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Letter

Synthesis and luminescent properties of color-tunable lanthanide complexes with 5-(pyridin-4-yl)isophthalic acid

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ABSTRACT

In this work, a T-shape organic molecule 5-(pyridin-4-yl)isophthalic acid was synthesized via a Suzuki coupling reaction and used as the ligand for a serial of mixed-lanthanide complexes. The chemical compositions of the lanthanide complexes were determined as $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ by elemental analysis (EA) and thermo gravimetric analysis (TGA). The luminescent properties of the as-synthesized complexes were investigated and the intramolecular energy transfer mechanisms involved, were discussed. Efficient energy transfer from Tb^{3+} to Eu^{3+} was observed and controlled by changing the molar ratio of Tb^{3+} to Eu^{3+} ions, allowing the color tuning on the luminescent emission of the mixed-lanthanide complexes.

1. Introduction

Solid state light emitting materials have diverse applications in extensive areas such as lighting, imaging, and medicine [1–4]. During the past several decades, the most commonly used solid state lighting materials were inorganic oxides and organic molecules [5–8]. In recent years, lanthanide organic complexes have attracted intensive research interests by scientists in this field. These materials were composed of lanthanide ions and organic ligands by coordination bonds, which brought them the benefits and advantages of both inorganic and organic parts, including the characteristics narrow emission bands, high photoluminescence quantum efficiencies and good brightness of lanthanide ions, together with the numerous choices of organic ligands, resulting in almost unlimited diversities on luminescent properties, and the efficient sensitization on lanthanide ions by organic moieties via the well-known “Antenna effect”. For all these reasons, lanthanide organic complexes have the potential to be solid state light emitting materials, which can be applied in biomedicine, agriculture and lighting [9–16].

As two of the most frequently employed lanthanide ions for light emitting materials, the dominant emission bands of Eu^{3+} and Tb^{3+} are in the red and green regions of the visible respectively, with good color purity. In concerns to improve the luminescent properties of the lanthanide complexes, ways for the sensitization of lanthanide ions, e.g. Eu^{3+} include the adoption of novel ligands which may have stronger absorption or better energy level compatibility for efficient intramolecular energy transfer, and the mixing or co-doping of other lanthanide ions which may result in the energy transfer between various kinds of lanthanide ions. In the latter case, the concentration-dependence of energy transfer processes makes the emission color of mixed-lanthanide ions complexes being easily tuned, which may cover the whole visible region theoretically. In our previous reports, energy transfer among various lanthanide ions have been observed in both lanthanide complexes and metal–organic frameworks, and the energy transfer mechanisms have been studied, which may also be applied as a novel temperature sensor potentially [12,17–19].

As another effort to improve the luminescent properties of lanthanide ions, in this work, a T-shape ligand 5-(pyridin-4-yl)isophthalic acid (L), which can sensitize the Eu^{3+} and Tb^{3+} efficiently, is synthesized and a serial mixed-lanthanide ions complexes $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ ($x = 1$, 0.5, 0.2, 0.15, 0.1, 0.075, 0.05, 0.04, 0) are developed based on it. The spectroscopic properties of the mixed-lanthanide ions complexes are systematically investigated and discussed in details. The luminescent color tuning from the red to green is observed by changing the value of x easily, indicating their potential as novel color-tunable light emitting materials.

2. Experimental section

2.1. Materials and methods

The commercially available europium (III) nitrate hexahydrate (99.99%), terbium(III) nitrate hexahydrate (99.99%) and other chemicals were used as received, without further purification.

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The Fourier transform infrared (FTIR) spectra were measured with a Nicolet Thermo Scientific Nicolet iS10 spectrometer using KBr pallets. Absorption bands then were labeled as follows: strong (s), medium (m), and weak (w). EA for C, H, and N was recorded on a ThermoFinnigan Instruments Flash EA1112 microelemental analyzer. ^{1}H NMR spectra were obtained with Bruker Advanced DMX500 spectrometer. TGA was carried out on a Netzsch TG209 F3 system at a heating rate of 10 °C/min under N_2 atmosphere. Photoluminescence (PL) spectra were recorded by a Hitachi F4500 spectrophotometer. The photomultiplier tube voltage was 700 V, and the slit widths for excitation and emission spectra were kept at both 1.0 nm.

