

Synthesis and optical character of novel rare earth Tb, Eu(III) complexes with β -Diketone

XIAOMING REN, CHANGPING WEI*, GUO CHENG

Collage of Materials Science and Engineering, Changchun University of Science and Technology,
Weixing Road 7186, Changchun 130022, Jilin Province, China

A novel β -diketone 1-(4-aminophenyl)-3-phenylpropane-1, 3-dione (L) was synthesized by classical claisen condensation reaction. With L as the first ligand and imidazo [5, 6-f] phenanthroline (IP) as the secondary ligand, two new Tb, Eu(III) ternary complexes were prepared by precipitation method. The ligands and complexes were characterized by elemental analysis, IR spectra, UV spectra. Fluorescence spectra demonstrated that the complexes could emit characteristic fluorescence of rare earth ions and the fluorescence intensity of Tb(L)₃IP was obviously higher. Further investigation showed that the fluorescence intensity was influenced with the matching situation of energy level between the lowest triplet state of the ligand L and the emission energy of rare earth ion. It suggested that the energy difference was well matched and the intramolecular energy could transfer efficiently to central Tb³⁺ ion in Tb(L)₃IP, which was an excellent green-emitter and would be regarded as a valuable material.

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1. Introduction

The study of rare earth complexes with luminescence properties began in 1942 when Weissman reported that europium β -diketone complexes displayed luminescence when irradiated with ultraviolet light [1]. Since then, the rare earth complexes with β -diketone attracted considerable attention because of their high and sharply spiked fluorescence emission efficiency, long lifetime caused by the high absorption coefficient of β -diketone structure [2-5]. This kind of complexes have promising applications in material science such as luminescent probes [6], organic light-emitting devices (OLEDs) [7-9] and laser materials [10-13]. Many β -diketone type ligands and their Eu, Tb(III) ternary complexes have been investigated such as benzoylacetone (BA), dibenzoylmethane (DBM) and thenoyltrifluoroacetone (HTTA) [14-18], however, either their absorption coefficients of the optical transitions for these ions are low, or the fluorescence and mechanical properties of the complexes are poor, which limit their practical applications. In order to overcome these drawbacks, the novel β -diketone 1-(4-aminophenyl)-3-phenylpropane-1, 3-dione (L) was synthesized as the first ligand. Then, our team prepared Tb, Eu (III) complexes using imidazo [5, 6-f] phenanthroline (IP) as the secondary ligand because IP obviously enhanced the fluorescent intensity of the complexes as an assistant antenna group. In addition, the various spectral properties of all complexes in solid state were investigated in detail.

2. Experimental

2.1. Materials

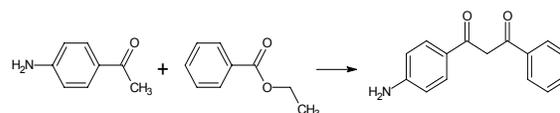
All starting materials were of AR grade. Solvents were purified with conventional methods.

2.2. Instrumentation

Elemental analysis (C, H, N) was performed on an Elemental vario EL elemental analyzer. The lanthanide content was determined by EDTA titration. Infrared spectra were recorded on a Nicolet NEXUS 670 FTIR spectrometer between KBr plate. UV absorption spectra were recorded with a Shimadzu UV-2401PC. ¹H NMR spectra were measured with a Bruker-400MHz nuclear magnetic resonance instrument using CDCl₃ as solvent. Fluorescence and phosphorescence spectra were recorded on a Hitachi F-4500 spectrometer.

2.3. Synthesis of L

Synthetic route to L was as follows:

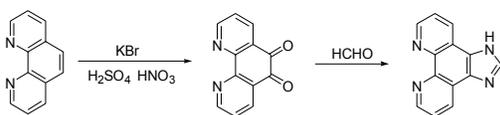


NaNH₂ (1.56 g, 0.04 mol) was dissolved in dry benzene (80 ml) under Ar, and heated to 50 °C, 4-acetylaniline (1.35 g, 0.01 mol) was added in portions. To the above stirred solution, benzoic acid ethyl ester (5.72 ml, 0.04 mol) was added dropwise, and the mixture was refluxed under Ar for 10 h, then left to cool to the room temperature. The reaction mixture was added to ice water (50 ml), and the pH was adjusted to 2.5 with hydrochloric acid. The mixture was then extracted with benzene (20 ml×3). The combined organic phase was washed with H₂O, dried over NaSO₄ for 10 h and filtered. The fil-

