

Synthesis and characterization of the novel color-tunable Eu/Tb(BPA)₃phen composites

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Abstract. The new color-tunable luminescent Eu/Tb(BPA)₃phen composites have been successfully fabricated by the solvothermal reactions. The characterization of the final products have been investigated by field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), Thermogravimetric analysis (TG-DSC) and Ultraviolet and visible (UV-Vis) spectrophotometer. It is found that the geometry of the composite particles is regular by scanning electron microscopy image. Thermogravimetric analysis indicates that the initial decomposition temperature of the final products is 334 °C, approximately. The results demonstrate that Eu/Tb(BPA)₃phen composites have excellent thermal stability. And the products after decomposition are stable oxides (Eu₂O₃ and Tb₂O₃). Furthermore, Eu and Tb ions complexes exhibit strong red and green luminescence, respectively. Emitting color of physically blended Eu(BPA)₃phen and Tb(BPA)₃phen composites can be tuned in a wide range from red to yellow to green under the excitation of 350 nm single-wavelength ultraviolet light. The CIE coordinates of C_{Tb}, C₁, C₂, C₃, C₄, C₅, C₆ and C_{Eu} are calculated as (0.24, 0.60), (0.31, 0.56), (0.33, 0.55), (0.38, 0.52), (0.40, 0.51), (0.43, 0.48), (0.54, 0.41) and (0.65, 0.34), respectively. The color-tunable luminescent materials can be widely applications in many fields, such as the optical and electronic devices, fluorescent probe and labels.

Keywords: Luminescence; Color-tunable; Thermal stability; 1, 10-Phenanthroline; Bisphenol A

1 Introduction

Recently, the color-tunable luminescent materials for their potential applications in flat panel display systems, full-color displays [1], next-generation lighting sources [2], biomarkers, imaging [3, 4] and so on, has been paid much attention. Many kinds of color-tunable materials have been investigated, including inorganic phosphors [5, 6], metal-organic frameworks [7, 8], functional organic materials [9, 10], rare earth (RE) organic complexes [11], etc. Among which, rare earth ions possess luminescence characteristics like narrow spectral widths, long luminescence lifetimes, large Stokes shifts and large strong binding with biological molecules. Luminescent rare-earth complexes have potential technological applications in fluorescence devices from the intense luminous properties of rare-earth complexes [12, 13]. Their application has also been reported in electroluminescent devices [14] and as fluorescence probes and labels in a variety of biological systems [15].

In order to enhance the fluorescence properties of the rare-earth complexes, co-luminescence system with two kinds of rare-earth elements has been successfully fabricated. Several authors have also indicated that the addition of the certain second rare-earth ions, such as Gd (III) and La (III), could change the fluorescence properties of the rare-earth complexes [16], for example,

SHAH [17] and Zhao [18] found Gd³⁺ ions in the mixed complex could remarkably increased the luminescent intensities of the terbium complex; Zhai [19] found the intrinsic fluorescence of Eu³⁺ could be enhanced by add Tb³⁺ ions and this is primarily due to an energy transfer from the ⁵D₄ level of Tb(III) to the ⁵D₀ level of Eu(III) ions. The luminescence mechanism is an intra-molecular energy transfer between Gd³⁺ and the central Tb³⁺ ions and from Tb³⁺ to Eu³⁺, that is called “antenna effect”. However, in the above mentioned co-luminescence system, the color of the emission light was single. Therefore, physically blended of the complexes with different RE (III) was conducted to realize multicolor [20, 21]. In the previous literature [22, 23], benzoic acid was widely used as the first ligand. In this paper, Bisphenol A (BPA) was used as the first ligand. As we know, BPA has not been mentioned in previous articles. The luminescence efficiency of BPA to Eu³⁺ and Tb³⁺ was studied, results show that it has excellent coordination ability to Eu³⁺ and Tb³⁺.

