

Saccharide Control of Energy-transfer Luminescence of Lanthanide Ions Encapsulated in Calix[4]arenes: A Novel Discrimination Method for the Energy-transfer Route

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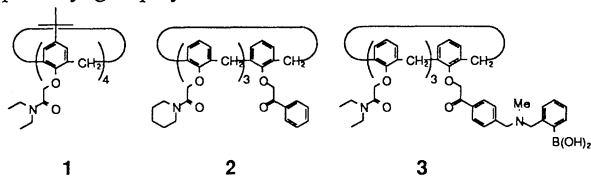
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A calix[4]arene bearing three amide groups (composing a lanthanide binding site) and one sensitizer (phenacyl group) bearing an (*o*-boronylphenyl)methylaminomethyl group (acting as a sugar-binding site) was synthesized. The energy-transfer to Eu^{3+} was significantly enhanced whereas that to Tb^{3+} was only slightly enhanced, indicating that in the Eu^{3+} complex the energy is mainly transferred from the sensitizer whereas in the Tb^{3+} complex it is mainly transferred from the calix[4]arene aromatic rings. This is a novel method for discriminating the energy-transfer path.

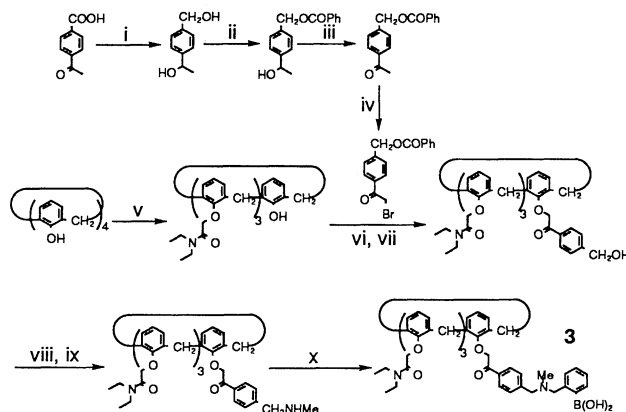
The luminescence properties of lanthanide ions have been of much interest because of their potential use as probes and labels for a variety of chemical and biological applications. To design a good emitting system one has to take two prerequisites into consideration: (i) lanthanide ions must be shielded from solvent molecules through encapsulation into the ligand and (ii) the ligand must have the lowest excited-state sufficiently high for the energy-transfer to lanthanide ions.¹⁻⁷ More recently, Sabbatini *et al.*⁸ found that Eu^{3+} and Tb^{3+} are strongly encapsulated into 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(diethylcarbamoylmethoxy)calix[4]arene (**1**)⁹; interestingly, the **1**• Tb^{3+} complex exhibited a remarkably high luminescence quantum yield ($\Phi = 0.2$). They proposed that **1** possesses a $^3\pi$, π^* level from which the energy-transfer to $^5\text{D}_3$ or $^5\text{D}_4$ in Tb^{3+} can take place.⁸ On the other hand, the luminescence quantum yield for **1**• Eu^{3+} is extremely low ($\Phi = 2 \times 10^{-4}$).⁸ This peculiar finding is rationalized by the presence of the C=O-to- Eu^{3+} charge-transfer band which efficiently deactivates the excited state of the phenol unit.⁸ To obviate this problem one has to seek for the sensitizer that has an energy level lower than the charge-transfer band but higher than the emission band. We synthesized compound **2** bearing a phenacyl group, the Eu^{3+} complex of which gave $\Phi = 0.060$ suggesting the significant contribution of the energy transfer process from this group.^{10,11}

To obtain further insights into the energy transfer mechanism we newly synthesized compound **3**. In **3** the excited state of the phenacyl group is efficiently quenched by the intramolecular amine whereas in the presence of saccharides this amine cannot act as a quencher because of the B-N interaction intensified by boronic acid-saccharide complexation.¹² Hence, one can selectively discriminate the energy-transfer path including the phenacyl group by added saccharides.



