

$\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}(x=0, 0.218, 0.799, 0.896, 0.987, 1)$ 配合物的近红外发光性能

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摘要: 采用 4,4,4-三氟-1-苯基-1,3-丁二酮(TPB)为第一配体,4,7-二苯基-1,10-菲咯啉(Bath)为第二配体,分别制备了配合物 $\text{Er}(\text{TPB})_3\text{Bath}$ 和 $\text{Yb}(\text{TPB})_3\text{Bath}$,以及它们的混合配合物 $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}(x=0.218, 0.799, 0.896, 0.987)$,并对所制得配合物的发光性能进行了系统研究。研究结果表明,所有配合物均能发射所含稀土离子的近红外特征光,并且可以通过调节混合配合物中的 $n_{\text{Er}}/n_{\text{Yb}}$ 来调控 $\text{Yb}^{3+}/\text{Er}^{3+}$ 之间的能量传递,进而提高 Er^{3+} 离子在 1 530 nm 处的发光。

关键词: 稀土配合物; 近红外发光; 能量传递

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Near Infrared Luminescence Properties of the Complexes of $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}(x=0, 0.218, 0.799, 0.896, 0.987, 1)$

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Abstract: A series of near infrared (NIR) luminescent complexes based on $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ (where TPB=4,4,4-tri-fluoro-1-phenyl-1,3-butanedione, Bath=4,7-diphenyl-1,10-phenanthroline, $x=0, 0.218, 0.799, 0.896, 0.987, 1$, respectively) were prepared by selecting TPB and Bath as the first and second ligands, respectively. Luminescence properties of these complexes were investigated in detail. All these complexes exhibit the characteristic emission of the Yb^{3+} and/or Er^{3+} ion in the NIR region, and the emission intensity of Er^{3+} ion can be enhanced by modulating the $n_{\text{Er}}/n_{\text{Yb}}$, which is related to the energy transfer from Yb^{3+} to Er^{3+} ions.

Keywords: rare earth complex; near infrared luminescence; energy transfer

0 Introduction

Rare earth (RE) complexes are the most promising luminescent materials with appealing features, such as large stock shift, sharp emission bands, long lifetimes, and high quantum efficiency, etc., which render them potential applications in the fields of bio-imaging, laser systems, optical amplification, organic light-

emitting diodes, and pressure/disorder sensors^[1-9], etc. Among rare earth complexes, the near infrared emitting complexes, such as Yb^{3+} , Er^{3+} , Nd^{3+} , Ho^{3+} , Pr^{3+} complexes, etc., have been intensely studied in the past decades^[10-15]. There are two particular driving forces for these researches: one is the rapid development of telecommunication networks; the other is the vivo sensing and imaging in bio-applications^[16]. Er^{3+} -based

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materials play a special role in telecommunication technologies since they emit characteristic emission at $\sim 1.55\ \mu\text{m}$ (0.8 eV), thus covering a spectroscopic window in which glass optical fibers show high transparency (the so-called third-communication window)^[17]. The organic erbium complexes have also attracted ever-increasing attention in recent years due to their advantages of easy processing and flexible molecular design, etc., compared with their inorganic glass fibers counterparts^[18]. But for practical application in the fields of telecommunication, optical communication systems, or optical amplifiers, the NIR yield and efficiency of the organic RE complexes should still be improved enormously.

Because of their small energy gaps between the emissive states and the ground states, the NIR luminescent RE^{3+} ions usually suffer the problem of quenching from many phonon-related nonradiative processes, especially the vibrations of the C-H, N-H and O-H bonds in the organic complexes^[19-20]. To achieve high yield of NIR emission, one of the strategies is to use heavy atoms to replace the H atom in the ligands, and fluorination is a beneficial method^[19-20]. Another drawback of the RE-based NIR emitting complexes is the pervasive energy mismatch between the ligands and the center ions. For most RE complexes, their absorption or excitation bands locate mainly in ultraviolet region, which means that the excited states energy levels of ligands are much higher than the RE NIR emitting levels, thus giving rise to inefficient energy transfer from the ligand to the center ion, and therefore the unsatisfactory NIR quantum efficiency^[21]. In the past decade, many groups have devoted to designing and synthesizing novel RE complexes with low exciting energy levels, such as large conjugated systems, heterometallic complexes, etc. Among them, *d-f* block complexes are feasible choices, in which long-lived ³MLCT states of *d-f* transition metals (e.g. Ru^{2+} , Re^+ , Os^{2+} , Au^+ , Pt^{2+} , Ir^{3+}) can be excited by visible light and transfer efficiently their energy onto the $4f^n$ manifolds, thus providing an efficient pathway for energy migration within heterometallic complexes^[7,21-23]. Mixed RE complexes, which

