Energy-transfer Luminescence of Lanthanide Ions Encapsulated in Sensitizer-modified Calix[4]arenes

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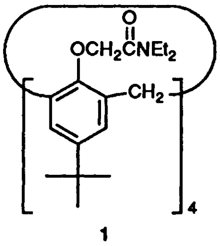
To induce the light-emitting properties of Tb^{3+} and Eu^{3+}, calix[4]arenes bearing three amide groups (composing a metal-binding site) and one sensitizer group (phenacyl group or diphenacylcarbonyl group) on the lower rim have been synthesized. The high luminescence quantum yields ($\varphi = 0.27$ for Tb^{3+} and 0.061 for Eu^{3+}) were attained by both the metal-encapsulation effect of calix[4]arenes and the selection of a sensitizer with a proper energy gap. The possible energy-transfer mechanisms from the sensitizer group to the encapsulated metal ions are discussed.

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. Current research has demonstrated that crown-ether derivatives,[1-3] 2,2′-bipyridine-containing tripode and tetrapode ligands[4,5] and 2,2′-bipyridine-based cryptands[6] are useful as potential ligands for the encapsulation of lanthanide ions. More recently, Sabbatini *et al.*[7] 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**); interestingly, the $\mathbf{1}\cdot Tb^{3+}$ complex exhibited a remarkably high luminescence quantum yield ($\varphi = 0.2$). They proposed, on the basis of the mechanistic considerations, that fortunately, **1** possesses the $^3\pi\pi^*$ level from which the energy-transfer to $^5D_3$ or $^5D_4$ in Tb^{3+} can take place.[7] This finding implies that **1** is an ideal ligand for energy-transfer luminescence of Tb^{3+}. It also means, on the other hand, that it is useful only for Tb^{3+}. In fact, the luminescence quantum yield for the $\mathbf{1}\cdot Eu^{3+}$ is extremely low ($\varphi = 2 \times 10^{-4}$).[7]



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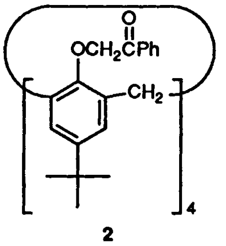

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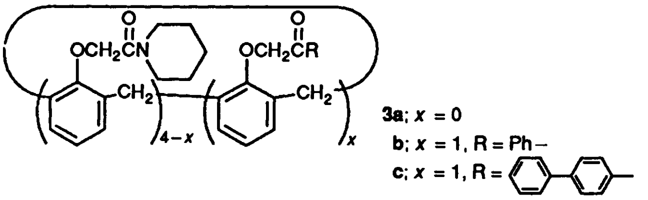
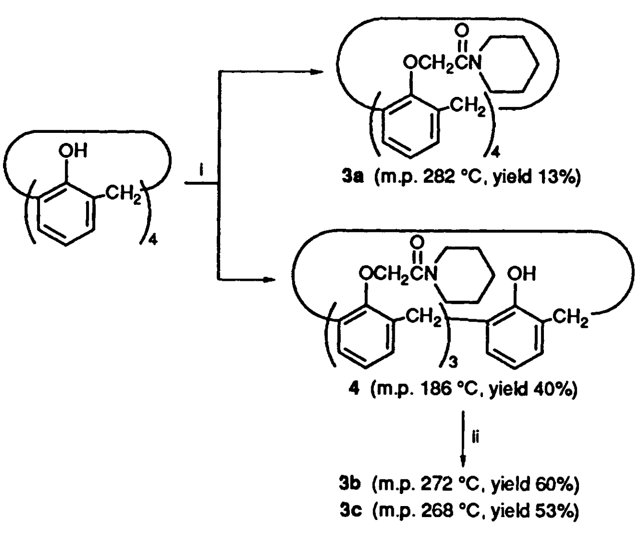