Compound **3** was synthesized according to Scheme 1 and identified by ^1H NMR, IR and mass spectral evidence and elemental analysis. MeOH (containing 0.2 vol% MeCN) which

can solubilize both **3** and saccharides was used in the luminescence measurements. Emission and excitation spectra were corrected precisely by the use of a Hitachi F-4500 fluorescence spectrophotometer.



Scheme 1. Reagents and conditions: i, LiAlH_4 , THF; ii, $\text{C}_6\text{H}_5\text{COCl}$, NEt_3 , CH_2Cl_2 ; iii, DDQ, dioxane; iv, Br_2 , CHCl_3 ; v, $\text{ClCH}_2\text{CONEt}_2$, BaO , DMF; vi, K_2CO_3 , acetone; vii, LiOH , MeOH, H_2O ; viii, $(\text{MeSO}_2)_2\text{O}$, CHCl_3 ; ix, MeNH_2 , MeOH; x, *o*- $\text{BrCH}_2\text{C}_6\text{H}_4\text{B}(\text{OH})_2$, Cs_2CO_3 , MeCN.

The measurements were carried out in MeOH:MeCN = 500:1 v/v at 25 °C. We plotted the emission intensity (λ_{em} 543 nm for the **3**• Tb^{3+} complex and 614 nm for the **3**• Eu^{3+} complex) against the metal concentration while the concentration of **3** was maintained constant ($[\text{3}] = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$). It was found that the emission intensity is gradually saturated and reaches a plateau above $3 \times 10^{-4} \text{ mol dm}^{-3}$. Hence, we fixed the metal concentration to $5.00 \times 10^{-4} \text{ mol dm}^{-3}$ in the following experiments.

In Figure 1, we compared the emission spectra of the complexes **3** with the complexes **2**. Since the absorbance between **2** and **3** at excitation wavelength region is different and the determination of Φ in these complex system is not so easy, we used I/ϵ (I , relative fluorescence intensity; ϵ , extinction coefficient) as a measure of Φ . It is seen from Figure 1 that the spectra have four bands; when compared at 543 nm for Tb^{3+} and at 614 nm for Eu^{3+} , the I/ϵ values for the complexes **3** are smaller by a factor of 18 in Tb^{3+} and by a factor of 30 in Eu^{3+} than those for the complexes **2**.

Here, we estimated the influence of the saccharide-binding on the emission spectra. We chose D-fructose which is known to show the highest affinity with the boronic acid group.¹² The absorption spectra of the **2**• Tb^{3+} and **2**• Eu^{3+} complexes were slightly changed with the isosbestic points (285 nm for **2**• Tb^{3+} and 282 nm for **2**• Eu^{3+}). The spectral change is attributable to the interaction between the free lanthanide ions and saccharide¹³ or to the weak interaction between saccharides and the complexes. In

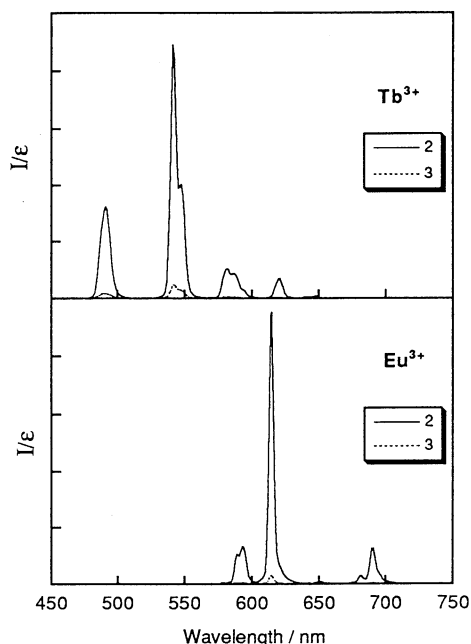


Figure 1. Emission spectra of the Tb^{3+} (upper) and Eu^{3+} (lower) complexes: 25 °C, MeOH:MeCN = 500:1 v/v, $[\text{2}] = [\text{3}] = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{TbCl}_3] = [\text{EuCl}_3] = 5.00 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{ex}} = 270 \text{ nm}$. The shorter wavelength light in emission is filtered with Toshiba Y-43. The absorbances for the complexes are fully small (0.156 for $\text{2} \cdot \text{Tb}^{3+}$, 0.228 for $\text{2} \cdot \text{Eu}^{3+}$, 0.102 for $\text{3} \cdot \text{Tb}^{3+}$, and 0.180 for $\text{3} \cdot \text{Eu}^{3+}$). One can thus regard that the emission intensity can be approximately compared with I/I_0 .