In the present paper, Eu(BPA)₃phen and Tb(BPA)₃phen were firstly prepared, in which Bisphenol A (BPA) was used as the first ligand and 1, 10-phenanthroline (phen) as the cooperative ligand. Besides, the novel color-tunable [Eu(BPA)₃phen + Tb(BPA)₃phen] composite were also fabricated by physical mixture action. The emission color of the as-prepared complexes

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are tuned by adjusting the mass ratio of $\text{Eu}(\text{BPA})_3\text{phen}$ to $\text{Tb}(\text{BPA})_3\text{phen}$. The morphology and fluorescence properties of the composites were systematically investigated. The resulting compounds are promising materials to fabricate various optoelectronic devices such as OLED.

2 Experimental sections

2.1 Materials

All experiment manipulations were performed in air using commercial grade solvents. Europium(III) nitrate hexahydrate ($\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Terbium(III) nitrate hexahydrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Bisphenol A (BPA), phenanthroline (phen), Ethanol absolute were used. All the reagents were of analytical grade and directly used as received without further purification. The purity of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was 99.99%.

2.2 Synthesis of rare earth complexes

$\text{Eu}(\text{BPA})_3\text{phen}$ powders were synthesized according to the solvothermal reactions. 0.0025 mol of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 ml of anhydrous ethanol at room-temperature. Then 0.03 mol of BPA and 0.01 mol of phen were dissolved in 30 ml of ethanol. $\text{Eu}(\text{NO}_3)_3$ ethanol solution was then added to the mixture solution of BPA and phen under magnetic stirring for 3 hour at 60 °C. The precipitates were collected by filtration and dried for 12 hour at 60 °C. The synthesis method of $\text{Tb}(\text{BPA})_3\text{phen}$ complex was similar to the above method. $\text{Eu}(\text{BPA})_3\text{phen}$ and $\text{Tb}(\text{BPA})_3\text{phen}$ complexes were marked as C_{Eu} and C_{Tb} , respectively.

2.3 Preparation of $[\text{Eu}(\text{BPA})_3\text{phen} + \text{Tb}(\text{BPA})_3\text{phen}]$ composite

By adjusting different mass ratios of $\text{Eu}(\text{BPA})_3\text{phen}$ to $\text{Tb}(\text{BPA})_3\text{phen}$, a series of $[\text{Eu}(\text{BPA})_3\text{phen} + \text{Tb}(\text{BPA})_3\text{phen}]$ composite were prepared, and the mass ratios of $\text{Eu}(\text{BPA})_3\text{phen}$ to $\text{Tb}(\text{BPA})_3\text{phen}$ were 1: 30, 1: 15, 1: 8, 1: 6, 1: 3 and 1: 1, in sequence. And these samples were respectively marked as C1, C2, C3, C4, C5 and C6. All samples were listed in Table 1.

Table 1. Composition of the composites.

Composite	$m(\text{C}_{\text{Eu}}):m(\text{C}_{\text{Tb}})$	$m(\text{C}_{\text{Eu}})/\text{g}$	$m(\text{C}_{\text{Tb}})/\text{g}$
C ₁	1:30	0.0333	1.0000
C ₂	1:15	0.0667	1.0000
C ₃	1:8	0.1250	1.0000
C ₄	1:6	0.1667	1.0000
C ₅	1:3	0.3333	1.0000

C ₆	1:1	1.0000	1.0000
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2.4 Characterization methods

The morphologies of samples were observed by field emission scanning electron microscope (FESEM, JSM-6460LV). The infrared spectra were recorded by a Fourier infrared spectrometer (FTIR, Waltham) in the range of 4000-400 cm^{-1} . Thermogravimetry and differential scanning calorimetry (TG-DSC) were carried out by a differential analyzer at the rate of 10 °C min^{-1} from room temperature to 700 °C. The fluorescent properties of the samples were investigated by a Hitachi fluorescence spectrophotometer (F-7000).

3 Results and Discussion

3.1 Characterization

The morphologies of the sample C_{Tb} , C2 and C_{Eu} were presented in figure 1(a), figure (b) and figure 1(c), respectively. It was shown that the three kinds of the samples are similar in morphology and they are similar to the quadrangular prism unit structure, the structure is relatively uniform. The above characteristics indicate that the preparation of the complex is crystal.