2.2. Synthesis of 5-(pyridin-4-yl)isophthalic acid

5-(pyridin-4-yl)isophthalic acid was obtained via Suzuki coupling of dimethyl 5-bromoisophthalate and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine, Fig. 1. (Suzuki coupling reaction is the Palladium-catalyzed cross-coupling reaction of organoboron compounds with alkenyl or aryl halides [20].) Dimethyl 5-bromoisophthalate was synthesized according to the work published by other researchers [21].

4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine was synthesized by stirring the mixture of pyridin-4-ylboronic acid (11.76 g, 96 mmol), pinacol (13.57 g, 115 mmol), 1,4-dioxane (300 ml) and $MgSO_4$ (15 g) at 110 °C for 1 day. The precipitate was removed by filtration, and after the removal of solvent under reduced pressure, **6** was obtained.

3 (10.92 g, 40 mmol), **6** (9.84 g, 48 mmol) and K_2CO_3 (76.64 g) were then mixed in 1,4-dioxane (260 ml) and the mixture was deaerated using N_2 for 30 min. Palladium(II)bis(triphenylphosphine) dichloride (0.128 g, 0.18 mmol) was added to the mixture. The mixture was heated at 65 °C for 1.5 day under N_2 atmosphere. The resultant mixture was extracted with ethyl acetate and water, and the water phase was then removed. Organic solvent was removed under reduced pressure, and the crude product was purified by silica column chromatography to yield **7.7** was hydrolyzed by adding NaOH, and then excess HCl was added. **L** was obtained after filtration.

High agreement between the experimental and calculated data were found from the EA results (Experiment/Calculated) for ester **6**: C, 66.64/66.42, H, 4.79/4.80, N, 5.06/5.17; and for **L**: C, 63.89/64.20, H, 3.68/3.70, N, 5.42/5.76.

The results of ^{1}H NMR experiments were shown in Fig. 2. ^{1}H NMR of ester **6** (500 MHz, $CDCl_3$, δ ppm): 8.74(d, 3H), 8.51(d, 2H), 7.59(t, 2H), 4.00(s, 6H). ^{1}H NMR of **L** (500 MHz, DMSO-d_6, δ ppm): 13.58(m, 2H), 8.75(d, 2H), 8.56(d, 1H), 8.51(d, 2H), 7.91(d, 2H).

The results of FTIR experiments were shown in Fig. 3. The absorption bands of **L** are at (cm^{-1}): 3102(m), 1710(s), 1630(s), 1509(m), 1402(m), 1303(m), 1193(s), 920(m), 835(s), 762(s), 723(m), 682(s), 616(w), 568(w).

2.3. Synthesis of lanthanide complexes

The $Eu(NO_3)_3$ and $Tb(NO_3)_3$ were dissolved in water at the concentration of 0.08 M. The ligand 5-(pyridin-4-yl)isophthalic acid was dissolved in dilute aqua ammonia at the concentration of 0.1 M, and the pH value of the solution was then adjusted to ca. 6 with dilute ammonia. The prepared solution was mixed by corresponding molar ratio (M^{3+}:L = 1:1) and stirred in water bath at 70 °C for 2 h and a white suspension was obtained. After vacuum filtration, the precipitates were washed by deionized water and alcohol for several times, and then dried at 80 °C for 1 day in vacuum oven to yield white powder.