3a; $x = 0$
b; $x = 1$, R = Ph–
c; $x = 1$, R =

It thus occurred to us that if one could introduce an appropriate sensitizer near the metal-binding site, one might be able to transfer the excited-state energy from the sensitizer to various kinds of encapsulated lanthanide ions. We first introduced several sensitizers into the ethyl group(s) in **1** but could not find any calix[4]arenes which could exceed the luminescence quantum yield of **1**. Although the mechanistic consideration taught us that the sensitizer covalently linked to calix[4]arene *via* the ketone group (*i.e.*, **2**) might transfer the excited-state energy, **2** could not form a stable lanthanide complex because of the poor coordination ability.[8] We have recently established a new method for the synthesis of tri-*O*-substituted calix[4]arenes.[9-11] We found, fortunately, that calix[4]arene-triacetamide derivatives can stably retain lanthanide ions in the ionophoric cavity. Thus, one can introduce a desired sensitizer *via* the ketone linkage into the residual OH group. We have recently synthesized calix[4]arenes **3a–c** and found that the excited-state energy can be efficiently transferred from the sensitizer appended near the ionophoric cavity. This discovery opens the door to a new methodology for the induction of energy-transfer luminescence of lanthanide ions in a calix[4]arene system, which has been so far limited to Tb^{3+} ion.



Scheme 1 *Reagents and conditions:* i, 1-bromoacetylpiperidine (3.7 equiv.), BaO, DMF, 70 °C, 18 h; ii, $RCOCH_2Br$ (1.2 equiv.), K_2CO_3, acetone, reflux, 24 h

Experimental

Materials.—We used de-*tert*-butylated calix[4]arene-25,26,27,28-tetraol as the starting material because *O*-alkylation of this compound can be stopped at the tri-*O*-substituted stage in the presence of $Ba(OH)_2$ or BaO, a process that is difficult in 5,11,17,23-tetra-*tert*-butylcalix[4]arene-25,26,27,28-tetraol.[11]

25,26,27,28-*Tetrakis*(*piperidinocarbonylmethoxy*)*calix*[4]*arene* **3a**.—A DMF solution (100 cm^3) containing calix[4]-

Table 1 Emission maxima (nm) at 25 °C

Complex	Acetonitrile	Methanol
3a·Tb^{3+}	492, 543, 582, 621, 649	491, 543, 584, 621, 647
3b·Tb^{3+}	491, 543, 582, 621, 648	490, 543, 583, 620
3c·Tb^{3+}	491, 543, 586, 621	489, 543, 584, 621, 646
3a·Eu^{3+}	594, 614, 690	592, 614, 690
3b·Eu^{3+}	594, 614, 650, 691	592, 614, 690
3c·Eu^{3+}	594, 614, 651, 691	593, 614, 689

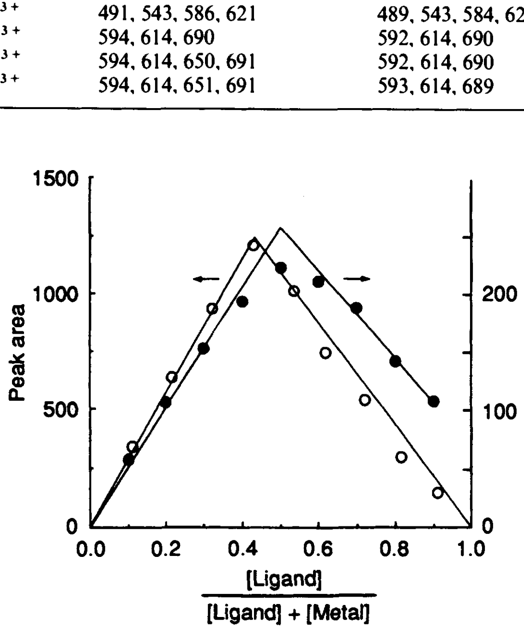


Fig. 1 Continuous variation plots in acetonitrile at 25 °C: ○, **3a** + $TbCl_3·6H_2O$ (total concentration 8×10^{-5} mol dm^{-3}), excitation 270 nm; ●, **3c** + $EuCl_3·6H_2O$ (total concentration 4×10^{-5} mol dm^{-3}), excitation 325 nm

