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稀土–间苯二甲酸–乙酰丙酮三元配合物的合成及发光性能

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摘 要：在乙醇体系中，由双配体间苯二甲酸(H_2PIA)和乙酰丙酮(Hacac)与稀土硝酸盐反应合成了相应的 4 种稀土三元配合物 [$Ln_2(PIA)_2(acac)_2$] (Ln = Sm (**1**)，Eu (**2**)，Tb (**3**)，Dy (**4**))，用元素分析、红外光谱、热重分析进行表征，并推断了其可能的结构。为便于比较三元配合物的发光性能，同时也制备了相应的稀土间苯二甲酸[$Ln_2(PIA)_3(H_2O)_4$]和稀土乙酰丙酮二元配合物[$Ln(acac)_3(H_2O)$]。室温下，测定了三元和二元配合物的荧光光谱，结果表明，所有配合物均显示稀土中心离子特有的发射，三元配合物的发光强度好于二元配合物(除了镝配合物)，说明双配体对中心离子有协同敏化作用，其实验结果用配体最低三重态能级 T_1 (来自 Gauss 理论计算)与中心金属离子最低激发态能级的匹配情况予以解释。

关键词：稀土配合物；间苯二甲酸；乙酰丙酮；荧光光谱
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Synthesis and Luminescent Property of Rare Earth Complexes Constructed by Isophthalic Acid and Acetylacetone

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Abstract: Four ternary complexes [$Ln_2(PIA)_2(acac)_2$] (Ln=Sm (**1**), Eu (**2**), Tb (**3**), Dy (**4**)) were synthesized with isophthalic acid (H_2PIA, $C_8H_6O_4$), acetylacetone(Hacac, $C_5H_8O_2$) and $Ln(NO_3)_3{\cdot}nH_2O$ in ethanol solution. These complexes were characterized by elemental analysis, infrared (IR) spectra, and thermogravimetric analysis (TG). Their possible structures were proposed. In order to compare the luminescent properties between ternary complexes and corresponding binary complexes, the binary complexes [$Ln_2(PIA)_3(H_2O)_4$] and $Ln(acac)_3(H_2O)$ (Ln=Sm, Eu, Tb, Dy) were also prepared. The fluorescent spectra of the ternary and binary complexes were determined at room temperature. The results show that all complexes displayed the characteristic emissions of rare earth center ions. The luminescent intensities of the ternary complexes (except the dysprosium complex) were stronger than that of the binary complexes, indicating that the synergistic sensitization effect had occurred for the center ions from the double ligands. These experimental results can be explained by the energy matching of the lowest triplet energy level T_1 of the two ligands (calculated from Gaussian theory) and the lowest excited state energy level of the central metal ions.

Keywords: rare earth complex; isophthalic acid; acetylacetone; luminescent property

1 Introduction

Rare earth complexes have the characteristics of a narrow band and pure color. Various compounds that have emitting light of different wavelengths (colors) and lights of different intensities can be obtained by selecting different rare earth metal ions and different organic ligands. Studies have shown that most of these compounds have excellent luminescent properties and are widely used in photoluminescence, electroluminescence, optical communication, laser and solar energy conversion systems, anti-counterfeiting, fluorescent probes, and biomedical and other

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fields[1–16]. These compounds have been become one of the "hot spots" in the development and application of rare earths.

In order to obtain rare earth complexes with excellent luminescent properties, selection of luminescent rare earth ions and organic ligands is naturally very important. However, the types of luminescent rare earth ions are limited, whereas the variety of organic ligands are almost unlimited. Therefore, the selection, design, and synthesis of organic ligands are highly specific.

