

Lipophilic Phenylphosphonic Acid-Lanthanide Ion Complexes Which Show Efficient Energy-Transfer Luminescence

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Abstract: Lipophilic phenylphosphonic acids with a Ar-P linkage form stable complexes with lanthanide ions such as Tb³⁺ and Eu³⁺ and the complexes show the very high luminescence quantum yields ($\Phi = 0.25 - 0.30$ for Tb³⁺ and $0.09 - 0.13$ for Eu³⁺) due to the efficient energy-transfer through the Ar-P linkage and the metal encapsulation effects.

The luminescence properties of lanthanide ions have been of much recent concern because of their potential use as probes and labels for a variety of chemical and biological applications. To design an efficient emitting system with the high quantum yield one has to take two prerequisites into account: that is, (i) desolvation of lanthanide ions through encapsulation into the ligand and (ii) efficient energy-transfer from a sensitizer with a high excited-state to lanthanide ions.¹⁻³ Current research has demonstrated that certain tetrapode ligands^{1,2} and macrocyclic ligands³⁻⁵ are useful as potential ligands for the encapsulation of lanthanide ions. Meanwhile, the recovery and purification of lanthanide ions are effected by solvent extraction using lipophilic extractants. Among them, most potential extractants are phosphate [(R₁O)(R₂O)P(=O)OH] and phosphonate [(R₁O)R₂P(=O)OH] derivatives.⁶ We recently exploited several arylphosphonate derivatives [(R₁O)ArP(=O)OH], which showed the high affinity toward lanthanide ions probably because of Ar-P conjugation.⁷ Here, it occurred to us that these compounds might be useful for energy-transfer luminescence of lanthanide ions because (i) they form stable complexes with lanthanide ions, (ii) the excited-state energy of Ar may be directly transferred to complexed lanthanide ions, and (iii) in most cases they form 1:3 metal/ligand complexes in which ions are considerable encapsulated. We thus planned to investigate the potential of efficient energy-transfer to Tb³⁺ and Eu³⁺ from the Ar group in these lipophilic phenylphosphonic acids.

We first measured the emission spectra of the Tb³⁺ and Eu³⁺ complexes in methanol-acetonitrile (3:2 v/v). The complexes with **2** and **3** scarcely showed luminescence. In contrast, the complexes with **1**, **4**, **5**, and **6** showed strong luminescence with three-to-five structures (Table 1). Compounds **2** and **3** have no aryl group whereas **1**, **4**, **5**, and **6** have a chromophoric benzene ring. The difference indicates that emission of Tb³⁺ and Eu³⁺ is induced according to the energy-transfer luminescence mechanism. We plotted the intensity of the strongest peak (548 nm for Tb³⁺ and 613nm for Eu³⁺) against [ligand]/[metal] where the metal concentration was maintained constant (6.40 x

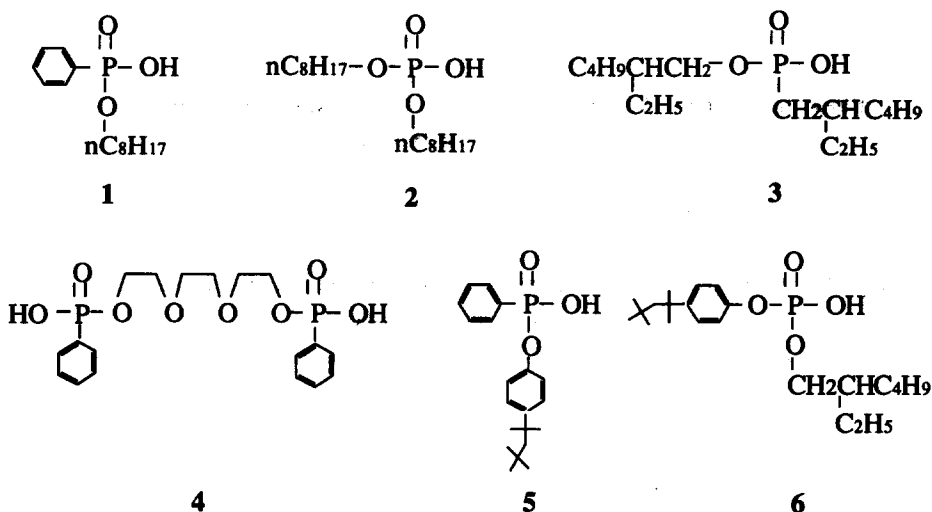


Table 1. Emission maxima (nm) at 25 °C (excitation wavelength 265 nm)

