Effects of the structure of ligands and their Ln^{3+} complexes on the luminescence of the central Ln^{3+} ions

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Abstract

According to the literature and our experimental results, it was found that (1) the suitability of the energy gap between the excited triplet energy level of the ligands and the lowest excited energy level of Ln^{3+} is a critical factor for sensitized luminescence of the central Ln^{3+}; (2) the high intensity of the sensitized luminescence of Ln^{3+} should be caused by a rigid planar molecular structure of the complex; (3) the existence of both a suitable conjugated system and ideal coordinating groups should be considered for ligand-design.

1. Introduction

The luminescence of lanthanides has been reviewed by several authors recently [1–5]. Horrocks and Albin have detailed the luminescence properties of Ln^{3+} complexes of β-diketonates and other organic ligands [4]. For designing new ligands that can sensitize the luminescence of the Tb^{3+} ion efficiently, we repeated the sensitization measurements of several well known β-diketonates [6–9] and aromatic carboxylates [10]. Based on the above-mentioned reviews and our repeated measurements, we designed a series of indole-derived acetylacetones and investigated their sensitization for the luminescence of Ln^{3+} ions [11–14]. In this paper, according to the reviews and our experimental results, the effects of the structure of the ligands and their Ln^{3+} complexes on the luminescence of the central Ln^{3+} ions are discussed.

2. Details of the effects of the structure of ligands and complexes on sensitized emission from central Ln^{3+} ions

2.1. Suitability of the energy gap between the excited triplet energy level of the ligand $[T^*(L)]$ and the lowest excited energy level of Ln^{3+} $[1^*(Ln^{3+})]$

It was found that only acetylacetone (Acac) and trifluoroacetylacetone (TFA) can sensitize the luminescence of Tb^{3+} among the well known β-diketones that are shown in Fig. 1. However, Acac cannot sensitize Eu^{3+}, while the other β-diketones can [6–9]. It was also found that Tb^{3+} is sensitized by most of the aromatic acids while the sensitization for Eu^{3+} is very weak [10].
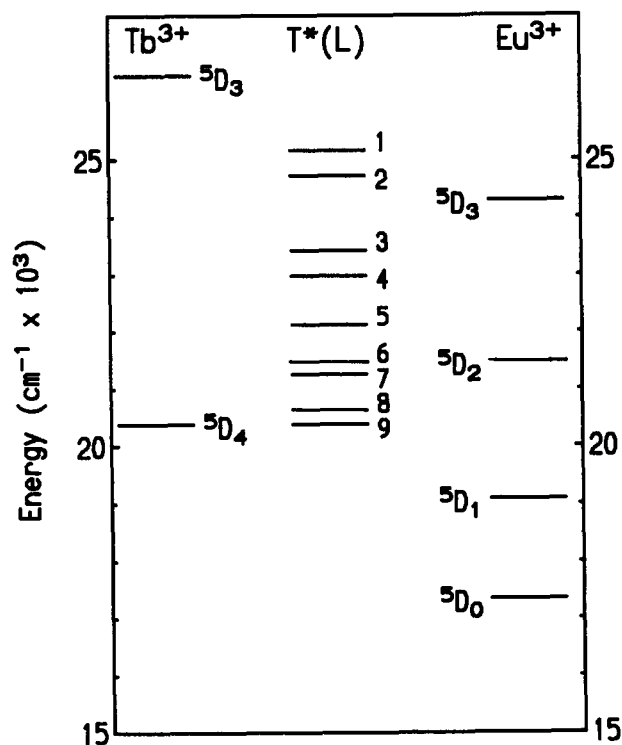

Fig. 1. Relation between T*(L) and ^5D_J of Eu^{3+} or Tb^{3+}. Ligands: 1, acetylacetone (Acac); 2*, benzoic acid (Ben); 3*, salicylic acid (Sal); 4, trifluoroacetylacetone (TFA); 5, hexafluoroacetylacetone (HFA); 6, benzoylacetone (BA); 7, benzoyltrifluoroacetone (BFTA); 8, dibenzoylmethane (DBM); 9, thenoyltrifluoroacetone (TTA). *Calculated from the phosphorescence spectra. All the other levels are from the literature [16].