So far, the reported luminescent rare earth complexes have a wide variety of ligands. In comparison, rare earth complexes formed by *β*-diketones and aromatic carboxylic acids have the most outstanding luminescent properties. Both types of ligands have a high absorption coefficient in the ultraviolet region and high-energy transfer efficiencies[17–25]. After many years of accumulation, the research results of these two aspects are extensive. The study found that most rare earth *β*-diketone complexes have relatively high luminous intensity, but their thermal stability is relatively poor. The luminescent effect of rare earth aromatic carboxylic acid complexes is not as good as that of rare earth *β*-diketone complexes, but these complexes have high thermal stability; thus, the two types of complexes have their own advantages. It is worth noting that the study of combining these two types of ligands to synthesize the corresponding ternary mixed complexes has rarely been reported. Therefore, the advantages of *β*-diketone and aromatic carboxylic acid ligands to combine organically for the synthesis of ternary mixed rare earth luminescent complexes is a very significant subject. In this paper, the mixed ligand ternary complexes were prepared by reacting isophthalic acid and acetylacetone as ligands with nitrates of samarium, europium, terbium, and dysprosium. The complexes were characterized by elemental analysis, infrared (IR) spectroscopy and thermogravimetric (TG) analysis. The composition and structure of the products were inferred. The fluorescent spectra of the solid products for ternary and binary complexes at room temperature were measured. The synergistic sensitivity of the double ligands to the central ions was calculated based on Gaussian theory.

2 Experimental methods

2.1 Materials and measurements

All reagents (isophthalic acid, acetylacetone, hydrated rare earth nitrates, sodium hydroxide) and solvents were of commercially available quality without purification before use.

The contents of rare earth were determined using the gravimetric analysis method. Elemental analyses of C and H were performed on elemental analyzer (Elementar Vario EL III, Germany). Fourier-transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4 000 to 400 cm^{-1}.The peak intensities are represented by strong (s), medium (m), and weak (w). A Netszch STA 449 F5 thermal analyzer from Germany was used to carry out the TG analysis with a heating rate of 10 ℃·min^{-1} from 30 to 700 ℃ in a normal air atmosphere. Fluorescent spectra of solid powder products were measured at room temperature by an Edinburgh FL-FS 920 time-correlated single photon counting (TCSPC) system. Both excitation and emission slits were 1 nm.

2.2 Synthesis of complexes

Synthesis of ternary complexes $[Ln_2(PIA)_2(acac)_2]$ (Ln=Sm (**1**), Eu (**2**), Tb (**3**), Dy (**4**)): A mixture of H_2PIA (0.164 g, 1.00 mmol), 5 mL 1.0 mol·L^{-1} NaOH solution, 10 mL absolute ethanol, and 10 mL (100.00 mmol) freshly distilled acetylacetone was stirred until the solid dissolved. An additional 0.450 g (about 1.00 mmol) $Ln(NO_3)_3·6H_2O$ was dissolved in 10 mL ethanol, and the ligand solution was then slowly dropped into the ethanol solution of rare earth nitrates. After addition of the ligand solution was completed, the pH of the mixture solution was adjusted to 6.5 by 1.0 mol·L^{-1} NaOH solution and the mixture was then heated under reflux for 24 h. During this process, precipitation gradually formed, which was allowed to stand. The precipitate was then filtered, washed with ethanol several times, and dried. White powder products were obtained.

A yield of 40% was found for complex 1. Anal. Calcd for $[Sm_2(PIA)_2(acac)_2]$: Sm, 36.36%; C, 37.75%; H, 2.68%. Found: Sm, 36.09%; C, 37.53%; H, 2.66%. IR (KBr) ν/cm^{-1}: 3 408 (w), 1 602 (s), 1 540 (s), 1 450 (m), 1 364 (s), 1 260 (w), 1 160 (w), 1 021 (w), 924 (w), 740 (w), 655 (w), 529 (w).

A yield of 35% was found for complex 2. Anal. Calcd for $[Eu_2(PIA)_2(acac)_2]$: Eu, 36.61%; C, 37.60%; H, 2.67%. Found: Eu, 36.34%; C, 37.41%; H, 2.69%. IR (KBr) ν/cm^{-1}: 3 434 (w), 1 600 (s), 1 540 (s), 1 138 (m), 1 384 (s), 1 261 (w), 1 160 (w), 1 025 (w), 925 (w), 739 (w), 656 (w), 531 (w).

A yield of 38% was found for complex 3. Anal. Calcd for $[Tb_2(PIA)_2(acac)_2]$: Tb, 37.64%; C, 36.99%; H, 2.63%. Found: Tb, 37.95%; C, 36.63%; H, 2.67%. IR (KBr) ν/cm^{-1}: 3 424 (w), 1 602 (s), 1 542 (s), 1 518 (m), 1 366 (s), 1 263 (w), 1 021 (w), 924 (w), 716 (w), 531 (w).

