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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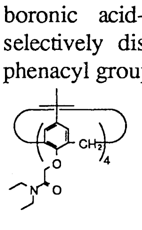
(Received November 30, 1995)

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 $^3\pi, \pi^*$ level from which the energy-transfer to $^5D_3$ or $^5D_4$ 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 deactives 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.



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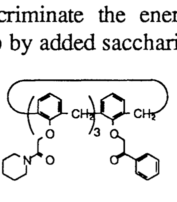

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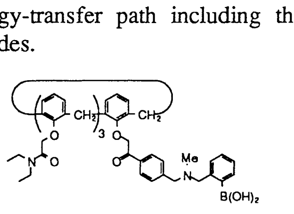

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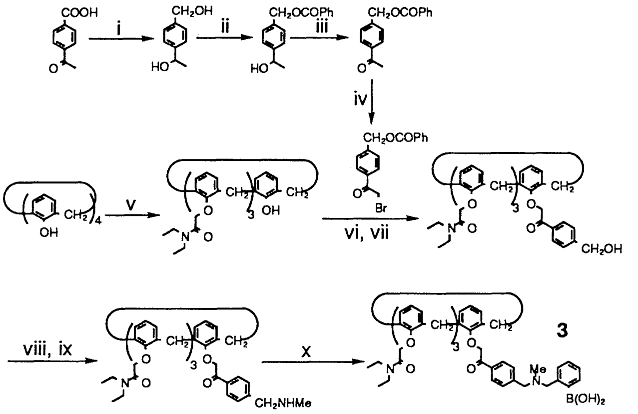
Compound **3** was synthesized according to Scheme 1 and identified by ^1H NMR, IR and mass spectral evidence and elemental analysis. MeOH (containing 0.2 vol% MeCN) which can solubilize both **3** and saccharides was used in the luminescence measurements. Emission and excitation spectra were corrected precisely by the use of a Hitachi F-4500 fluorescence spectrophotometer.



Scheme 1. *Reagents and conditions*: i, $LiAlH_4$, THF; ii, C_6H_5COCl, NEt_3, CH_2Cl_2; iii, DDQ, dioxane; iv, Br_2, $CHCl_3$; v, $ClCH_2CONEt_2$, BaO, DMF; vi, K_2CO_3, acetone; vii, LiOH, MeOH, H_2O; viii, $(MeSO_2)_2O$, $CHCl_3$; xi, $MeNH_2$, MeOH; x, *o*-$BrCH_2C_6H_4B(OH)_2$, 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 ($[\mathbf{3}] = 1.00 \times 10^{-5}$ mol dm^{-3}). It was found that the emission intensity is gradually saturated and reaches a plateau above 3×10^{-4} mol dm^{-3}. Hence, we fixed the metal concentration to 5.00×10^{-4} 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 saccharide[13] or to the weak interaction between saccharides and the complexes. In

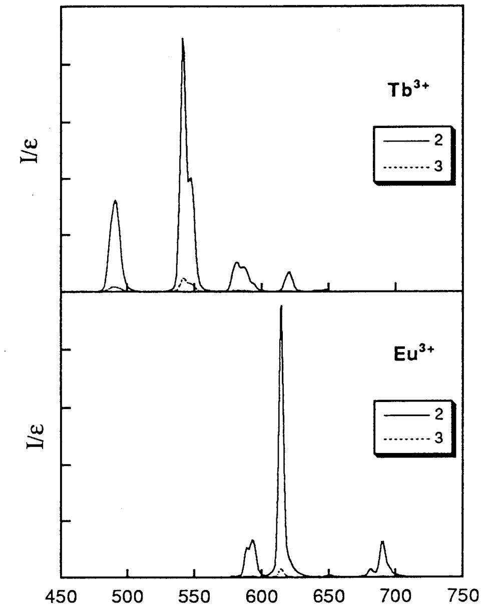
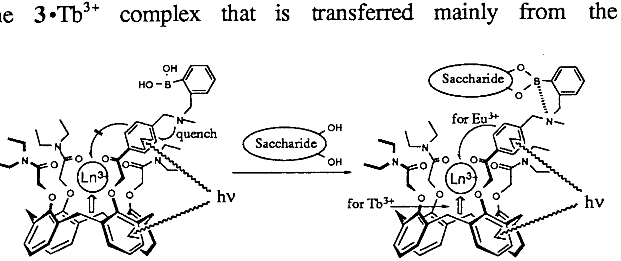


Figure 1. Emission spectra of the Tb^{3+} (upper) and Eu^{3+} (lower) complexes: 25 °C, MeOH:MeCN = 500:1 v/v, [**2**] = [**3**] = 1.00 x 10^{-5} mol dm^{-3}, [TbCl$_3$] = [EuCl$_3$] = 5.00 x 10^{-4} mol dm^{-3}, λ_{ex} 270 nm. The shorter wavelength light in emission is filtered with Toshiba Y-43. The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