arene-25,26,27,28-tetraol (1.67 g, 3.93 mmol), bromoacetopiperidine (2.97 g, 14.4 mmol) and BaO (12.0 g, 78.6 mmol) was stirred at 60 °C for 18 h under a nitrogen stream. The mixture was concentrated under reduced pressure to dryness, the residue being then dissolved in chloroform. The solution was washed twice with aqueous 0.1 mol dm^{-3} HCl and twice with water and dried over $MgSO_4$. The solution was evaporated to dryness and the residue was subjected to column chromatography (silica gel; chloroform). We thus isolated **3a** in 13% yield and 25-hydroxy-26,27,28-tris(piperidinocarbonylmethoxy)calix[4]arene (**4**) in 40% yield.

3a: m.p. 280–282 °C (Found: C, 72.7; H, 7.35; N, 5.65. $C_{56}H_{68}N_4O_8$ requires C, 72.70; H, 7.40; N, 6.06%); ν_{max}(KBr)/cm^{-1} 1667 (C=O); δ_H(250 MHz; $CDCl_3$; 25 °C; $SiMe_4$) 1.45–1.65 (24 H, m, CH_2-CH_2-CH_2), 3.24 (4 H, d, *J* 13.7, one H of Ar-CH_2-Ar), 3.35–3.60 (16 H, m, N-CH_2-CH_2), 4.87 (8 H, s, O-CH_2-CO), 5.09 (4 H, d, *J* 13.6, one H of Ar-CH_2-Ar) and 6.60 (12 H, s, Ph); *m*/*z* 925 (M + H) and 947 (M + Na).

4: m.p. 174–177 °C (Found: C, 72.8; H, 7.05; N, 5.2. $C_{49}H_{57}N_3O_7$ requires C, 73.57; H, 7.18; N, 5.25%); ν_{max}(KBr)/cm^{-1} 1655 (C=O); δ_H(250 MHz; $CDCl_3$; 25 °C; $SiMe_4$) 1.45–1.65 (18 H, m, CH_2-CH_2-CH_2), 3.29 (4 H, dd, *J* 13.5 and 13.3, one H of Ar-CH_2-Ar), 3.35–3.65 (12 H, m, N-CH_2-CH_2), 4.54 (4 H, d, *J* 13.7, two O-CH_2-CO), 5.03 (4 H, dd, *J* 13.8 and 13.1, one H of Ar-CH_2-Ar), 5.12 (2 H, s, one O-CH_2-CO), 6.52–6.95 (12 H, m, Ph) and 7.38 (1 H, s, OH).

25-*Phenacyloxy*-26,27,28-*tris*(*piperidinocarbonylmethoxy*)-*calix*[4]*arene* **3b**.—An acetone solution (25 cm^3) containing **4** (0.25 g, 0.313 mmol), phenacyl bromide (0.125 g, 0.626 mmol) and K_2CO_3 (0.695 g, 6.26 mmol) was stirred at reflux temperature for 18 h under a nitrogen atmosphere. After filtration the mixture was concentrated to dryness and the residue was dissolved in chloroform. The solution was washed twice with aqueous 0.1 mol dm^{-3} HCl and twice with water and dried over $MgSO_4$. The solution was concentrated to dryness and the residue was subjected to column chromatography (silica gel; chloroform). Finally, the product was recrystallized from methanol: yield 60%, m.p. 268–271 °C (Found: C, 74.1; H, 6.9; N, 4.35. $C_{57}H_{63}N_3O_8$ requires C, 74.57; H, 6.92; N, 4.58%); ν_{max}(KBr)/cm^{-1} 1667 (N-C=O) and 1705 (Ph-C=O); δ_H(90 MHz, $CDCl_3$; 25 °C, $SiMe_4$) 1.15–1.75 (18 H, m, CH_2-CH_2-CH_2), 3.26 (4 H, dd, *J* 13.6 and 13.4, one H of Ar-CH_2-Ar), 3.05–3.65 (12 H, m, N-CH_2-CH_2), 4.77 (4 H, s, two O-CH_2-CO-N), 5.00 (4 H, d, *J* 13.1, one H of Ar-CH_2-Ar), 5.23 (2 H, s, one O-CH_2-CO-N), 5.72 (2 H, s, O-CH_2-CO-Ph), 6.38–6.93 (12 H, m, OPh) and 7.42–8.12 (5 H, m, COPh); *m*/*z* 918 (M + H) and 940 (M + Na).