A yield of 45% was found for complex 4. Anal. Calcd for $[Dy_2(PIA)_2(acac)_2]$: Dy, 38.17%; C, 36.67%; H, 2.60%. Found: Dy, 38.41%; C, 36.63%; H, 2.57%. IR (KBr) ν/cm^{-1}: 3 539 (w), 1 604 (s), 1 540 (s), 1 452 (m), 1 403 (s), 1 262 (w), 1 165 (w), 1 020 (w), 921 (w), 746 (w), 657 (w), 530 (w).

Synthesis of binary complexes $Ln_2(PIA)_3(H_2O)_4$ (Ln=Sm, Eu, Tb, Dy). These complexes were prepared and characterized according to reference [26]. A

mixture of H_2PIA (0.123 g, 0.75 mmol), $Ln(NO_3)_3{\cdot}6H_2O$ (0.223 g, 0.50 mmol), NaOH (0.040 g, 1.00 mmol), and H_2O (15 mL) was added to a Teflon-lined stainless steel autoclave (25 mL), which was heated to 160 ℃ for 72 h. After the sample was cooled to room temperature at a rate of 10 ℃·h^{-1}, colorless block crystals suitable for physical measurements were obtained, washed with distilled water and ethanol, and the air-dried. The yield was 45%.

Synthesis of binary complexes $Ln(acac)_3(H_2O)$ (Ln=Sm, Eu, Tb, Dy): These complexes were prepared and characterized according to reference Zhang [27]. A mixture of $Ln(NO_3)_3{\cdot}6H_2O$ (0.223 g, 0.50 mmol), 10 mL ethanol, and 10 mL (100.00 mmoL) acetylacetone was put into a 50 mL vessel and stirred. The pH of the solution was then adjusted with 1.0 mol·L^{-1} NaOH until it reached 6.0–7.0. After refluxing for 24 h, it was cooled to room temperature, allowed to stand while filtering, and washed with ethanol. A solid powder was obtained with a yield of about 40%.

The elemental analysis data of two series binary complexes are shown in Table 1 in supporting material.

3 Results and discussion

3.1 Elemental analysis

The composition of ternary complexes is in accordance with the proportional relationship of a central metal ion, an isophthalate ligand, and an acetylacetonate from the elemental analysis results of the products. The chemical formula was determined as Ln(PIA)(acac).

3.2 Thermogravimetric analysis

The series of ternary complexes 1–4 were thermally stable with an initial decomposition temperature of about 300 ℃. Their thermal decompositions were very similar. The europium complex $[Eu_2(PIA)_2(acac)_2]$ (Fig. 1) was taken as an example for illustration. The weight loss interval ranged from 300 to 580 ℃. After oxidative decomposition of the ligand, a rare earth oxide remained with a residual amount of 42.89%, which was basically consistent with the residue Eu_2O_3 (theoretical value 42.39%).

3.3 IR spectra

In the series complexes of $[Ln_2(PIA)_2(acac)_2]$, the C═O stretching vibration peak of the original free isophthalic acid (H_2PIA) ligand at 1 708 cm^{-1} disappeared, and the both the antisymmetric stretching vibration and symmetric stretching vibration peaks (1 516–1 520 and 1 399–1 413 cm^{-1}, respectively) of carboxylate appeared with a $\Delta\nu$ value of about 117 cm^{-1}, which was less than the frequency of free COO^- symmetry and antisymmetric vibration in Na_2PIA ($\Delta\nu$=232 cm^{-1}). This finding indicates that the carboxyl group of the isophthalate was coordinated with the central metal ion *via* a bidentate chelate coordination mechanism[26–28]. A strong C═O vibrational absorption peak appeared near 1 595–1 602 cm^{-1} as compared with $\nu_{C=O}$ (1 728, 1 624 cm^{-1}) in the acetylacetone ketone and enol isomers. Blue shifts of about 133 and 29 cm^{-1} indicate that the central metal ion coordinated with both the carbonyl and enol oxygens of acetylacetonate to form a six-membered chelated ring[29].