have $\text{RE}^{3+}/\text{RE}^{3+}$ couples and possible mutual energy transfer, are another useful approach to enhance the expected NIR yield^[24-27]. Yb^{3+} ion is usually a prime candidate of the sensitizer to be chosen due to its high luminescent efficiency and relatively simple electronic structure of two energy level manifolds: the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state around at $10\ 000\ \text{cm}^{-1}$ in the NIR region, especially for the Er^{3+} complexes. Thanks to the energy match between the $^4I_{11/2}$ level of Er^{3+} and the $^2F_{5/2}$ level of Yb^{3+} , the energy transfer between excited state Yb^{3+} ion and ground state Er^{3+} ion can occur resonantly. This process is very efficient since the absorption cross section of Yb^{3+} (about $10^{-20}\ \text{cm}^2$) is one order of magnitude higher than that of Er^{3+} (about $10^{-21}\ \text{cm}^2$)^[28]. In this case, the Yb^{3+} ion functions as the bridge between ligands and Er^{3+} ion, thus enhancing the emission intensity of Er^{3+} .

Herein we synthesized erbium and ytterbium complexes using fluorinated ligand TPB and large conjugated ligand Bath as the first and the second ligands, respectively. In addition, the mixed complexes $\text{Er}_x\text{Yb}_{1-x}(\text{TfB})_3\text{Bath}$ ($x=0.218, 0.799, 0.896$, and 0.987 , respectively) were also prepared aiming to improve the Er^{3+} emission intensity. Photoluminescence properties of the as-prepared complexes were investigated in detail, and the experimental results reveal that all the complexes exhibit the characteristic transition of the Er^{3+} and/or Yb^{3+} ion. In the Er^{3+} - Yb^{3+} mixed systems, the emission intensity of Er^{3+} ion can be enhanced by modulating the $n_{\text{Er}}/n_{\text{Yb}}$ to facilitate the energy transfer from Yb^{3+} to Er^{3+} ion.

1 Experimental

1.1 Materials and instruments

Ytterbium(III) nitrate pentahydrate (99.9%), and erbium(III) nitrate pentahydrate (99.9%), 4,4,4-trifluoro-1-phenyl-1,3-butanedione (99.9%), 4,7-diphenyl-1,10-phenanthroline (98%) were obtained commercially from Aladdin company and used as received without further purification. Excitation and emission spectra were measured with an Edinburgh FLSP 920 fluorescence spectrophotometer. The Er^{3+} and Yb^{3+} ion contents were measured by Thermo iCAP6300 ICP-OES.

1.2 Preparation of $\text{Er}(\text{TPB})_3\text{Bath}$

0.648 g (3 mmol) TPB and 0.332 g (1 mmol) Bath were dissolved in 15 mL ethanol, and NaOH aqueous ($1 \text{ mmol} \cdot \text{L}^{-1}$) was added into it under stirring and heating to adjust the pH value to 6~8. Then, the solution of 0.449 g $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (1 mmol) in 10 mL ethanol was dropped into the above solution. A lot of precipitates appeared. The reaction was kept under reflux for 3 h. After that, the precipitates were filtered and washed by de-ionized water and ethanol for several times, respectively. Finally, the precipitates were dried and recrystallized with acetone/ethanol mixed solvent, and the resulted products were dried at 80°C under vacuum. Yield: 0.78 g (68%).

1.3 Preparation of $\text{Yb}(\text{TPB})_3\text{Bath}$

The same procedure as that of $\text{Er}(\text{TPB})_3\text{Bath}$. Yield: 76%.