25-(4-*Phenyl*)*phenacyloxy*-26,27,28-*tris*(*piperidinocarbonylmethoxy*)*calix*[4]*arene* **3c**.—This compound was synthesized from **4** and *p*-phenylphenacyl bromide in a manner similar to that described for **3b**: yield 53%, m.p. 264–268 °C (Found: C, 76.0; H, 6.95; N, 4.05. $C_{63}H_{67}N_3O_8$ requires C, 76.17; H, 6.79; N, 4.23%); ν_{max}(KBr)/cm^{-1} 1664 (N-C=O) and 1702 (Ph-C=O); δ_H(90 MHz; $CDCl_3$; 25 °C, $SiMe_4$) 1.15–1.75 (18 H, m, CH_2-CH_2-CH_2), 3.28 (4 H, dd, *J* 13.8 and 13.9, one H of Ar-CH_2-Ar), 3.05–3.65 (12 H, m, N-CH_2-CH_2), 4.78 (4 H, s, two O-CH_2-CO-N), 5.02 (4 H, d, *J* 12.7, one H of Ar-CH_2-Ar), 5.21 (2 H, s, one O-CH_2-CO-N), 5.76 (2 H, s, O-CH_2-CO-C_6H_4-Ph), 6.40–6.94 (12 H, m, OPh), 7.42–8.20 (9 H, m, CO-C_6H_4-Ph).

Luminescence Measurements.—MeOH and MeCN (Luminasol from Dojindo Lab.) were used for the luminescence measurements. Absorption spectra were measured with a Shimadzu UV-2200 spectrophotometer. Emission and excitation spectra were corrected precisely by use of a Hitachi F-4500 fluorescence spectrophotometer. For all luminescence measurements Toshiba cut-off filters (L-39 or Y-43) were set in front of a monochromator. Luminescence quantum yields were determined by using aquo ions of Tb^{3+} ($\varphi = 0.08$ for 376 nm excitation)[12] or Eu^{3+} ($\varphi = 0.0074$ for 394 nm excitation)[13] as standards.

Results and Discussion

Ligands **3a**–**c** were synthesized according to Scheme 1.* They were identified on the basis of IR, NMR spectral evidence and elemental analysis (see the Experimental section). We first isolated the lanthanide complexes with **3a**–**c** but soon noticed that their emitting properties in solution are identical with those of mixtures of **3a**–**c** and lanthanide salts. It took about 1 h to reach the equilibria at room temperature and the mixtures finally gave absorption and excitation spectra identical with those of the isolated complexes. We thus employed the latter method and measured the spectra after 4 h.

We first estimated the stoichiometry of the complexes by the continuous variation method. To choose the wavelength for ordinate we measured the emission spectra of the complexes. As summarized in Table 1, the Tb^{3+} complexes display four to five structures. Of them, we chose the strongest peak at 543 nm. The Eu^{3+} complexes display three to four structures, the strongest peak being at 614 nm. We plotted the intensity of these peaks