$\text{3} \cdot \text{Tb}^{3+}$ and $\text{3} \cdot \text{Eu}^{3+}$ complexes, the absorption spectra were also changed slightly with the isosbestic points (282 nm for $\text{3} \cdot \text{Tb}^{3+}$ and 274 nm for $\text{3} \cdot \text{Eu}^{3+}$). The isosbestic wavelengths were used for excitation in making plots of (I/I_0) versus $[\text{D-fructose}]$ (Figure 2). It is seen from Figure 2 that the emission intensity of the complexes **2** is scarcely enhanced by the addition of D-fructose (less than 1.4 fold). In contrast, the emission intensity of the complexes **3** is enhanced with increasing D-fructose concentration, the enhancement magnitude being ca. 9 times for the $\text{3} \cdot \text{Eu}^{3+}$ complex and ca. 2 times for the $\text{3} \cdot \text{Tb}^{3+}$ complex. As the D-fructose-binding to the boronic acid moiety should change only the energy-transfer efficiency from the phenacyl group, one can confidently conclude that in the $\text{3} \cdot \text{Eu}^{3+}$ complex the excited energy is transferred mainly from the phenacyl group whereas in the $\text{3} \cdot \text{Tb}^{3+}$ complex that is transferred mainly from the

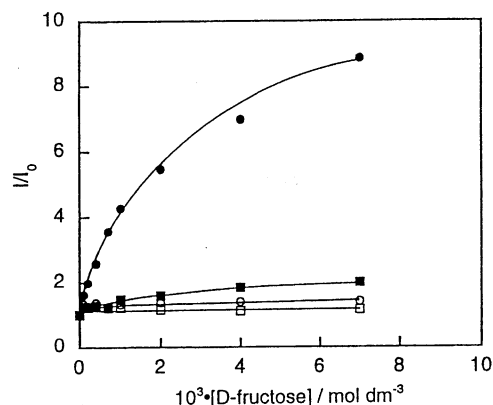


Figure 2. Plots of the emission intensity (I/I_0) versus $[\text{D-fructose}]$. λ_{ex} and λ_{em} are 285 and 542 nm for $\text{2} \cdot \text{Tb}^{3+}$ ($\square$), 282 and 614 nm for $\text{2} \cdot \text{Eu}^{3+}$ ($\circ$), 282 and 543 nm for $\text{3} \cdot \text{Tb}^{3+}$ ($\blacksquare$) and 274 and 614 nm for $\text{3} \cdot \text{Eu}^{3+}$ ($\bullet$), respectively. Other measurement conditions are the same as those in Figure 1.

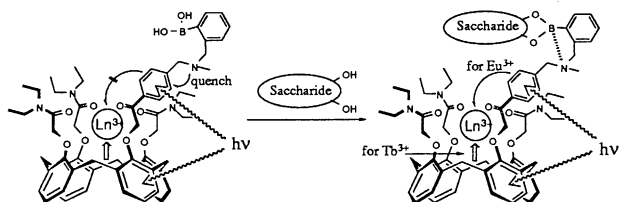
calix[4]arene's aromatic rings.¹⁴

In conclusion, the present study has offered a novel and unique methodology which is useful not only for the selective control of the energy-transfer efficiency by saccharides but also for the discrimination of the energy-transfer path. We believe that this method is applicable more generally to the mechanistic studies of the energy-transfer path.

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- 14 This means that the smaller I/I_0 of the complexes **3** relative the the complexes **2** in the absence of saccharide is due to the phenylboronic acid group which is useless for the energy-transfer.



Scheme 2.