trate was concentrated under reduced pressure, and the residue was purified to afford the product 1.28 g (53.56%) as pale yellow crystals. Elemental analysis for $C_{15}H_{13}NO_2$ (calcd. %): C: 75.25 (75.31), H: 5.28 (5.44), N: 5.65 (5.86). 1H NMR ($CDCl_3$) δ : 4.03(s, keto CH_2), 6.63(s, enol CH), 7.21(d, 2H), 7.45-7.53(m, 2H), 7.79(t, 2H), 7.94(d, 2H), 8.31(s, 1H), 17.02(s, enol OH). The characteristic chemical shift of β -diketone enol hydroxyl proton appeared at 17.02, substantiated that the product L mainly existed as the enol structure.

2.4. Synthesis of IP

Synthetic route to IP was as follows:



IP was prepared based on the method in [19]. Elemental analysis for $C_{13}H_9N_4$ (calcd. %): C: 70.25(70.59), H: 3.80(3.62), N: 25.05(25.33). 1H NMR ($CDCl_3$) δ : 9.1(s, 4H), 8.6(s, 1H), 8.1(d, 2H), 3.4(N-H).

2.5. Synthesis of the complexes

The Tb(III) and Eu(III) complexes were synthesized by mixing the Tb(III) or Eu(III) chloride with L and IP in 1:3:1 ratio in anhydrous ethanol which was adjusted to pH 6-7 by aqua ammonia at 298 K. The white-solid state complexes were filtrated, washed with anhydrous ethanol and dried at 60 °C. Elemental analysis for $Tb(L)_3IP$ (calcd.%) C: 69.74(69.96), H: 4.51(4.38), N: 9.82(9.65), Tb: 15.93(15.65); for $Eu(L)_3IP$ (calcd.%)C: 70.23(70.16), H: 4.54(4.36), N: 9.89(9.78), Eu: 15.34(15.36).

3. Results and discussion

3.1. Elemental analysis

The results of elemental analysis indicated that the composition of the complexes conformed to $Tb(L)_3IP$ and $Eu(L)_3IP$.

3.2. IR spectra

The IR spectral of the ligands and complexes were measured in the region between 4000 and 400 cm^{-1} . The main data were presented in Table 1.

For the ligand L, the band at 1684 cm^{-1} could be attributed to the keto $C=O$. In addition, the band at 1593 cm^{-1} was assigned to the enolic $C=O$. The enolic $C=O$ stretching absorption was observed at 1267 cm^{-1} . These bands confirmed the presence of the keto-enol tautomer in Fig.1. It was consistent with the result of 1H NMR spec-

troscopy analysis.

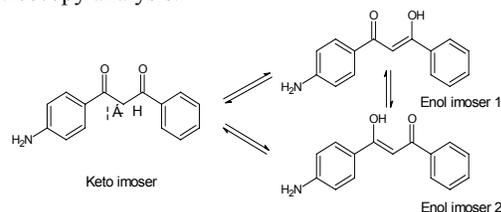


Fig.1. Keto-enol tautomer of L

Table 1. IR spectra data of the comp. (cm^{-1})

comp.	$\nu_{C=O}$	ν_{C-O}	$\nu_{C=N}$	δ_{C-H}	ν_{N-H}	ν_{Re-O}
L	1684,1593	1267		709	3358	
IP			1592	814,722	3045	
$Tb(L)_3IP$	1688,1598		1558	821,736	3349	554
$Eu(L)_3IP$	1685,1597		1546	835,744	3352	485

In the case of $Tb(L)_3IP$, the band appeared around 1267 cm^{-1} disappeared in the complex, which was ascribed to enolic $C-O$, the fact confirmed that the oxygen atoms coordinated to Tb^{3+} ion via the deprotonation of enol hydroxyl groups successfully. The band appeared around 1592 cm^{-1} in IP, due to $C=N$, downshifted to 1558 cm^{-1} in the complex. The shift indicated that the $C=N$ groups of the IP coordinated to the Tb^{3+} ion through nitrogen atoms. The bands appeared around 554 cm^{-1} assigned to $Tb-O$ mode. The above facts indicated that rare earth ions were coordinated with oxygen atoms of the first ligand L and nitrogen atoms of the secondary ligand IP. The IR spectra results of $Eu(L)_3IP$ was similar to that of $Tb(L)_3IP$. The elemental analysis and IR spectra results led us to speculate the general structures of $Re(L)_3IP$ ($Re=Tb, Eu$). It was shown in Fig. 2.