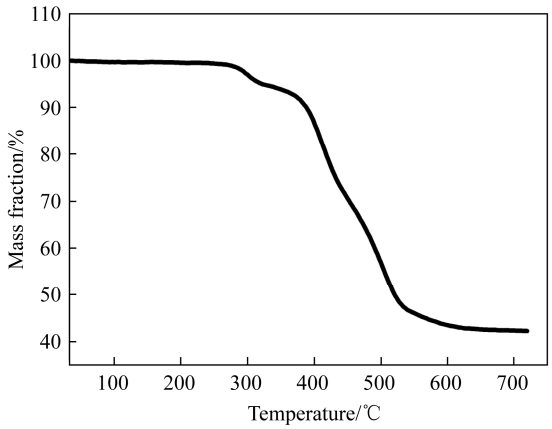


Fig. 1　Thermogravimetric curve of complex $[Eu_2(PIA)_2(acac)_2]$

3.4 Suggested structure of the ternary complexes

From the elemental analysis data, IR spectra and thermogravimetric analysis mentioned above, it is concluded that every central metal ion in the complexes is coordinated with two oxygen atoms from one acetylacetonate and four oxygen atoms from two carboxyl groups of two isophthalates. The coordination number is 6, and a two-core structure is formed. The suggested structure of ternary complexes 1–4 are shown in Fig. 2.

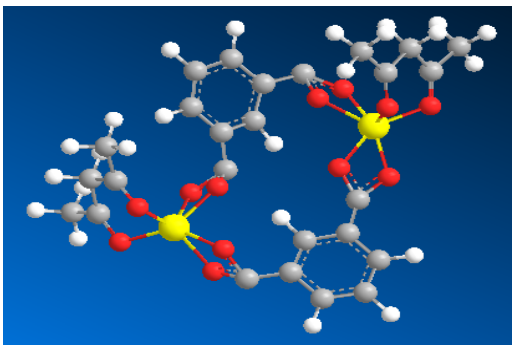


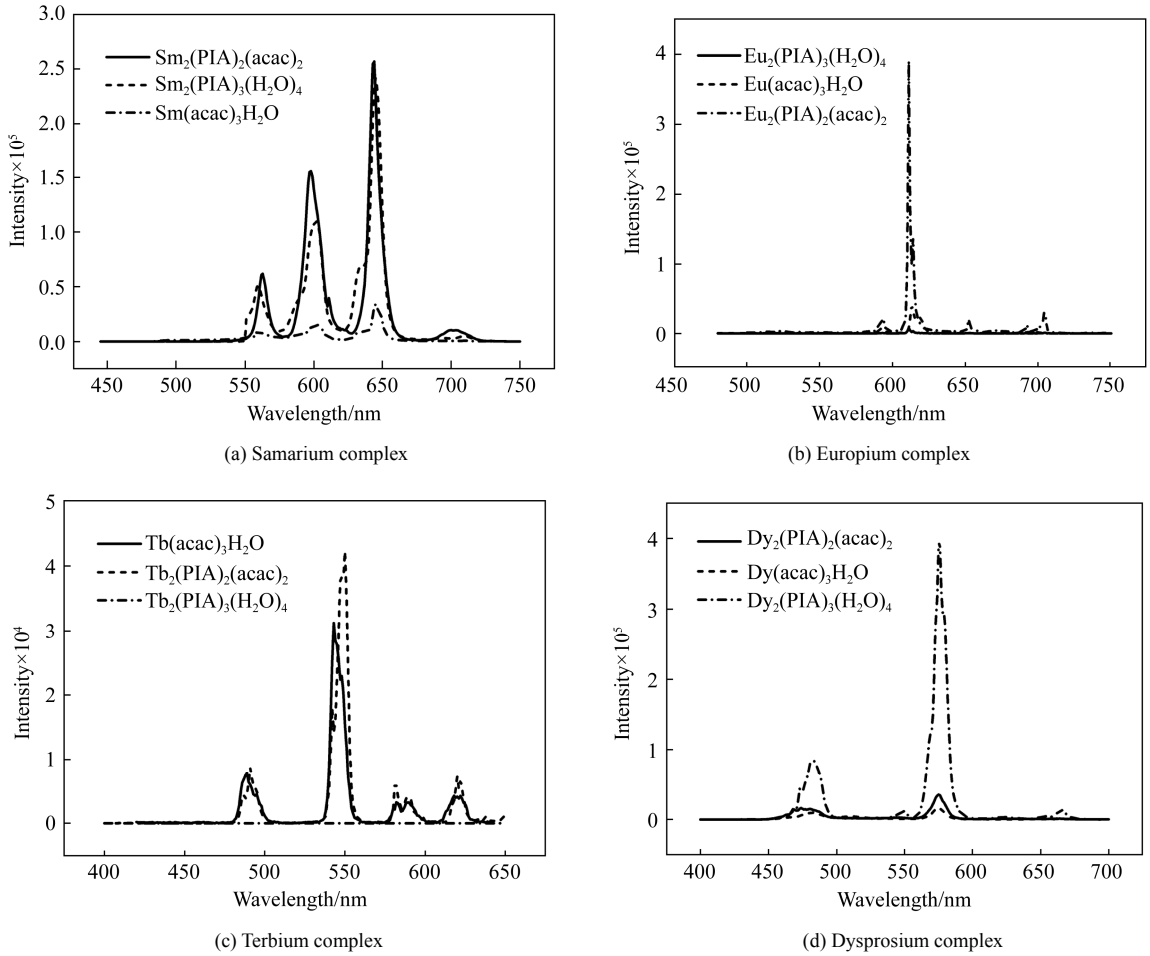
Fig. 2　Suggested structure of complexes 1–4