3. Results and discussion

High agreement between the experimental and calculated data are found from the EA results (Experiment/Calculated) for the Eu

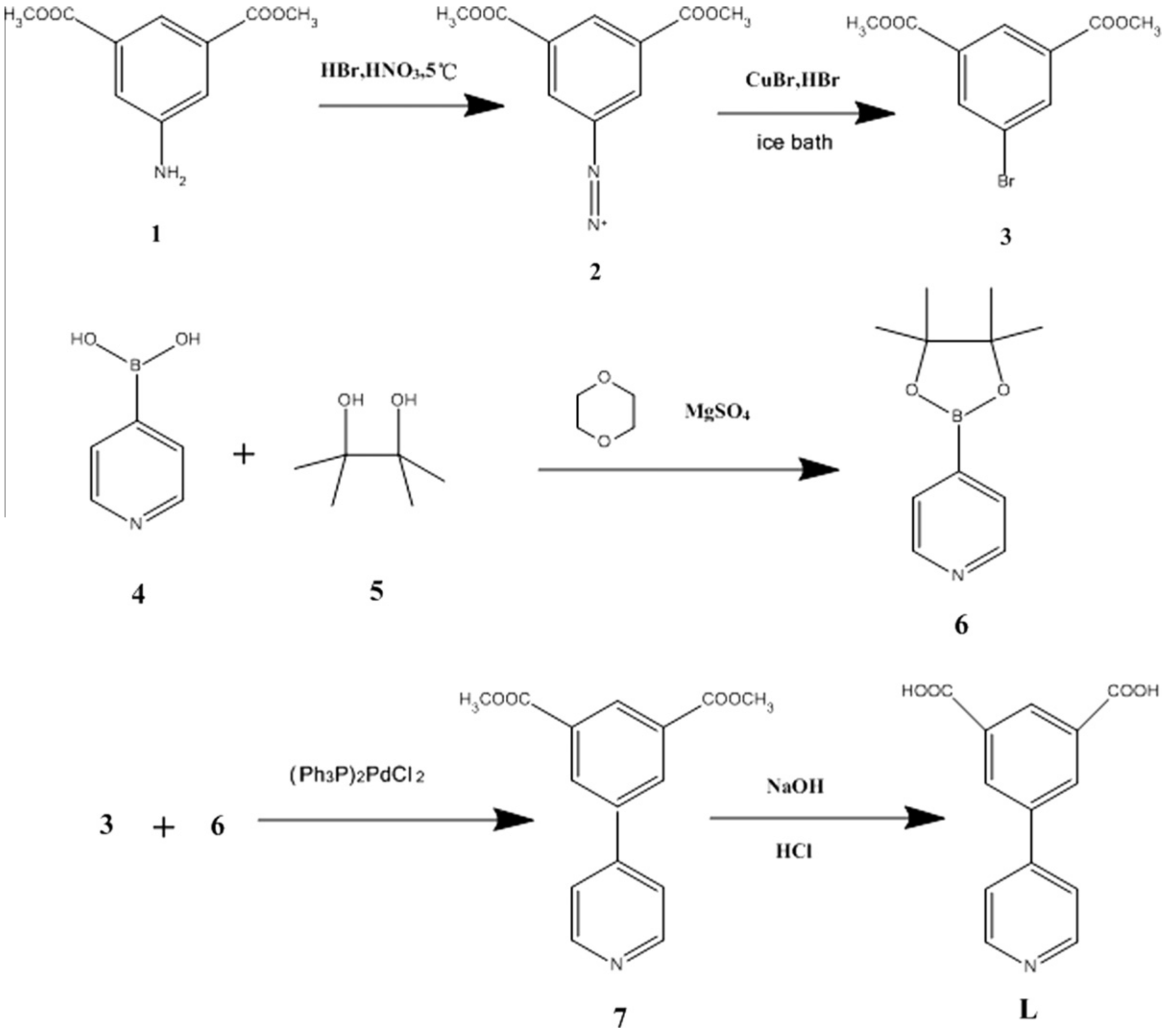

Fig. 1. The synthesis process of the ligand.