Ligand	Tb ³⁺ (nm)	Eu ³⁺ (nm)
1	487 549 582 620 651	591 609 654 702
4	488 549 582 619 650	591 609 654 701
5	487 548 581 621 652	590 609 653 700
6	489 548 583 621	590 610 700

10⁻⁶ M: the plots for Tb³⁺ are shown in Fig. 1). It is seen from Fig. 1 that monofunctional 1, 5, and 6 form 1:3 complexes whereas bifunctional 4 form a 1:2 complex. The stoichiometries for the Eu³⁺ complexes were also 1:3 for 1, 5 and 6 and 1:2 for 4. These stoichiometries are in good accord with those obtained in a solvent-extraction system.⁸

Absorption and excitation spectra for the Tb³⁺ and Eu³⁺ complexes with 1 and 4 are illustrated in Fig. 2. The absorption spectra with λ_{\max} at 258, 264, and 271 nm are similar to the excitation spectra with λ_{\max} at 260, 265, and 272 nm. Absorption and excitation spectra of the Tb³⁺ and Eu³⁺ complexes with 5 and 6 are also similar with each other. The results support again that the excited-state energy can be transferred from the phenyl groups to bound Tb³⁺ or Eu³⁺.

The luminescence quantum yields were determined by using aquo ions of Tb³⁺ ($\Phi = 0.08$ for 308 nm excitation) and Eu³⁺ ($\Phi = 0.0074$ for 394 nm excitation) as standards. The luminescence intensities were

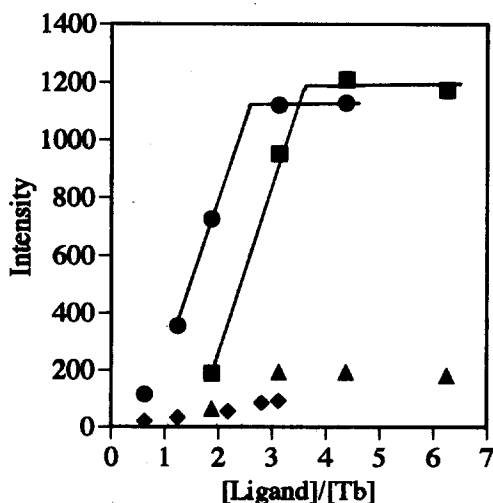


Fig. 1. Plots of intensity v s. [Ligand]/[Tb]
 ■ ; 1, ● ; 4, ▲ ; 5, ◆ ; 6,
 [Tb]=6.4x10⁶M, Ex 265nm, Em 548nm