3.5 Luminescent properties of complexes

3.5.1　Fluorescent spectra of complexes

The fluorescent spectra of a series of mixed ligands ternary complexes, a single isophthalic acid ligand binary complexes, and a single acetylacetone ligand binary complexes were tested at room temperature (Fig. 3). As shown in Fig. 3, all of the complexes

presented the characteristic luminescence of the central metal ions themselves. The emission peaks of samarium ternary complexes and binary complexes at 565, 605 nm and 650 nm were attributed to the $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$, and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ of Sm^{3+} ions, respectively. The strongest fluorescent peak at 650 nm (red fluorescence) corresponded to the $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition of Sm^{3+} emitting. The emission peaks of the europium complexes at 592, 612, 652 nm and 704 nm were assigned to $^5D_0\rightarrow{}^7F_1$, $^5D_0\rightarrow{}^7F_2$, $^5D_0\rightarrow{}^7F_3$, and $^5D_0\rightarrow{}^7F_4$ transition of Eu^{3+}, respectively, and its strongest emission peak was located at 612 nm. Eu^{3+} was at the asymmetric center position at which the characteristic transition belongs to the electric dipole transition of Eu^{3+}. These complexes emitted a red color. The emission peaks of terbium complexes appeared at 492, 543, 584 nm and 622 nm, corresponding to the $^5D_4\rightarrow{}^7F_6$, $^5D_4\rightarrow{}^7F_5$, $^5D_4\rightarrow{}^7F_4$, and $^5D_4\rightarrow{}^7F_3$ transition of Tb^{3+}, respectively. The strongest emission peak position was observed at 543 nm, indicating that the complexes emitted a green color. The emission peaks of dysprosium complexes at 484 and 575 nm were attributed to $^4F_{9/2}\rightarrow{}^6H_{15/2}$ and $^4F_{9/2}\rightarrow{}^6H_{13/2}$ transition of Dy^{3+}, respectively. The strongest emission peak appeared at 575 nm, indicating that the complex emitted yellow fluorescence.



(a) Samarium complex (b) Europium complex

(c) Terbium complex (d) Dysprosium complex

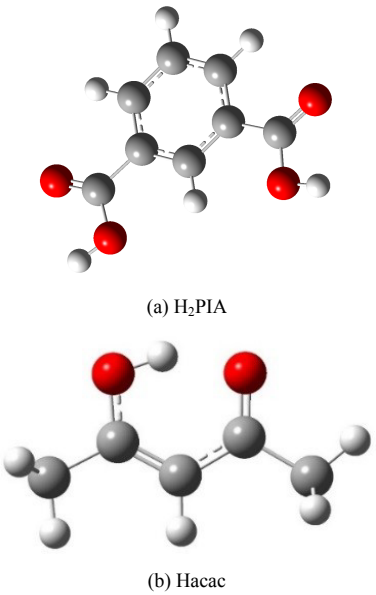
Fig. 3 Fluorescent emission curve of ternary and binary complexes