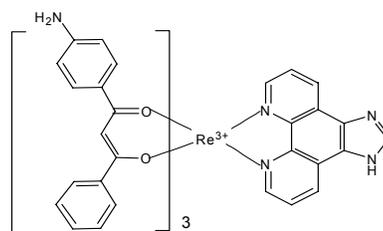


Fig.2. The general structures of $Re(L)_3IP$ ($Re= Tb, Eu$)

3.3. UV spectra

Fig. 3 showed the UV absorption spectra of ligands and complexes at 298 K. Comparing the UV absorption spectra of the complexes with L, the similar position of peak substantiated that the main absorption of the complexes came from the first ligand[20]. The main absorption bands were located at 230 nm and 265nm. Among the UV absorption spectra, the absorption intensity of the complex

was stronger than that of corresponding ligand, which indicated that the energy transfer occurred between ligand and rare earth ion and more extensive conjugating system was formed due to the effect of the electronic exchange. In the complexes, the absorption band of IP was not appeared, which showed that the secondary ligand was acted as the synergistic coordination.

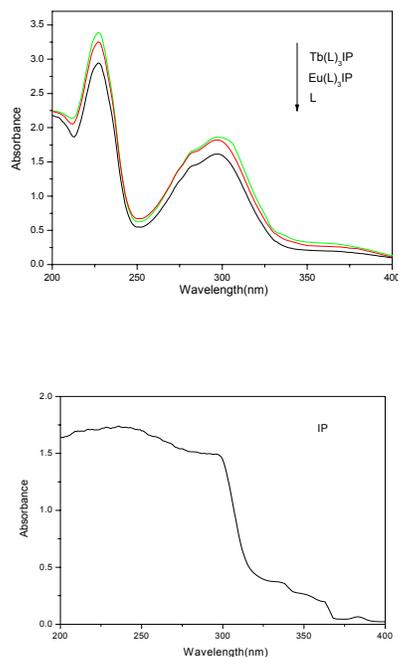


Fig. 3. UV spectra of ligands and complexes

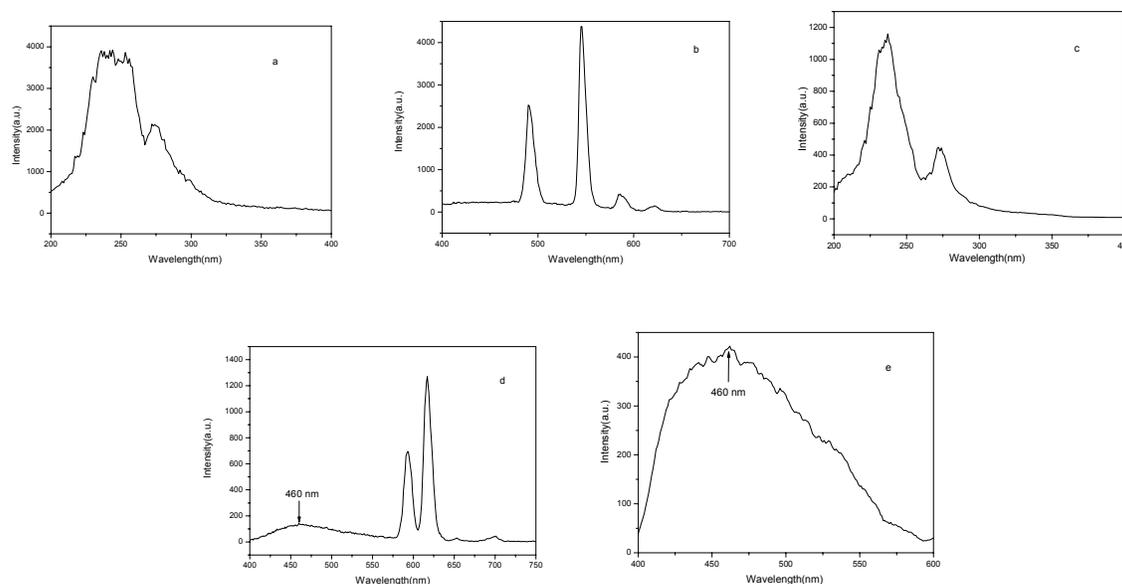


Fig. 4. Fluorescence spectra of L and complexes a. Excitation spectra of $Tb(L)_3IP$ b. Emission spectra of $Tb(L)_3IP$ c. Excitation spectra of $Eu(L)_3IP$ d. Emission spectra of $Eu(L)_3IP$ e. Emission spectra of L.