1.4 Preparation of $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$

The same procedure as that of $\text{Er}(\text{TPB})_3\text{Bath}$, but herein the $\text{Er}(\text{NO}_3)_3/\text{Yb}(\text{NO}_3)_3$ mixed solution with different $n_{\text{Er}}/n_{\text{Yb}}$, instead of pure $\text{Er}(\text{NO}_3)_3$ or $\text{Yb}(\text{NO}_3)_3$, was added.

$\text{Er}_{0.218}\text{Yb}_{0.782}(\text{TPB})_3\text{Bath}$: 0.2 mmol $\text{Er}(\text{NO}_3)_3$ +0.8 mmol $\text{Yb}(\text{NO}_3)_3$ was added. Yield: 65%. Elemental analysis: Er: $28\,540 \mu\text{g} \cdot \text{g}^{-1}$, Yb: $106\,200 \mu\text{g} \cdot \text{g}^{-1}$.

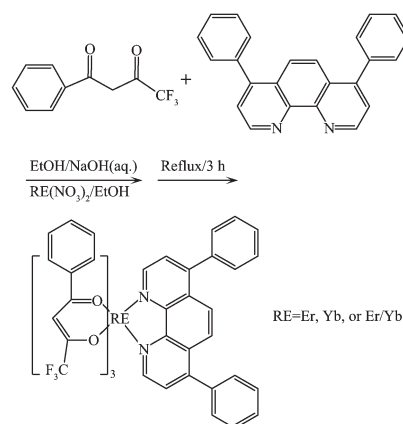
$\text{Er}_{0.896}\text{Yb}_{0.104}(\text{TPB})_3\text{Bath}$: 0.5 mmol $\text{Er}(\text{NO}_3)_3$ +0.5 mmol $\text{Yb}(\text{NO}_3)_3$ was added. Yield: 72%. Elemental analysis: Er: $88\,020 \mu\text{g} \cdot \text{g}^{-1}$, Yb: $11\,300 \mu\text{g} \cdot \text{g}^{-1}$.

$\text{Er}_{0.799}\text{Yb}_{0.201}(\text{TPB})_3\text{Bath}$: 0.8 mmol $\text{Er}(\text{NO}_3)_3$ +0.2 mmol $\text{Yb}(\text{NO}_3)_3$ was added. Yield: 70%. Elemental analysis: Er: $137\,800 \mu\text{g} \cdot \text{g}^{-1}$, Yb: $2\,036 \mu\text{g} \cdot \text{g}^{-1}$.

$\text{Er}_{0.987}\text{Yb}_{0.013}(\text{TPB})_3\text{Bath}$: 0.9 mmol $\text{Er}(\text{NO}_3)_3$ +0.1 mmol $\text{Yb}(\text{NO}_3)_3$ was added. Yield: 66%. Elemental analysis: Er: $155\,300 \mu\text{g} \cdot \text{g}^{-1}$, Yb: $11\,300 \mu\text{g} \cdot \text{g}^{-1}$.

2 Results and discussion

The preparation routes of these complexes are shown in Scheme 1.



Scheme 1 Preparation routes of $\text{RE}(\text{TPB})_3\text{Bath}$

The mixed complexes $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ were synthesized by using the $\text{Er}(\text{NO}_3)_3/\text{Yb}(\text{NO}_3)_3$ mixed solution with different $n_{\text{Er}}/n_{\text{Yb}}$ as the rare earth sources. The actual Er^{3+} and Yb^{3+} content in the as-prepared complexes were detected by means of ICP. And the mixed $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ complexes were denoted by the detected results, as shown in Table 1.

The photoluminescence properties of the $\text{Er}(\text{TPB})_3\text{Bath}$ and $\text{Yb}(\text{TPB})_3\text{Bath}$ were investigated firstly. Fig. 1 shows the excitation and emission spectra of $\text{Er}(\text{TPB})_3\text{Bath}$ and $\text{Yb}(\text{TPB})_3\text{Bath}$. There are three obvious bands in the excitation spectrum of $\text{Er}(\text{TPB})_3\text{Bath}$, locating at 374, 463 and 520 nm, respectively. The strongest one at 374 nm can be ascribed to the $\pi-\pi^*$ transition of the ligands. And the band at 463 nm can be ascribed to the additive contribution from the ligands and the transition of $^4I_{15/2} \rightarrow ^4H_{7/2}$ from Er^{3+} ion^[26]. The sharp peak at 520 nm can be contributed to the transition of