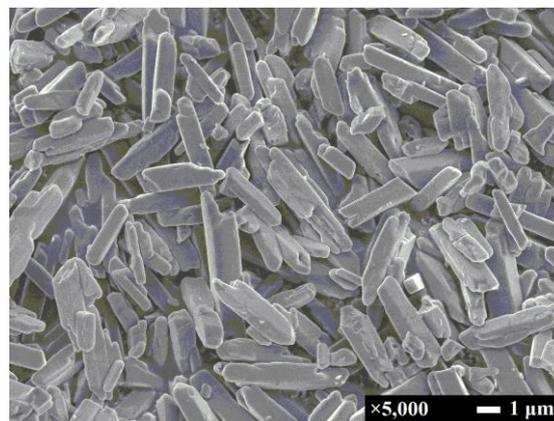


Figure 1(a). SEM images of C_{Tb} .

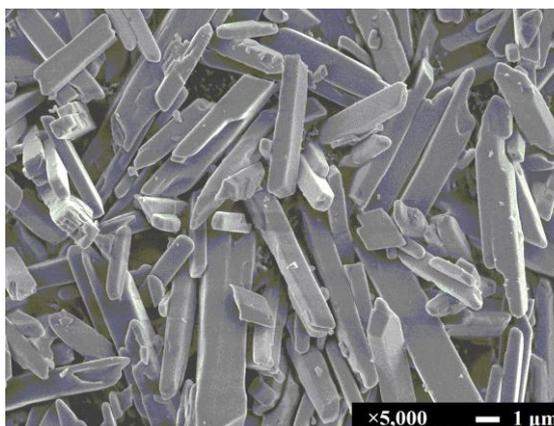


Figure 1(b). SEM images of C2.

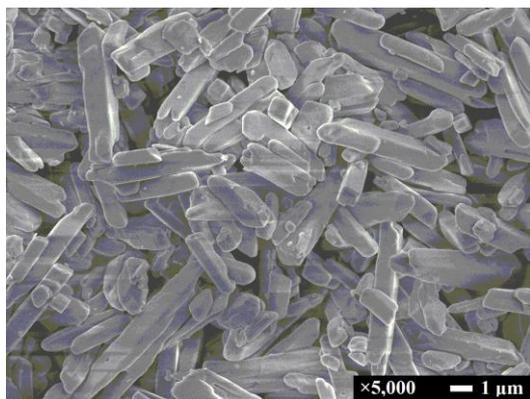


Figure 1(c). SEM images of C_{Eu} .

FTIR spectra of the ligands BPA and phen, the complexes C_{Tb} , C2 and C_{Eu} were recorded in the range of $4000-400\text{ cm}^{-1}$, as shown in figure 2. It can be easily seen from figure 2 that, the disappearance of absorption peak at 551 cm^{-1} (ν_{O-H}) for the pure BPA, and the appearance of new peak at 638 cm^{-1} of the title complex assign to symmetric absorption peaks indicate that the oxygen atoms of BPA coordinate to Eu(III) and Tb(III) ions. Besides, the appearance of absorption band for $\nu(Eu-O)$ and $\nu(Tb-O)$ at 420 cm^{-1} accounts for above-mentioned conclusion. In addition, the absorption bands of $\nu_{CN}(1585\text{ cm}^{-1})$, $\delta_{CC}(1085\text{ cm}^{-1})$ and $\delta_{CH}(840\text{ cm}^{-1})$ of phen ligand shift to higher wave number around at 1625 cm^{-1} , 1106 cm^{-1} and 855 cm^{-1} in the spectra of the complex, respectively, suggesting that the nitrogen atoms of a phen ligand coordinate to Eu^{3+} or Tb^{3+} ions [12, 24]. It was also proved by the appearance of the absorption band at 472 cm^{-1} . On the basis of the above analyses and referencing other articles [25], the coordination structure of the as-prepared complexes C_{Eu} and C_{Tb} are shown in figure 3 and figure 4, respectively.