3.4. Fluorescence spectra of the complexes and L

The fluorescence spectra of the complexes were measured at 298 K in solid state (Tb complex : λ_{ex} :245 nm, λ_{em} :545 nm; Eu complex : λ_{ex} :237 nm, λ_{em} :617nm). In Fig. 4(b), $Tb(L)_3IP$ showed four characteristic emission bands of Tb^{3+} ion which were assigned to the $^5D_4 \rightarrow ^7F_6$ (490 nm), $^5D_4 \rightarrow ^7F_5$ (546 nm), $^5D_4 \rightarrow ^7F_4$ (584 nm) and $^5D_4 \rightarrow ^7F_3$ (621 nm), respectively. The $^5D_4 \rightarrow ^7F_5$ transition is a typical electric dipole transition and strongly varies with the local symmetry of Tb^{3+} ions, while the $^5D_4 \rightarrow ^7F_6$ transition corresponds to a partly allowed magnetic dipole transition. In addition, among these transitions, the $^5D_4 \rightarrow ^7F_5$ transition showed the strongest emission, suggesting the chemical environment around Tb^{3+} ion was in low symmetry.

In Fig. 4(d), $Eu(L)_3IP$ displayed four characteristic emission bands of Eu^{3+} ion, which were assigned to the $^5D_0 \rightarrow ^7F_J$ ($J=1, 2, 3, 4$) transitions at 592 nm, 617 nm, 652 nm and 702 nm, respectively. The emission band $^5D_0 \rightarrow ^7F_2$ was obviously higher than the other emission bands. Moreover, an emission band at 460 nm was also observed.

The emission spectra of L was measured at 298 K in solid state (λ_{ex} :275 nm). The highest emission band was located at 460 nm in Fig.4(e), so it could be predicted that the emission band at 460 nm in Fig.4(d) was from the luminescence of L. The fluorescence data of the complexes and L were shown in Table 2.

Compared with the fluorescence intensity of the complexes in Table 2, $Tb(L)_3IP$ was obviously stronger. To explain the difference of the fluorescence intensity and define the assignment of the emission band at 460 nm, the lowest triplet state of L was given next.

Table 2 The fluorescence data of the comp.

comp.	Assignment(nm)				PI*(a.u.)
Tb(L) ₃ IP	⁵ D ₄ → ⁷ F ₆ 490	⁵ D ₄ → ⁷ F ₅ 546	⁵ D ₄ → ⁷ F ₄ 584	⁵ D ₄ → ⁷ F ₃ 621	4380
Eu(L) ₃ IP	⁵ D ₀ → ⁷ F ₁ 592	⁵ D ₀ → ⁷ F ₂ 617	⁵ D ₀ → ⁷ F ₃ 652	⁵ D ₀ → ⁷ F ₄ 702	1270

*PI: peak intensity

3.5. Triplet state of the ligand and energy transfer

The phosphorescence spectra of Gd-L was measured at 77 K (λ_{ex} : 275 nm) [21]. Gd complex was selected as the model complex for the determination of the triplet state energy of the ligand owing to their high phosphorescence-fluorescence ratios. Taken the reciprocal of the shortest emission wavelength at 404 nm, the lowest triplet state energy level of L was confirmed at 24152 cm⁻¹.

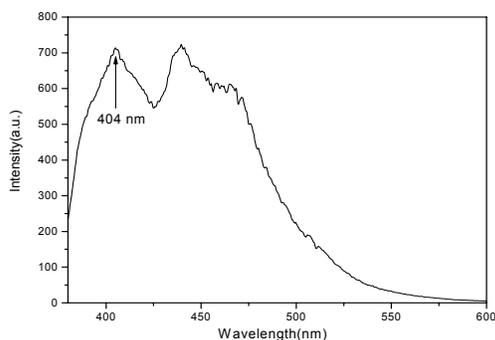


Fig.5. Phosphorescence spectra of Gd-L

From the fluorescence spectra of the complexes, it was clearly observed that the fluorescence intensity of Tb(L)₃IP was much stronger than that of Eu(L)₃IP. UV spectra showed that the absorption was mainly from the first ligand L in the complexes. According to the intramolecular energy transfer mechanism[22], the fluorescence intensities are influenced by the intramolecular energy transfer efficiency between the ligand L and the rare earth ion, which depends on the Dexter electron exchange from the lowest triplet level of ligand to the excited energy level of rare earth ion[23], the rate constant of energy transfer K_{ET} is:

$$K_{ET} = KJ \exp(-2R_{DA}/L)$$

Where K is a constant, R_{DA} is intermolecular distance between energy donor and energy acceptor, L is van der Waals radius, both R_{DA} and L are considered to be constant for intramolecular energy transfer, so:

$$K_{ET} = CJ = C \int F_D(E) \cdot E_A(E) dE$$

Where $F_D(E)$ is the luminescence spectrum of energy donor (ligand) and $E_A(E)$ is the absorption spectrum of energy acceptor (Re³⁺ ion) separately. The integral of spectra

overlap in this equation represents the energy difference between the lowest triplet state energy level of ligand and the excited energy level of rare earth ion. So K_{ET} consists with the energy difference matching between the lowest triplet state energy level of ligand and the excited energy level of rare earth ion. Thus, the energy difference is neither too large nor too small, and can be assumed that there existed an optimal value[24].

Based on the above analysis, the process of energy transfer in the complexes was given in Fig.6. In Tb(L)₃IP, the energy difference ΔE (T_1 -Tb³⁺) between the lowest triplet state energy level T_1 of L (24152 cm⁻¹) and the excited energy level of Tb³⁺ (⁵D₄, 20500 cm⁻¹) was 3652 cm⁻¹, and the emission of Tb³⁺ ion was stronger and characteristic. So, it could be concluded that the lowest triplet state energy level T_1 of L was suitable for the luminescence of Tb³⁺ ion.

In Eu(L)₃IP, the energy difference ΔE (T_1 -Eu³⁺) between the lowest triplet state energy level T_1 and the excited energy level of Eu³⁺ (⁵D₀, 17260 cm⁻¹) was 6892 cm⁻¹. Compared with the energy difference ΔE (T_1 -Tb³⁺), ΔE (T_1 -Eu³⁺) was larger, this larger energy difference could not sensitize Eu³⁺ ion effectively, and some of the energy was consumed as the luminescence of L, which was appeared at 460 nm in Fig.4(d). Thus, Eu(L)₃IP showed lower luminescence intensity and competitive luminescence of L also appeared.

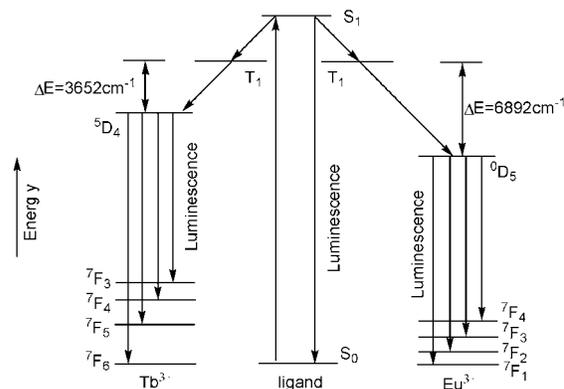


Fig.6. Conventional diagram of energy transfer * S_0 : ground state; S_1 : excited singlet state; T_1 : lowest triplet state; ΔE : energy difference

4. Conclusions

In this paper, our team synthesized a novel β -diketone 1-(4-aminophenyl)-3-phenylpropane-1, 3-dione (L) which

mainly existed as an enol isomer. Then, its rare earth ternary complexes Tb(L)₃IP and Eu(L)₃IP were prepared. The ligands and complexes were characterized. IR spectra showed that the rare earth ion was coordinated with six oxygen atoms of the first ligand L and two nitrogen atoms of the second ligand IP in the complex. UV spectra demonstrated that the main absorption was from the first ligand L in the complexes. Fluorescence and phosphorescence spectra confirmed that the luminescence intensity was influenced by the energy difference between the lowest triplet level of the ligand L and the excited energy level of the rare earth ions, and the energy difference was well matched in Tb(L)₃IP. So, Tb(L)₃IP exhibited much higher emission than Eu(L)₃IP. The Tb(L)₃IP was an excellent green-emitter which would be considered as a promising material with bright green fluorescence.

Acknowledgements

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*Corresponding author: changpingwei@hotmail.com