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* We have found that in calix[4]arene-25,26,27,28-tetraol the *O*-alkylation reaction in the presence of BaO or CaH_2 stops at the tri-*O*-substituted stage[9–11] whereas the tri-*O*-substitution selectivity is not so reproducible in 5,11,17,23-tetra-*tert*-butylcalix[4]arene-25,26,27,28-tetraol. The reason is not well understood. Here, we employed calix[4]arene-25,26,27,28-tetraol as the starting material but the reaction did not stop 'perfectly' at the tri-*O*-substituted stage as observed for the reaction with alkyl bromides or $BrCH_2CO_2Et$.[9–11]

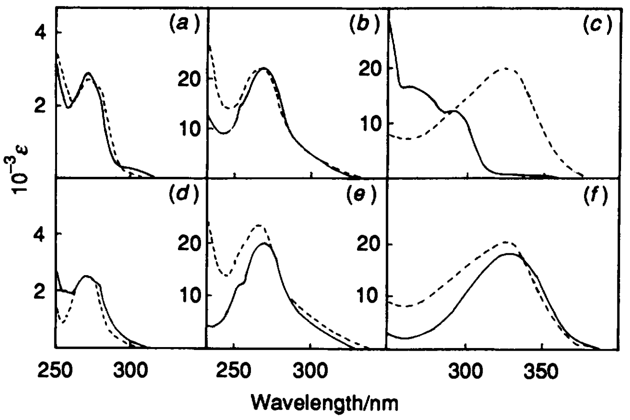

Fig. 2 Absorption (– – – –) and excitation (——) spectra of six complexes: acetonitrile, 25 °C, emission 543 nm for the Tb^{3+} complexes and 614 nm for the Eu^{3+} complexes: (*a*) **3a** (1×10^{-5} mol dm^{-3}) + $TbCl_3{\cdot}6H_2O$ (4×10^{-5} mol dm^{-3}); (*b*) **3b** (3×10^{-6} mol dm^{-3}) + $TbCl_3{\cdot}6H_2O$ (3×10^{-5} mol dm^{-3}); (*c*) **3c** (1×10^{-5} mol dm^{-3}) + $TbCl_3{\cdot}6H_2O$ (5×10^{-5} mol dm^{-3}); (*d*) **3a** (1×10^{-5} mol dm^{-3}) + $EuCl_3{\cdot}6H_2O$ (5×10^{-5} mol dm^{-3}); (*e*) **3b** (5×10^{-6} mol dm^{-3}) + $EuCl_3{\cdot}6H_2O$ (5×10^{-5} mol dm^{-3}); (*f*) **3c** (5×10^{-6} mol dm^{-3}) + $EuCl_3{\cdot}6H_2O$ (5×10^{-5} mol dm^{-3})

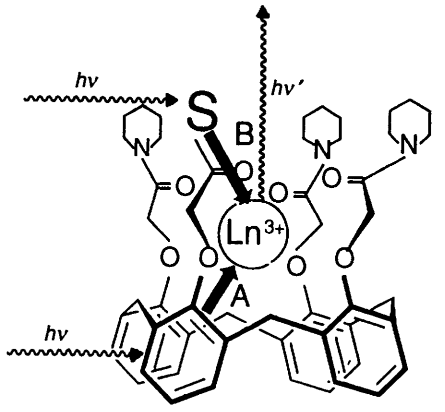

Fig. 3 Path A (excitation of the phenol units in calix[4]arene followed by the energy transfer to Ln^{3+}) is allowed only for Tb^{3+}. Path B [excitation of the sensitizer (S) followed by the energy transfer to Ln^{3+}] is allowed for Tb^{3+} encapsulated in **3b** and for Eu^{3+} encapsulated in **3b** or **3c**.