complex: C, 42.43/42.58, H, 2.85/2.91, N, 3.64/3.82; and for the Tb complex: C, 41.83/42.05, H, 2.79/2.88, N, 3.60/3.71. The results indicate the chemical composition of the complexes are $Re_2L_3(H_2O)_4$ (Re = Eu, Tb). The results of TGA experiments are shown in Fig. 4, the weight loss of the coordinated water molecules of Eu complex and Tb complex corresponding to the first step in the TGA curves are 6.84% and 6.64% respectively, which are in good agreement with the calculated values of 6.55% and 6.47%. The thermal stability of the complexes is fairly good as concerning the relatively high decomposition temperature about 480 °C. The FTIR spectra for all

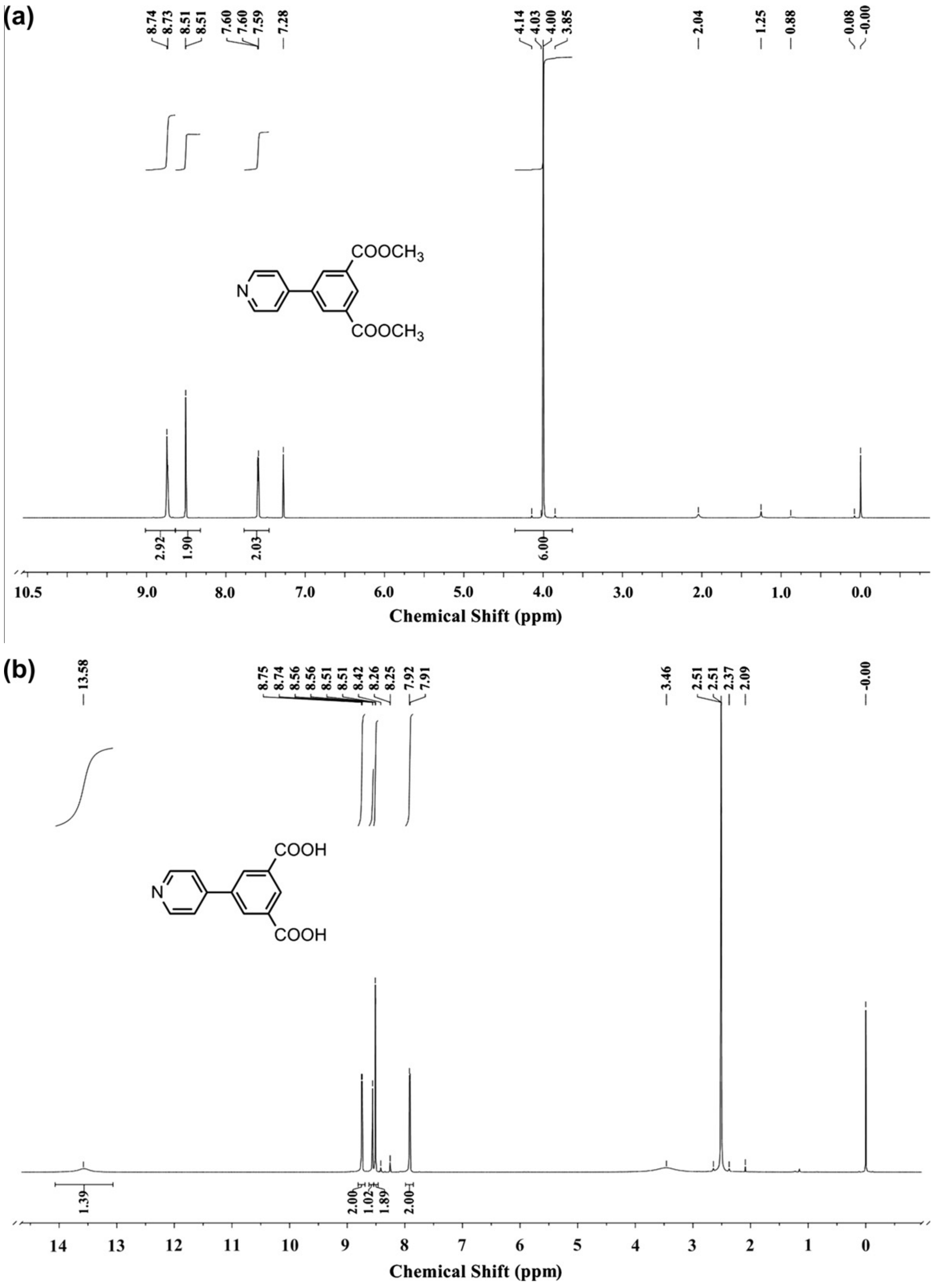

Fig. 2. ^{1}H NMR shift of ester **6** (a) and **L** (b).

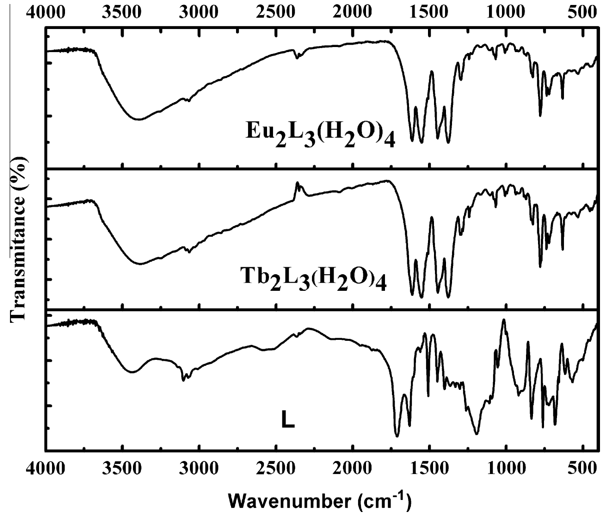