3•Tb^{3+} and **3**•Eu^{3+} complexes, the absorption spectra were also changed slightly with the isosbestic points (282 nm for **3**•Tb^{3+} and 274 nm for **3**•Eu^{3+}). The isosbestic wavelengths were used for excitation in making plots of (I/I_0) versus [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 **3**•Eu^{3+} complex and *ca.* 2 times for the **3**•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 **3**•Eu^{3+} complex the excited energy is transferred mainly from the phenacyl group whereas in the **3**•Tb^{3+} complex that is transferred mainly from the calix[4]arene's aromatic rings.[14]



Scheme 2.

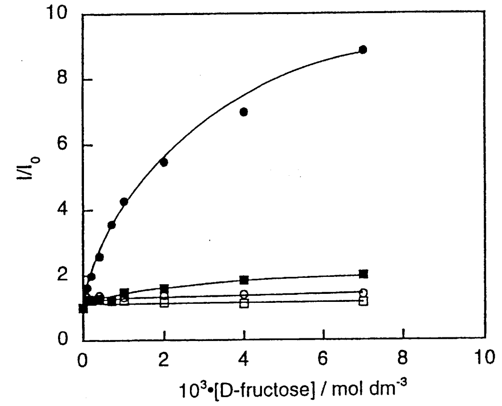


Figure 2. Plots of the emission intensity (I/I_0) versus [D-fructose]. λ_{ex} and λ_{em} are 285 and 542 nm for **2**•Tb^{3+} (□), 282 and 614 nm for **2**•Eu^{3+} (○), 282 and 543 nm for **3**•Tb^{3+} (■) and 274 and 614 nm for **3**•Eu^{3+} (●), respectively. Other measurement conditions are the same as those in Figure 1.

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.

We thank Miss R. Iguchi for technical assistance.

References and Notes

1 M. Sowinska, M. -T. Le Bris, and B. Valeur, *J. Photochem. Photobiol.*, **60**, 383 (1991).
2 N. Sabbatini, S. Dellonte, M. Ciano, A. Bonazzi, and V. Balzani, *Chem. Phys. Lett.*, **107**, 212 (1984).
3 N. Sabbatini, S. Dellonte, and G. Blasse, *Chem. Phys. Lett.*, **129**, 541 (1986).
4 V. Balzani, E. Berghmans, J. -M. Lehn, N. Sabbatini, R. Terodeand, and R. Ziessel, *Helv. Chem. Acta*, **73**, 2083 (1990).
5 V. Balzani, J. -M. Lehn, J. V. Loosdreeht, A. Meeati, N. Sabbatini, and R. Ziessel, *Angew. Chem., Int. Ed. Engl.*, **30**, 190 (1991).
6 M. Li and P. R. Selvin, *J. Am. Chem. Soc.*, **117**, 8132 (1995), and references cited therein.
7 B. Alpha, J. -M. Lehn, and G. Mathia, *Angew. Chem.*, **99**, 259 (1987).
8 N. Sabbatini, M. Guardigli, A. Mecati, V. Balzani, R. Ungaro, E. Ghidini, A. Casnati, and A. Pochini, *J. Chem. Soc., Chem. Commun.*, **1990**, 878; M. F. Hazenamp, G. Blasse, N. Sabbatini, and R. Ungaro, *Inorg. Chem. Acta*, **172**, 93 (1990).
9 For other examples for energy-transfer luminescence of Ln^{3+} in calix[4]arene systems see N. Sato, I. Yoshida, and S. Shinkai, *Chem. Lett.*, **1993**, 1261; S. Pappalardo, F. Bottino, L. Giunta, M. Pietraszkiewicz, and J. Karpiuk, *J. Inclusion Phenom.*, **10**, 387 (1991).
10 N. Sato and S. Shinkai, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 621.
11 H. Matsumoto and S. Shinkai, *Chem. Lett.*, **1994**, 901.
12 T. D. James, K. R. A. S. Sandanayake and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, **33**, 2207 (1994); Idem, *Nature*, **374**, 6520 (1995); K. R. A. S. Sandanayake and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, **1994**, 1083.
13 Z. Chen, N. Morel-Desrosiers, J. -P. Morel, and C. Detellier, *Can. J. Chem.*, **72**, 1753 (1994); N. Morel-Desrosiers, C. Lhermet, and J. -P. Morel, *J. Chem. Soc., Faraday Trans.*, **89**, 1223 (1993).
14 This means that the smaller I/ε 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.