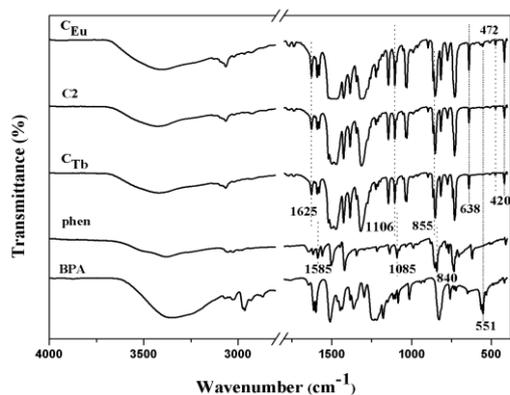


Figure 2. FTIR spectra of the sample C_{Tb} , C2 and C_{Eu} .

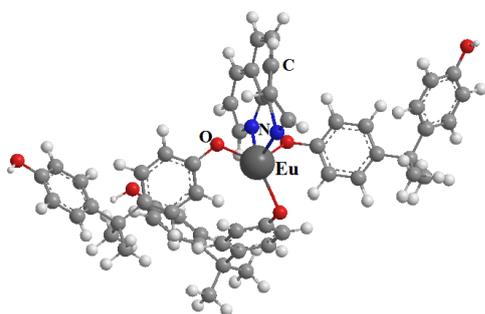


Figure 3. Coordination structure of C_{Eu} .

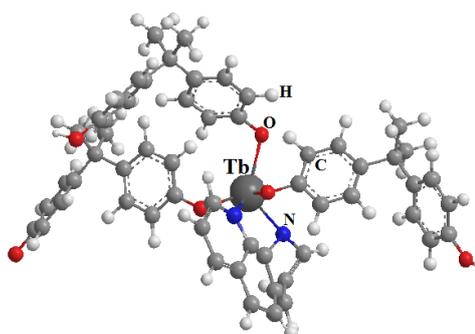


Figure 4. Coordination structure of C_{Tb} .

3.2 Thermal stabilities

The thermal stability of the sample C_{Tb} , C2 and C_{Eu} were investigated by analyzing the TG-DSC traces. The TG-DSC curves of $Eu(BPA)_3phen$ complexes are shown in figure 5. Thermogravimetric analysis indicates that $Eu(BPA)_3phen$ decomposed into two stages. The first weight loss is 51.09 % between the temperature of 334 and $400\text{ }^\circ\text{C}$, which may be due to the release of BPA molecules. As shown in the IR spectra of the residues, the bands of the asymmetric vibrations $\nu_s(O-Eu)$ at 638 cm^{-1} disappeared. In addition, the process is an endothermic reaction. The second weight loss is 22.83 % from 400 to $500\text{ }^\circ\text{C}$, which was due to the release of phen molecules. The IR spectra of the residue shows that the absorption band of $C=N$ at 1625 cm^{-1} disappears [26]. Furthermore, it can also be concluded that the melting point of $Eu(BPA)_3phen$ is about $480\text{ }^\circ\text{C}$. Due to the formation of thermally stable europium oxide (Eu_2O_3), the phenomenon of weight reduction does not occur in the next process of temperature rise [27].

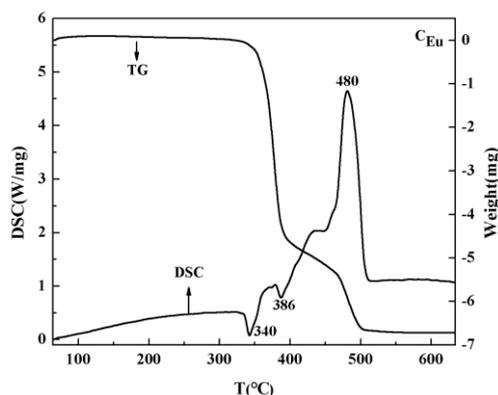


Figure 5. The TG-DSC curves of C_{Eu} .