Fig. 3. FTIR spectra of **L** and the lanthanide complexes.

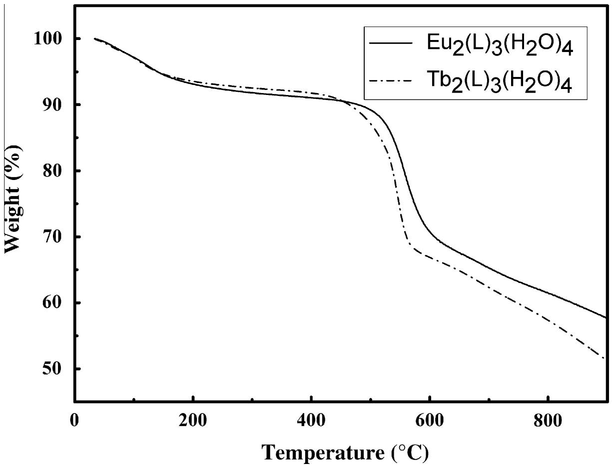

Fig. 4. TGA curves of the lanthanide complexes.

the lanthanide complexes were similar (shown in Fig. 3), in which the absorption bands are at (cm^{-1}): 3384(s), 3065(w), 1613(s), 1551(s), 1446(s), 1378(s), 779(s), 738(m), 722(m), 633(m). The absorption bands attribute to carboxyl groups in complexes (1613 cm^{-1}, 1446 cm^{-1}) are shifted to lower wave numbers in comparison with those of free ligands (1710 cm^{-1}, 1630 cm^{-1}), which suggests the deprotonated carboxyl groups have been coordinated to lanthanide ions. The strong broad absorption bands at 3384 cm^{-1} (ν_{O-H}) attributing to the stretching vibration mode of O–H bonds also indicates the coordinated water molecules.