From the above-described results for samarium complexes, the single ligand complex formed by isophthalic acid had stronger luminescence compared to the ligand complex formed by acetylacetone, which had the weaker luminescence. The ternary complex had a slightly stronger luminescence than the binary complex formed by isophthalic acid. For europium and terbium complexes, the luminescent intensities of binary complexes formed by acetylacetone were stronger than that of isophthalic acid complexes. The luminescent intensity of the same rare earth ion ternary complex was better than that of the binary complex. This finding indicates that the two ligands, isophthalic acid and acetylacetone, had synergistic sensitization to the central ions. Although the luminescence of the isophthalic acid binary complex was strong for the dysprosium complex, the luminescent intensity of the ternary complex was weaker than that of the binary complex.

These experimental results are basically consistent with the theory of energy transfer, that is, the transfer efficiency of the ligand to the rare earth ion in the complex depends on the degree of matching between the lowest excited state energy of the rare earth ion

and the lowest excited triplet states (T_1) of the ligand[30–33]. The energy transfer efficiency of organic ligands and central ions is the most important factor affecting the luminescent properties of the complexes. The difference between the lowest triplet energy level of the ligand and the resonance emission level of the central ion decreased while both the energy transfer rate and the inverse energy transfer rate increased. Thus the best match between the two values can be found; however, if the difference is too large or too small, the luminescent properties of the complexes will be reduced. Therefore, the triplet energy level of the ligand must be higher than the excited state energy level of the rare earth ions in order to produce energy resonance transmission; otherwise, no fluorescence will be generated. However, if the triplet energy level of the ligand is much higher than the lowest excited state energy level of the central ions, the effective resonance transfer of the energy cannot occur because the spectral overlap is small. If the difference between the triplet level of the ligand and the excited state of the rare earth ion is too small, the thermal deactivation rate of the triplet state of the ligand is larger than that of the energy transfer to the rare earth ions, and no effective energy transfer occurs.

To investigate the fluorescent properties of the title complexes, the lowest triplet energy level T_1 of the ligands (isophthalic acid and acetylacetone) was calculated using the Gaussian 09[34] quantum chemistry package. First, the density functional theory (DFT) was used to optimize the ground state of the ligand at the B3LYP/6-31G(d) level. Second, in the optimized configuration, the CIS/6-31(d) method was used to continue, and the excited state structure was optimized (Fig. 4). Finally, the lowest triplet energy level T_1 of the ligand was calculated by the TD-B3LYP/6-31G(d) method.



(a) H_2PIA

(b) Hacac

Fig. 4　Optimal geometries of the ligands in excited triplet state

From the calculation results, the lowest triplet energy level of isophthalic acid was 24 079 cm^{-1}, and the lowest triplet energy level of acetylacetone was 20 960 cm^{-1}. The lowest excited state energy levels of the central ions were calculated: 1) Sm^{3+} ($^4G_{5/2}$), 17 800 cm^{-1}; 2) Eu^{3+} ($^5D_0$), 17 250 cm^{-1}; 3) Tb^{3+} ($^5D_4$), 20 430 cm^{-1}; and 4) Dy^{3+} ($^4F_{9/2}$), 21 000 cm^{-1}. The ΔE for lowest triplet energy level of the two ligands and the lowest excited state energy level of the central ion are listed in Table 1. The energy transfer diagram is shown in Fig. 5.

Table 1　ΔE for lowest triplet state of the ligands and the lowest excited state energy level of the central ions (cm^{-1})

Ligand	T_1	ΔE/cm^{-1}			
		T_1–$^4G_{5/2}$ (Sm^{3+})	T_1–$^5D_0$ (Eu^{3+})	T_1–$^5D_4$ (Tb^{3+})	T_1–$^4F_{9/2}$ (Dy^{3+})
H_2PIA	24 079	6 279	6 829	3 649	3 079
Hacac	20 960	3 160	3 710	530	–40

It can be seen from the data in Table 1 that the lowest excited triplet energy level of the two ligands is higher than the lowest excited state energy level of samarium, europium, and terbium ions, and the energy absorbed by the ligand can be transferred to the central ions, and the final sensitizing center ion luminescence produces a fluorescence enhancement effect. Although the lowest excited triplet energy level of isophthalic acid was higher than the lowest excited state energy level of dysprosium ion for the dysprosium complex, the lowest triplet energy level of acetylacetone was lower than the $^4F_{9/2}$ energy level of Dy^{3+}. The absorbed energy to the central ion will be effectively transferred but also will weaken the luminescence of the central ion, causing the energy absorbed by the isophthalate ligand to transfer to the central ion and then transfer some energy from the central ion to the acetylacetonate. The end result is weaker luminescent intensity of the ternary complex than that of the isophthalic acid binary complex but stronger than the acetylacetonate binary complex.