Table 1 Raw and detected $n_{\text{Er}}/n_{\text{Yb}}$ for the mixed complexes $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$

Raw $n_{\text{Er}}/n_{\text{Yb}}$	Detected $n_{\text{Er}}/n_{\text{Yb}}^a$			Resulted complexes
	$C_{\text{Er}} / (\mu\text{g} \cdot \text{g}^{-1})$	$C_{\text{Yb}} / (\mu\text{g} \cdot \text{g}^{-1})$	$n_{\text{Er}}/n_{\text{Yb}}$	
2/8	28 540	106 200	0.218/0.782	$\text{Er}_{0.218}\text{Yb}_{0.782}(\text{TPB})_3\text{Bath}$
5/5	88 020	11 300	0.896/0.104	$\text{Er}_{0.896}\text{Yb}_{0.104}(\text{TPB})_3\text{Bath}$
8/2	137 800	35 860	0.799/0.201	$\text{Er}_{0.799}\text{Yb}_{0.201}(\text{TPB})_3\text{Bath}$
9/1	155 300	2 036	0.987/0.013	$\text{Er}_{0.987}\text{Yb}_{0.013}(\text{TPB})_3\text{Bath}$

^a Detected $n_{\text{Er}}/n_{\text{Yb}}$ is resulted from: $(C_{\text{Er}}/M_{\text{Er}})/(C_{\text{Yb}}/M_{\text{Yb}})$, where C_{Er} and C_{Yb} denote the detected contents of Er^{3+} and Yb^{3+} ion, M_{Er} and M_{Yb} is the atomic weight of the Er^{3+} and Yb^{3+} ion, respectively.

$^4I_{15/2} \rightarrow ^2H_{11/2}$ [26,29]. As depicted in its emission spectrum, the $\text{Er}(\text{TPB})_3\text{Bath}$ complex emit its characteristic emission peaked at 1 530 nm, which is originated from the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er^{3+} ion.

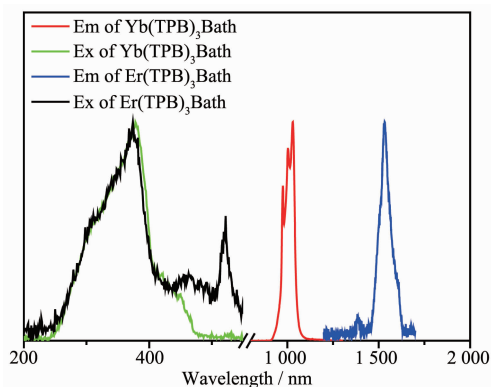


Fig.1 Excitation (Ex) and emission (Em) spectra of $\text{Er}(\text{TPB})_3\text{Bath}$ and $\text{Yb}(\text{TPB})_3\text{Bath}$

The $\text{Yb}(\text{TPB})_3\text{Bath}$ exhibit similar excitation spectrum with that of $\text{Er}(\text{TPB})_3\text{Bath}$, locating mainly at 378 nm with a shoulder band at about 445 nm, which can be ascribed to the contribution of ligands. However, the transition of the Yb^{3+} ion is not observed in the excitation spectrum, which is rational because the Yb^{3+} ion owns only one possible transition between its ground state and excited state locates in the NIR transition. As shown in Fig.1, the $\text{Yb}(\text{TPB})_3\text{Bath}$ complex shows a emission band in NIR region, split into three peaks at 976, 1 005 and 1 031 nm, respectively, which is related with the coordination field effect of the ligands [30-32].

To enhance the emission yield of the Er^{3+} ion, we prepared a series of mixed $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ ($x=0.218, 0.799, 0.896$, and 0.987 , respectively) compl-

exes because the presence of Yb^{3+} was expected to facilitate the energy transfer from ligands to Er^{3+} ions. The photoluminescence properties of these complexes were investigated. For better comparison, all the emission spectra were measured under the same conditions. Firstly, we investigate the effect of excitation source (374 or 378 nm) on the emission spectra, and the experimental results show that 378 nm excitation source causes slightly higher emission intensities of both Yb^{3+} and Er^{3+} ions than that from 374 nm source. Fig.2 compares the emission spectra of complexes $\text{Er}_{0.896}\text{Yb}_{0.104}(\text{TPB})_3\text{Bath}$ and $\text{Er}_{0.218}\text{Yb}_{0.782}(\text{TPB})_3\text{Bath}$ under the excitation of 374 and 378 nm, respectively.