According to the TG-DSC curves (as shown in figure 6), $Tb(BPA)_3phen$ complexes is stable up to $334\text{ }^\circ\text{C}$, afterwards it begin to decompose. When the temperature reaches $456\text{ }^\circ\text{C}$, the decomposition is terminated. The losing weight is 67.37 % with a high speed. The total process was decomposed in one-step, which may be due to the specially coordination between Tb^{3+} ions and the ligands. There is an exothermic peak on the DSC curves, and the melting point is about $412\text{ }^\circ\text{C}$.

The TG-DSC curves of C2 are shown in figure 7, TG analysis indicates that sample C2 decomposes into two stages. The initial decomposition temperature was $334\text{ }^\circ\text{C}$,

it was attributed to the release of Tb(BPA)₃phen and the release of BPA molecules in Eu(BPA)₃phen. With the temperature rising to 420 °C, the decomposition was terminated. The second weight loss was observed from the temperatures of 420 to 500 °C, which may be due to the release of phen molecules. Moreover, one exothermic peak appears on the DSC curves and the melting point is also 480 °C. Therefore, figure 7 indicated that Eu(BPA)₃phen and Tb(BPA)₃phen were physically blended and without chemical reaction with each other.

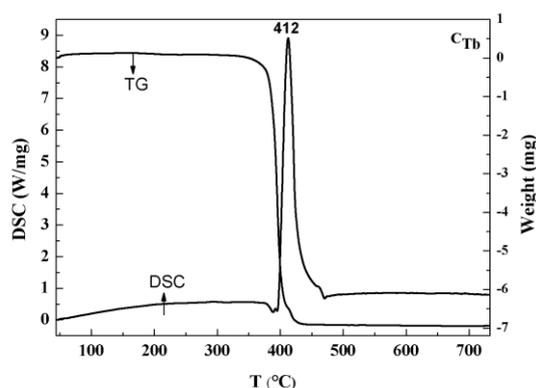


Figure 6. The TG-DSC curves of C_{Tb}.

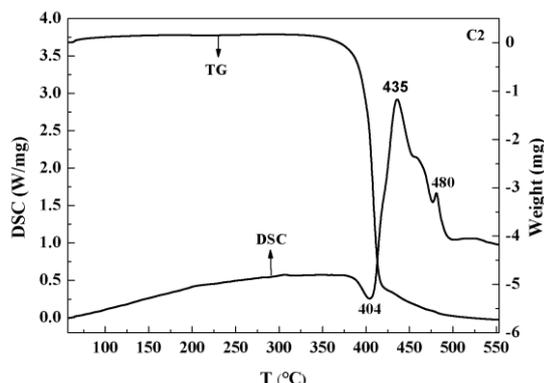


Figure 7. The TG-DSC curves of C₂.

3.3 Fluorescence properties

The luminescent characteristics of terbium (III) complexes and europium (III) complexes are investigated, firstly. The excitation and emission spectra of Tb(BPA)₃phen (C_{Tb}) are demonstrated in figure 8. When the monitoring wavelength of sample C_{Tb} is set as 544nm, a broad excitation band extending from 200 to 380 nm with the maximum at 350 nm can be observed, which is assigned to the $\pi \rightarrow \pi^*$ electron transition of the ligands. Under the excitation of 350-nm ultraviolet light, characteristic emission peaks of Tb³⁺ ions are observed, which are ascribed to the energy levels transitions of ⁵D₄→⁷F₆ (490 nm), ⁵D₄→⁷F₅ (544 nm), ⁵D₄→⁷F₄ (583 nm), and the ⁵D₄→⁷F₅ and ⁵D₄→⁷F₆ hypersensitive transitions at 544 and 490 nm are the predominant emission peaks.