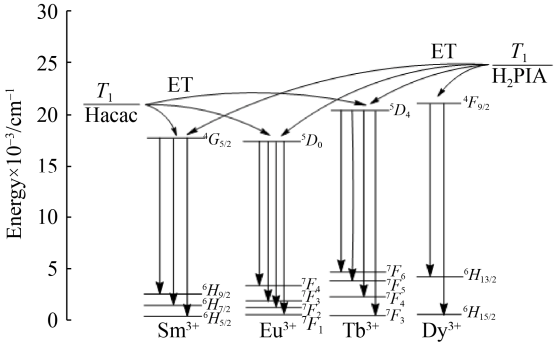


Fig. 5　Schematic of energy transfer in complexes

In addition to the above-described factors, a water is found in the binary complexes and the strong vibration of O—H in the water molecule has a certain quenching effect on the luminescence of the rare earth central ion while the ternary complex is anhydrous. This disadvantage may be eliminated in which the hydroxyl group vibration can reduce the luminescent intensity of the products. Therefore, in general, the luminescent properties of the anhydrous ternary complexes are better than those of the binary complexes with water.

3.5.2 Color coordinates of the ternary complexes

Fig. 6 depicts the emission colors of the complexes 1–4 as calculated from their emission spectra and validated by the Commission Internationale de Eclairage (CIE) diagram. The CIE coordinates of 1–4 were calculated as (0.424 2, 0.330 2), (0.643 0, 0.351 1), (0.346 6, 0.603 9), and (0.422 7, 0.461 2), respectively. The results based on the CIE diagram indicate that the complexes can be used as a potential orange, red, green, and yellow components in luminescent materials.

3.5.3 Fluorescent lifetime of the ternary complexes

Taking the strongest excitation wavelength of each ternary complex as the excitation wavelength and selecting its strongest emission wavelength as the detection wavelength, the solid-state fluorescent lifetime of the ternary complex was determined. As shown in Fig. 7, it can be seen from the fitting results, the fluorescent lifetime of the complex is first-order, and the values are 23.54 (**1**), 837.34 (**2**), 1 092.79 (**3**), and 20.15 μs (**4**). The fluorescent lifetime of the terbium complex exceeded 1 ms.

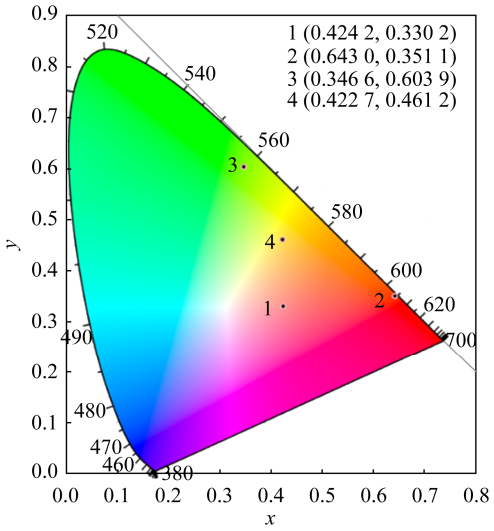
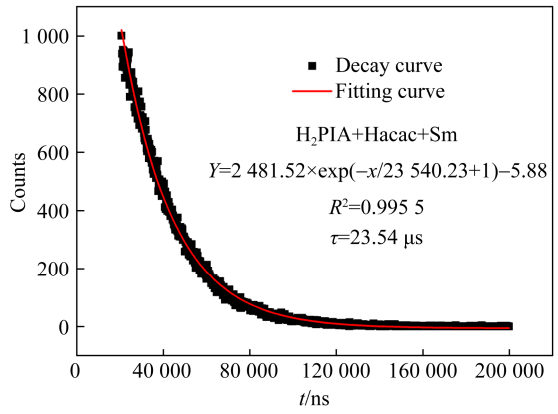
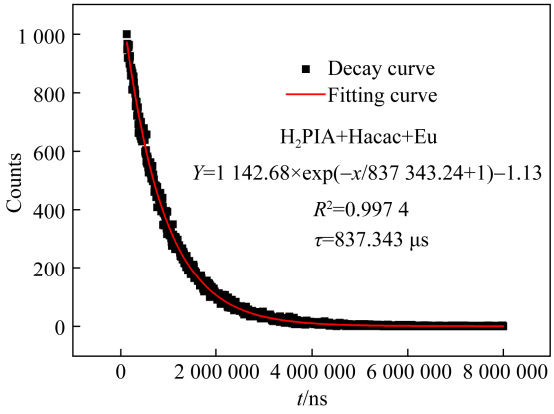


