirements into considerations, we are now designing new calix[4]arenes which can efficiently transfer the energy to Eu^{3+}.

References

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6) In Fig. 1c, the excitation spectrum at 250 nm region is a little weaker than the absorption spectrum. This is due to the excitation probability reduced by the presence of the strong absorption band and to the difficulty in the correction at this wavelength region.
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