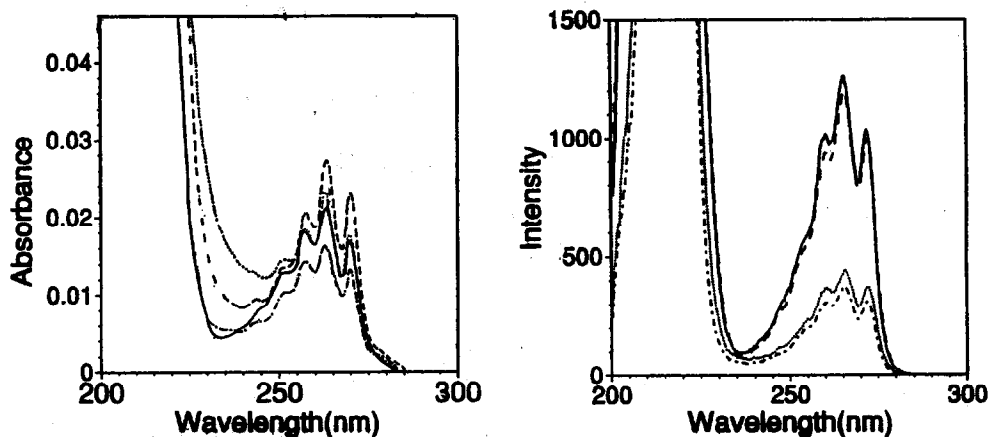


Fig. 2. Absorption and excitation spectra for Tb^{3+} and Eu^{3+} with 1 and 4

[Metal]= 6.4×10^{-6} M, [Ligand]= 2.8×10^{-5} M, Em 548 nm

1• Tb^{3+} (————), 4• Tb^{3+} (- - - - -), 1• Eu^{3+} (- · - · - ·), 4• Eu^{3+} (······)

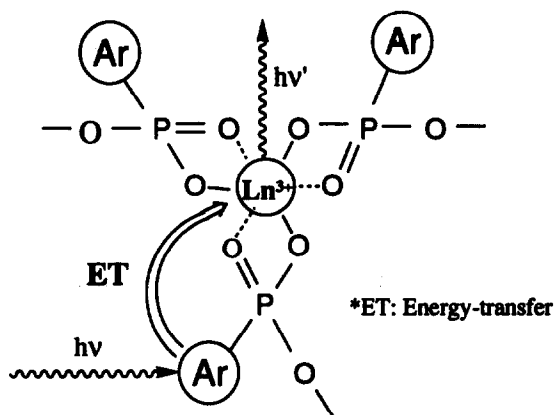
Table 2. Luminescence quantum yields of Tb^{3+} and Eu^{3+} complexes at 25 °C^a

Ligand	Excitation (nm)	F	
		Tb^{3+}	Eu^{3+}
1	265	0.25	0.09
4	265	0.30	0.13
5	265	0.02	0.005
6	265	0.02	0.001

^a The quantum yields were corrected for the light intensity at 265 nm which was used for excitation.

determined at the plateau region in Fig. 1 and corrected for the concentration of free ligands. The results are summarized in Table 2. The quantum yields for 1 and 4 ($\Phi = 0.25 - 0.30$ for Tb^{3+} complexes and $0.09 - 0.13$ for Eu^{3+} complexes) are very high and are comparable with those recently attained in calix[4]arene derivatives which are known to show an efficient metal-encapsulation effect ($\Phi = 0.16 - 0.27$ for Tb^{3+} complexes and $0.017 - 0.061$ for Eu^{3+} complexes).⁵ To the best of our knowledge, these complexes can be evaluated as the best complexes for energy-transfer luminescence.

The correlation between the ligand structure and the quantum yield provides an important clue to elucidate why efficient energy-transfer luminescence is attained in 1 and 4. Comparison of 1 with 6 reveals that the energy-transfer from Ar-P is about 12-90 times more efficient than that from ArO-P. This implies that the sensitizer should be "directly" linked to the ligation atom. Compound 4 which has two Ar-P groups within a molecule shows the highest quantum yield because of the high energy-transfer efficiency from two Ar-P groups and the podand-like metal-encapsulation effect. In contrast, the poor energy-transfer efficiency for 5 tells us that the excited-state energy of Ar-P is partially quenched by ArO-P.



In conclusion, the present paper demonstrated that in lanthanide complexes of phosphonate derivatives the excited-state energy is efficiently transferred from the appended sensitizer to the bound lanthanide ion and the high luminescence quantum yield is obtained. Important is the distance between sensitizer and lanthanide ion and molecular design for efficient encapsulation. We believe that by carefully choosing the sensitizer and skillfully designing the inclusion site, we can realize the further improved energy-transfer luminescence system.

References

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