What should be noted is the possible energy transfer from Yb^{3+} to Er^{3+} ion. As mentioned above, the 378 nm excitation source corresponds to the maximum excitation of the obtained Yb^{3+} complex. Compared with Er^{3+} ion, the Yb^{3+} ion possesses wider absorption cross section, which is helpful in harvesting the energy from ligands. In this case, part excited energy of Yb^{3+} ion would be transferred to the Er^{3+} ion, thus enhancing the emission of Er^{3+} ion. So, the enhanced Er^{3+} emission can be interpreted as the improved energy transfer from Yb^{3+} to Er^{3+} ion.

The energy transfer between $\text{Yb}^{3+}/\text{Er}^{3+}$ ions and the enhancement of Er^{3+} emission were found to be more obvious by comparing the emission spectra of the mixed $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ ($x=0.218, 0.799, 0.896$, and 0.987 , respectively) complexes with that of the pure $\text{Er}(\text{TPB})_3\text{Bath}$ complex. Under excitation at 378 nm, the emission intensity of the $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ varied with different $n_{\text{Er}}/n_{\text{Yb}}$ (Fig.3). Fig.3a depicts

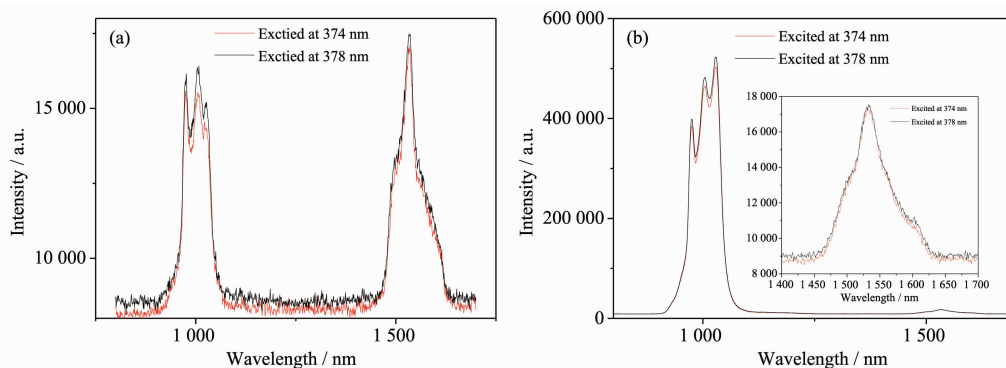


Fig.2 Emission spectra of (a) $\text{Er}_{0.896}\text{Yb}_{0.104}(\text{TPB})_3\text{Bath}$ and (b) $\text{Er}_{0.218}\text{Yb}_{0.782}(\text{TPB})_3\text{Bath}$

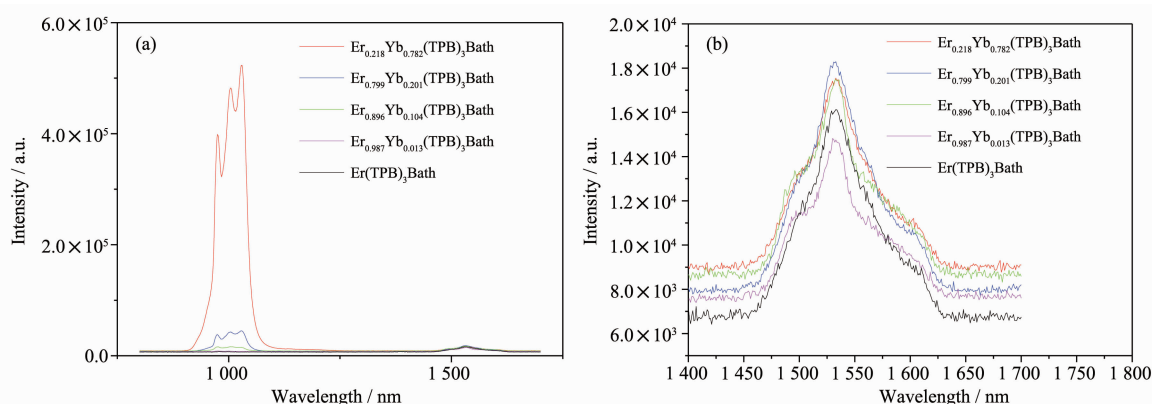


Fig.3 Emission spectra of the $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ ($x=0.218, 0.799, 0.896, 0.987, 1$, respectively) excited at 378 nm (a) whole emission spectra and (b) emission spectra of the Er^{3+} ion