The intensity of sensitized luminescence for Eu^{3+} decreases in the following order: TTA, BTFA ≫ TFA > DBMBA ≫ Ben > Sal ≫ Acac; and for Tb^{3+}: Acac >

Sal, Ben > TFA > BA, DBM, BTFA, TTA. These results confirm the conclusion given by Horrocks and Albin that the sensitized emission from Ln^{III} ion level in chelates arises from intramolecular transfer to the ion levels from a higher energy triplet state of the ligands [4]. The above-mentioned intensity order can be explained according to the idea given by Sato and Wada [15], who indicated that the fluorescence yield would be decreased either because of the thermal deactivation process while the energy gap is small, or due to the diminution in energy overlap while the energy gap is large. Consequently, the fluorescence yield shows a maximum for a proper energy gap between $T^*(L)$ and $^5D_0$ (Eu^{3+}) or $^5D_4$ (Tb^{3+}) levels, as shown in Fig. 1.

The suitability of the energy gap between $T^*(L)$ and $1^*(Ln^{3+})$ as a critical factor for the sensitized luminescence of Tb^{3+} was also confirmed in our studies on the RE^{III} complexes with indole-derived acetylacetones [11,12]. The oscillator data shown in Table 1 indicated that Tb^{3+} complexes with 3-indoleacetylacetone(L^3) are more stable than that with 1-indoleacetylacetone(L^1) [11]. Conversely, the intensity of sensitized luminescence of the former is much weaker than that of the latter. This indicates that the delocalization of π electrons in L^3 from the acetylaceto-chelating ring to the indole ring not only stabilizes the complex, but also lowers the energy level of $T^*(L)$ as determined from the phosphorescence spectra of Gd^{3+} complexes [12]. The fact that both L^1 and L^3 cannot sensitize luminescence of Eu^{3+}, and L^1 sensitizes luminescence of Tb^{3+} more intensely than L^3, can also be explained by comparing the energy gap, $\Delta E[T^*(L^1\text{ or }L^3)-1^*(Eu^{3+}$ or $Tb^{3+})]$ shown in Table 2, with the proper energy gap mentioned in Sato and Wada's paper [15].

It was found that the displacement of the benzene ring in BA by the indole ring not only increases the energy level of $T^*(L)$, but also increases the thermal stability of the complex. The different electron effect of the substituted groups on the indole ring does not influence the triplet state energy levels of the ligands evidently [13], as shown in Table 3, so all the ligands, L^1, 3-carboxylic acid-1-indoleacetylacetone (3C), 5-carboxylic acid-1-indoleacetylacetone (5C), 3-methyl-1-indoleacetylacetone (3M) 3-acetic acid-1-indoleacetylacetone (3A), 3-butanoic acid-1-indoleacetylacetone (3B) and 2-methyl-1-indoleacetylacetone (2M), can sensitize the luminescence of Tb^{3+} efficiently in ethanol solution (Table 4).

2.2. High intensity of the sensitized luminescence caused by a rigid planar molecular structure of the complexes

This rule has been confirmed in our earlier work [6], which shows that the fluorescence intensity of $Eu(TTA)_3Phen$ is much higher than that of $Eu(TTA)_3Bipy$. Recently, we found that 3C sensitizes Tb^{3+} luminescence more intensely than 3M in ethanol solution, while the complex with 3C exhibits weaker luminescence than that with 3M in the solid state [14]. In the solid state, the carboxylic group in 3C takes part in the coordination and destroys the planar molecular structure of the complex, so the efficiency of energy transfer is lowered, and the luminescence for this complex becomes weaker. As compared with 3C,