against [ligand]/([ligand] + [metal]). The typical examples are shown in Fig. 1. These results established that ligands **3a–c** form the 1 : 1 complex with Tb^{3+} and Eu^{3+} in acetonitrile or methanol. We then plotted the emission intensity against the metal concentration while the ligand concentration was maintained constant ([**3a**] = 1.0×10^{-5} mol dm^{-3}, [**3b**] = 3.0×10^{-6} mol dm^{-3} and [**3c**] = 1.0×10^{-5} mol dm^{-3} for Tb^{3+}; [**3a**] = 1.0×10^{-5} mol dm^{-3} and [**3b**] = [**3c**] = 5.0×10^{-6} mol dm^{-3} for Eu^{3+}). It was found that the emission intensity is gradually saturated and reaches a plateau above 3×10^{-5} mol dm^{-3} (in acetonitrile) and 3×10^{-4} mol dm^{-3} (in methanol) for Tb^{3+} and above 5×10^{-5} mol dm^{-3} (in acetonitrile) and 5×10^{-4} mol dm^{-3} (in methanol) for Eu^{3+}. The subsequent experiments were thus conducted above these metal concentrations where the ligands all exist as the metal complexes. Under these measurement conditions the emission intensity was not affected by free lanthanide metal salts present in excess.*

Absorption and excitation spectra for six complexes in acetonitrile are illustrated in Fig. 2. Similar spectra were observed in methanol. It is seen from Fig. 2(*a*) that in the **3a**·Tb^{3+} complex the absorption spectrum with λ_{max} = 270 nm (transition of the phenol units) is similar to the excitation spectrum. The result supports the view that the energy transfer can take place from the phenol units to bound Tb^{3+} (path A in Fig. 3). The excitation spectrum for the **3b**·Tb^{3+} complex features a maximum at 270 nm and a broad shoulder above 300 nm [Fig. 2(*b*)]. This result shows that the energy is transferred not only from the phenol units (270 nm) but also from the phenacyl unit (above 300 nm) (path A and path B). As a result, the luminescence quantum yield is significantly enhanced (see later). This finding means that the idea of transfer of excited-state energy from the sensitizer situated near the metal-binding site to the bound lanthanide ion is basically feasible. In contrast, the excitation spectrum for the **3c**·Tb^{3+} complex is largely different from the absorption spectrum [Fig. 2(*c*)]. The biphenylylcarbonyl group is excited at 325 nm but the emission band was not detected in this wavelength region. The significant energy-transfer occurs only from the phenol units (path A). One can thus expect that the magnitude of the luminescence quantum yield for the Tb^{3+} complex should appear in the order **3b** > **3a** > **3c**.

Table 2 Luminescence quantum yields (φ) of the Tb^{3+} and Eu^{3+} complexes (25 °C)

Ligand	Solvent	λ_{exc}/nm	φ	
			Tb^{3+}	Eu^{3+}
3a	MeCN	270	0.16	0.001 7
3a	MeOH	270	0.19	0.000 33
3b	MeCN	270	0.27	0.060
3b	MeCN	310	0.18	—
3b	MeOH	270	0.023	0.000 98
3c	MeCN	270	0.015	0.017
3c	MeCN	325	0.000 08	0.061
3c	MeOH	270	0.018	—
3c	MeOH	325	—	0.000 87

In the **3a**·Eu^{3+} complex the emission intensity was extremely weak although the excitation spectrum is similar to the absorption spectrum [Fig. 2(*d*)]. One can thus consider that the energy-transfer from the phenol units to bound Eu^{3+} is rather difficult. In contrast, we detected strong luminescence from the **2b**·Eu^{3+} and **2c**·Eu^{3+} complexes, and excitation bands which clearly support the energy-transfer from the phenacyl group [above 300 nm in Fig. 2(*e*)] or from the biphenylylcarbonyl group [at 325 nm in Fig. 2(*f*)] *via* path B appeared. These results further support the idea that the energy-transfer to Eu^{3+}, which otherwise is difficult in a conventional calix[4]arene system,[7] becomes possible by appropriate modification of the ionophoric cavity with the sensitizer.