The PL spectra of $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ excited at 350 nm are showed in Fig. 5. In the PL spectra of the complexes containing only one kind of lanthanide ion, $Eu_2L_3(H_2O)_4$ and $Tb_2L_3(H_2O)_4$, only the characteristic emission bands of each lanthanide ion were found without the broad-band emission of ligands. The emission bands peaked at 580, 594, 616, and 700 nm of Eu^{3+} can be assigned to the transitions between the first excited state ($^5D_0$) to the ground multiplet (^7F_J, J = 0–4) respectively, while those centered at 488, 545, 585, and 623 nm of Tb^{3+} can be ascribed to the transitions between the first excited state ($^5D_4$) to the ground multiplet (^7F_J, J = 6–3) respectively. The strongest emission bands of Eu^{3+} and Tb^{3+} are centered at 616 and 545 nm respectively, which lead to red and green color emission of the corresponding lanthanide complexes. In the mixed-lanthanide ions complexes, characteristic emission bands from both Eu^{3+} and Tb^{3+} can be observed. The splitting of emission bands is suggested to be due to the crystal field splitting of energy level, which indicates the lanthanide ions have different coordination environment in the complexes [22,23]. It should be noted that in all PL spectra, the broad emission bands of the ligands from ~380 to 480 nm are too weak to be observed easily, indicating the efficient energy transfer from the ligands to the lanthanide ions, and the good match on energy levels between the lowest triplet state of the ligands and the excited state of the lanthanide ions [24,25]. In other words, 5-(pyridin-4-yl)isophthalic acid can efficiently sensitize the lanthanide ions.

In our and other researcher's previous works, the energy transfer between lanthanide ions, e.g. from Tb^{3+} to Eu^{3+} in mixed-lanthanide ions complexes has been reported and discussed [12,26–28]. In this work, the energy transfer process between Tb^{3+} and Eu^{3+} ions in the mixed $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ complexes are also

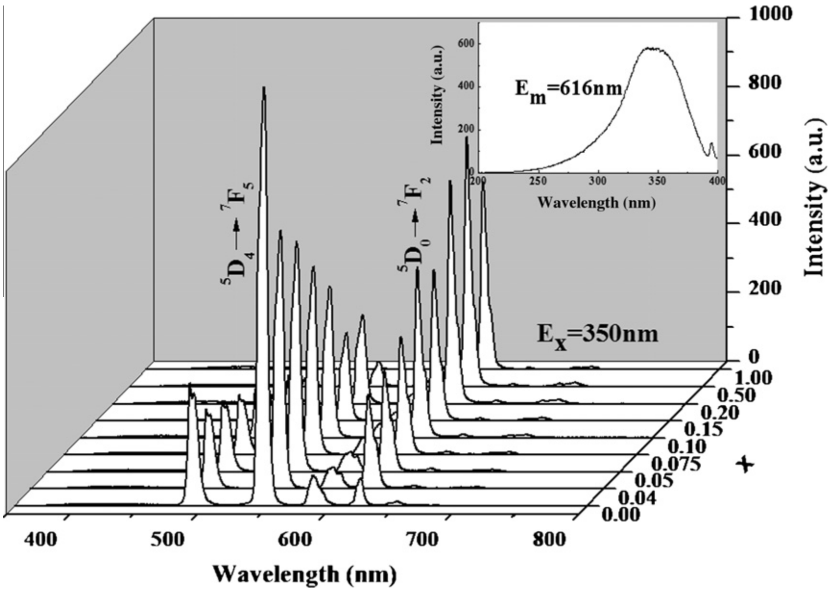

Fig. 5. PL spectra of $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ excited at 350 nm. (Inset) Excitation spectra of $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ (monitored at 616 nm).