TABLE 3. Energies of excited triplet state for the ligands

Ligands	Energies (cm^{-1})	Ligands	Energies (cm^{-1})
3C	23256	L^1	23474
3A	22989	3M	22462
3B	22936	2M	22322
5C	22727		

TABLE 1. Oscillator strengths (P) for the complexes[a]

Complexes	$P\times10^6$	Complexes	$P\times10^6$
$NdL^1_3\cdot2H_2O$	9..19	$NdL^3_3\cdot2H_2O$	37.44
$NdL^1_3\cdot Phen$	30.39	$NdL^3_3\cdot Phen$	39.21
$ErL^1_3\cdot2H_2O$	6.33	$ErL^3_3\cdot H_2O$	18.12
$ErL^1_3\cdot Phen$	9.14	$ErL^3_3\cdot Phen$	21.10

[a]Determined in 95% ethanol.

TABLE 4. Fluorescence intensity (I) for the Tb^{3+} complexes

Ligands	3C	3A	3B	5C	L^1	3M	2M
I^a	78.3	72.9	72.6	72.0	71.1	70.0	68.6
I^b	203	306	330	411	400	389	375

[a]In ethanol solution.
[b]In the solid state.

TABLE 2. $\Delta E[T^*(L)-{}^5D_J]$ for the indole-derived acetylacetones

Acetylacetones	$\Delta E[T^*(L)-{}^5D_1]$ (cm^{-1})	$\Delta E[T^*(L)-{}^5D_4]$ (cm^{-1})
HL^1	4456	2970
HL^3	2960	1478

TABLE 5. Fluorescence intensity for the solid ternary complexes of Tb^{3+}

2nd ligand	None	Bipy	TPPO	Et_4N^+	$PipH^+$
L^1	400	516	–	–	546
5C	411	440	469	461	469
3M	389	420	460	452	462

5C sensitizes luminescence of Tb^{3+} as intensely as 3M both in ethanol solution and in the solid state, which means that, as the carboxyl in 5C is far from the chelating ring, it cannot coordinate Tb^{3+}, so a planar structure can be kept in the complex, and the luminescence is not affected (Table 4).

The luminescence intensity for Tb^{3+} complexes with 3A and 3B in the solid state are also lower than that with 3M, while the intensity order for the complexes with L^1 and 2M is the same as that with 3M, both in ethanol solution and in the solid state (Table 4). These facts suggest that it is necessary to keep a rigid planar structure with a suitable conjugated π-electron system for designing new ligands that are able to sensitize luminescence of Ln^{3+}.

2.3. Enhancement of sensitized luminescence by addition of a suitable secondary ligand

It is well known that sensitized luminescence of some complexes is enhanced by addition of suitable secondary ligand. In our studies on Tb^{3+} complexes with L^1, 5C or 3M, it was found that addition of a suitable secondary ligand, such as Bipy, TPPO, Et_4N^+, and $PipH^+$, would enhance the sensitized luminescence of Tb^{3+} (Table 5). The neutral ligands, Bipy and TPPO, enhance the luminescence of Tb^{3+} complexes with L^1, 5C or 3M for reasons of both the displacement of coordinating H_2O and the increase in molecular rigidity. For the organic bases, Et_4N^+ and $PipH^+$, the luminescence enhancement is due to association of the cations with a coordinated anion, $(TbL_4)^-$ [13].

3. Conclusions

The suitability of the energy gap between the excited triplet energy level of ligands and the lowest energy level of Ln^{3+} is a critical factor for sensitized luminescence of the central Ln^{3+} ion. High intensity of sensitized luminescence of Ln^{3+} should be caused by

a rigid planar molecular structure of the complex. The existence of both a suitable conjugated system and ideal coordinating groups should be considered for ligand design. Based on these rules, ten new binary and ternary Tb^{3+} complexes have been synthesized. All the complexes exhibit both intense fluorescence at room temperature and high thermal stability even at 200 °C.

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