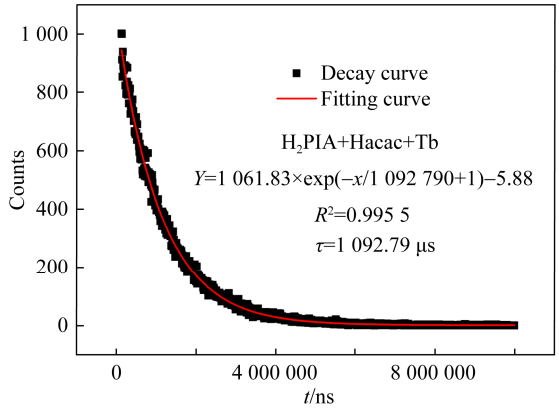
Fig. 6 CIE coordinates of complexes 1–4



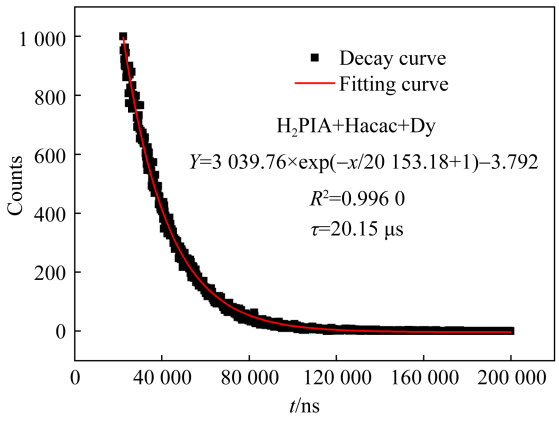
(a) Samarium complex



(b) Europium complex



(c) Terbium comple



(d) Dysprosium complex

Fig. 7 Fluorescent decay traces of the ternary complexes 1–4

4 Conclusions

The ternary complexes $[Ln_2(PIA)_2(acac)_2]$ and the binary complexes $[Ln_2(PIA)_3(H_2O)_4]$ and $Ln(acac)_3H_2O$ (Ln=Sm, Eu, Tb, Dy) were synthesized using isophthalic acid and acetylacetone as ligands. The fluorescent spectra of the solid products at room temperature and the fluorescent lifetime of the ternary complexes were determined. The experimental results show that the fluorescent intensities of the ternary complexes were much stronger than that of the binary complexes for Eu^{3+} and Tb^{3+}, that is, the sensitization of the double ligands was significantly stronger than the sensitization of a single ligand, indicating a synergistic enhancement effect. For Sm^{3+}, the fluorescent intensity of the ternary complex was only slightly stronger than that of the binary complex. The energy mainly originated from the energy absorbed by isophthalic acid. The effect of acetylacetone was not strong, and the energy transfer efficiency was not particularly high. However, a certain enhancement was present. For Dy^{3+}, the synergistic effect of the two ligands was poor. Since the lowest excited state level of acetylacetone was lower than the $^4F_{9/2}$ level of Dy^{3+}, the energy absorbed by isophthalic acid was lost, eventually leading to the less luminescent intensity of ternary complexes as found for the isophthalic acid binary complex. Otherwise, the strong vibration of O—H in the water molecule of binary complexes had a certain quenching effect on the luminescence of the rare earth central ions, thereby reducing their luminous intensity. In addition, the fluorescent lifetime of the europium and terbium ternary complexes were as long as 1 ms, which indicates that they are potential fluorescent powder materials.

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