the emission spectra of the $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ ($x=0.218, 0.799, 0.896$, and 0.987 , respectively) complexes and $\text{Er}(\text{TPB})_3\text{Bath}$. It could be found that the emission intensity of Yb^{3+} ion (Em-Yb) is dominated in the cases of $x=0.218$ and 0.799 , while Em-Yb and the emission intensity of Er^{3+} ion (Em-Er) is comparable when $x=0.896$ (Fig.2a).

As far as the Em-Er is concerned, it varies with the $n_{\text{Er}}/n_{\text{Yb}}$ also, but the variation should be distinguished carefully. As shown in Fig.3b, the intensity order of the Em-Er of the mixed complexes is $\text{Er}_{0.799}\text{Yb}_{0.201}(\text{TPB})_3\text{Bath} > \text{Er}_{0.896}\text{Yb}_{0.104}(\text{TPB})_3\text{Bath} = \text{Er}_{0.218}\text{Yb}_{0.782}(\text{TPB})_3\text{Bath} > \text{Er}(\text{TPB})_3\text{Bath} > \text{Er}_{0.987}\text{Yb}_{0.013}(\text{TPB})_3\text{Bath}$. With the increasing ratio of Er^{3+} ion from $x=0.218$ to 0.896 , the mixed complexes show enhanced Em-Er, which is higher than that of $\text{Er}(\text{TPB})_3\text{Bath}$. This result confirm the presence of energy transfer from Yb^{3+} ion to Er^{3+} ion in these cases. Based on theory and experimental results,

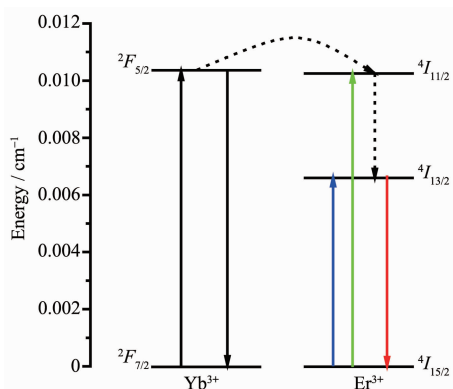
the energy processes involved in these mixed complexes was analyzed and depicted in Scheme 2. It is found that there is an optimal $n_{\text{Er}}/n_{\text{Yb}}$ for the mixed complexes. The Em-Er is most desirable when $x=0.799$, but further increasing x to 0.896 , it decreased to the level as that of the case of $x=0.218$, and further increasing x to 0.987 causes the rapid decrease of Em-Er to even lower than that of the $\text{Er}(\text{TPB})_3\text{Bath}$ complex. In this case, back energy transfer from Er^{3+} to Yb^{3+} ion was suggested to responsible for this phenomenon [26]. Further investigation about this phenomenon should be performed in future.

3 Conclusions

In summary, a series of complexes based on $\text{Er}_x\text{Yb}_{1-x}(\text{TPB})_3\text{Bath}$ ($x=0, 0.218, 0.799, 0.896, 0.987$, and 1 , respectively) with TPB and Bath as the first and second ligands, respectively, were prepared. Their luminescence properties of these obtained complexes were investigated experimentally. All the mixed complexes exhibit the characteristic emission of Yb^{3+} and Er^{3+} ion. Interestingly, the emission intensity of Er^{3+} ion can be enhanced by appropriately modulating the $n_{\text{Er}}/n_{\text{Yb}}$. When $x=0.799$, the correspond mixed complexes realize the highest emission intensity of Er^{3+} ion attributed to the energy transfer from Yb^{3+} to Er^{3+} ion.

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Scheme 2 Energy transfer between $\text{Yb}^{3+}/\text{Er}^{3+}$ ion, here the higher energy levels of Er^{3+} ion are omitted

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