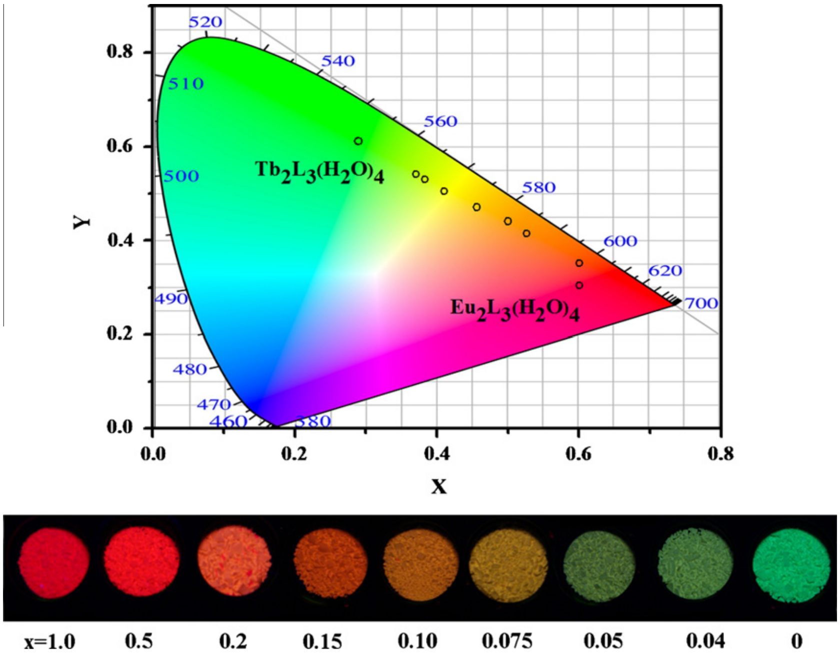

Fig. 6. CIE chromaticity coordinates and photographs of $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ with various *x*.

observed. While being excited at 485 nm which is the $^7F_6 \rightarrow {}^5D_4$ characteristic transition of Tb^{3+} ions, the characteristic emission at 616 nm of Eu^{3+} can be clearly observed in the PL spectra of the mixed $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ complexes, which confirms the energy transfer process from Tb^{3+} to Eu^{3+} in the complexes (Supplementary Fig. S1).

As shown in Fig. 5, with the increase of Tb^{3+} concentrations in the mixed-lanthanide ions complexes $(Eu_xTb_{1-x})_2L_3(H_2O)_4$, i.e. the value of *x* decreases from one, the luminescence intensities of Tb^{3+} increase gradually as the result of increased amount of Tb^{3+} ions, while those of Eu^{3+} varies in a mixed tendency which increases first, and then decreases generally. This is suggested to be due to the energy transfer from Tb^{3+} to Eu^{3+}, which enhances the emissions of Eu^{3+}, although the amount of which decreases.

Thus, the tuning on the emission colors by changing the lanthanide ions concentrations can be explained and predicted based on the energy transfer mechanism. Photographs of $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ complexes with various x values under the excitation of a 355 nm UV lamp are shown in Fig. 6. The corresponding CIE coordinates are also shown on CIE chromaticity diagram. As expected, with the decrease on the value *x* from 1 to 0, the emitting colors of complexes shift from red to yellow, and then to green as the result of various ratios of red emission by Eu^{3+} to green emission by Tb^{3+}. These luminescent properties of the mixed-lanthanide ions complexes indicate the systematic color-tuning on their emission from red to green, which may be potentially applied as light emitting materials in this region. For such an aim, the other luminescent properties of the mixed-lanthanide ions complexes such as the temperature-dependence of their luminescence should be further investigated. This work is now underway.

4. Conclusions

In this study, we synthesis mixed-lanthanide complexes by Eu^{3+}, Tb^{3+} and 5-(pyridin-4-yl)isophthalic acid. The antenna effect and energy transfer from Tb^{3+} to Eu^{3+} in the complexes have been observed and discussed in details. The luminescent color of the mixed-lanthanide ions complexes $(Eu_xTb_{1-x})_2L_3(H_2O)_4$ can be tuned from red to green by changing the ratio of Tb^{3+} to Eu^{3+}, which indicate them as promising light emitting materials potentially.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2012.12.030.

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