Luminescence quantum yields were determined by using aquo ions of Tb^{3+} (φ = 0.08 for 308 nm excitation) or Eu^{3+} (φ = 0.0074 for 394 nm excitation) as standards (see the Experimental section). The results are summarized in Table 2. As expected from a comparison of the absorption spectra with the excitation spectra, the order of the luminescence quantum yield for the Tb^{3+} complexes is **3b** > **3a** ≫ **3c**. The high luminescence quantum yield observed for **3a** is ascribed to both the phenol-to-metal energy-transfer (path A) and the efficient metal-encapsulation effect of the calix[4]arene-based ionophore.[7] Further improvement in the luminescence quantum yield for **3b** is ascribed to the additional energy-transfer from the phenacyl group (path B). In the Eu^{3+} series, the high luminescence quantum yields are observed only for **3b** and **3c** in acetonitrile. Clearly, the sensitizer-to-metal energy-transfer is the sole route to enhance the quantum yield of Eu^{3+}.

Taking the energy levels of each species into account,[7,14,15]

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* However, the emission intensity for the **3a**·Eu^{3+} complexes in acetonitrile and methanol was corrected for the free Eu^{3+} salt.

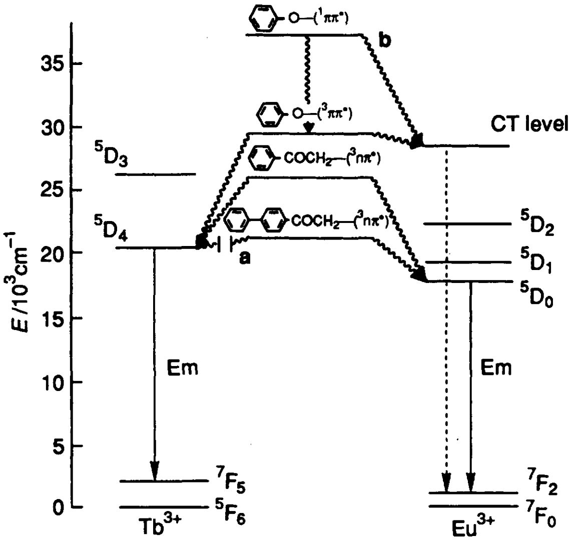

Fig. 4 Energy-transfer diagram for the present system. The excitation path is omitted for clarity: excitation wavelength, PhO– (λ = 270 nm), $PhCOCH_2$– (λ = 270 nm) and Ph–C_6H_4–$COCH_2$– (λ = 325 nm). One cannot transfer the energy to the Tb^{3+} ion levels from the triplet energy levels of the biphenylylcarbonyl (see mark **a** in the figure). As the C=O to Eu^{3+} charge-transfer band deactivates the excited-state of the phenol units to the ground state,[14] one cannot transfer the energy to the Tb^{3+} ion levels from the excited energy levels of the phenol units (see mark **b** in the figure).

we can now propose an energy-transfer diagram for the present system as shown in Fig. 4. The triplet energy levels of the phenol unit and the phenacyl group are high enough to transfer the energy to the Tb^{3+} ion levels whereas that for the biphenylylcarbonyl group is not sufficiently high. The energy levels for Eu^{3+} are lower than those for Tb^{3+} because the energy-transfer takes place efficiently even from the triplet energy level of the biphenylylcarbonyl group. Why, then, is the energy-transfer from the triplet energy level of the phenol unit to Eu^{3+} difficult? This peculiar finding is rationalized by the C=O-to-Eu^{3+} charge-transfer band which appears between PhO($^3\pi\pi^*$) and $PhCOCH_2$($^3n\pi^*$)[15] (see Fig. 4). This level efficiently deactivates the excited state of the phenol unit to the ground state.

In conclusion, the present paper demonstrates for the first time that in calix[4]arene-based ionophores that have excellent metal-encapsulation ability, the excited-state energy is efficiently transferred from the sensitizer to the bound lanthanide ion. It is important to choose a sensitizer which has an appropriate upper energy limit with regard to the lanthanide ion. We believe that this concept may eventually become useful for the excitation of *any lanthanide ions* and to obtain various kinds of colour emission.

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