The excitation and emission spectra of Eu(BPA)₃phen (C_{Eu}) are indicated in figure 9. When the monitoring wavelength of sample C_{Eu} is set as 615 nm, a broad excitation band extending from 200 to 380 nm with the

maximum at 290 nm is observed, which is assigned to the $\pi \rightarrow \pi^*$ electron transition of the ligands. Under the excitation of 350-nm ultraviolet light, it is found that characteristic emission peaks at 593 nm and 615 nm which attributed to the ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ energy levels transitions of Eu³⁺ ions, respectively.

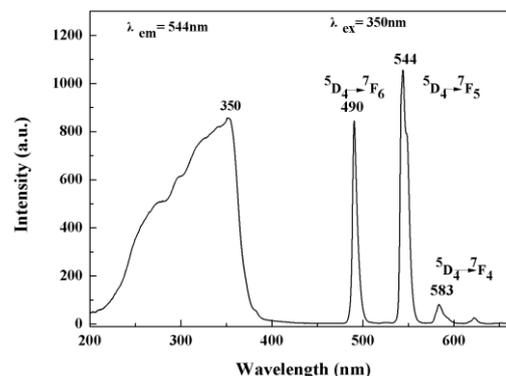


Figure 8. Excitation (left) and emission (right) spectra of C_{Tb}.

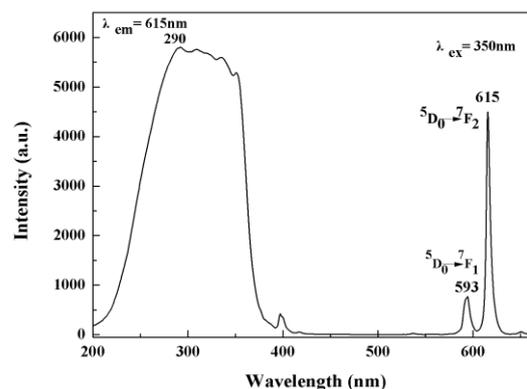


Figure 9. Excitation (left) and emission (right) spectra of C_{Eu}.

Figure 10 is the emission spectrum of all the composites. Four predominant peaks are observed for the [Eu(BPA)₃phen + Tb(BPA)₃phen] composite. The green, orange and red fluorescence emissions of predominant peaks at 490 nm, 544 nm, 593 nm and 615 nm can be observed, simultaneously. And with the decrease of the mass of Eu(BPA)₃phen, the orange and red fluorescence emissions at 593 nm and 615 nm gradually decrease. The variation of the PL intensity of Eu³⁺ and Tb³⁺ can be attributed to the energy distribution. Since the energy that the matrix absorbs and the content of RE(BPA)₃phen (RE= Eu and Tb) are constant, more energy is assigned to Eu³⁺ with the increase of the Eu(BPA)₃phen content, thus leading to stronger fluorescence peaks at 615 nm. Therefore, it is evidently found that the emission spectra of the samples could be tuned by adjusting the mass ratio of Eu(BPA)₃phen.

Generally, color can be represented by the Commission Internationale de L'Éclairage (CIE) 1931 chromaticity coordinates. Figure 10 reveals the CIE coordinate diagram of all the samples under the excitation of 350-nm ultraviolet light. It is clearly to see that the emitting color of samples could be tuned by adjusting the mass ratios of Eu(BPA)₃phen to Tb(BPA)₃phen complexes, the color is from red to yellow, yellow green, and green.

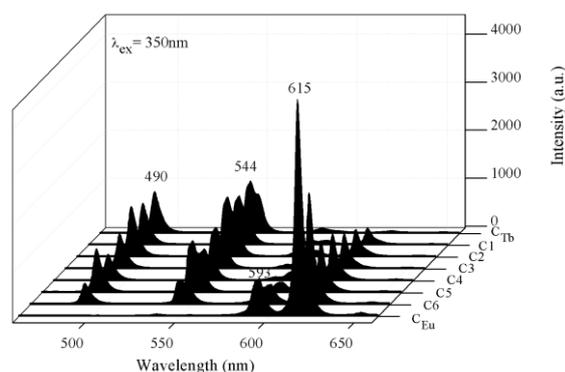


Figure 10. Emission spectra of all the samples.

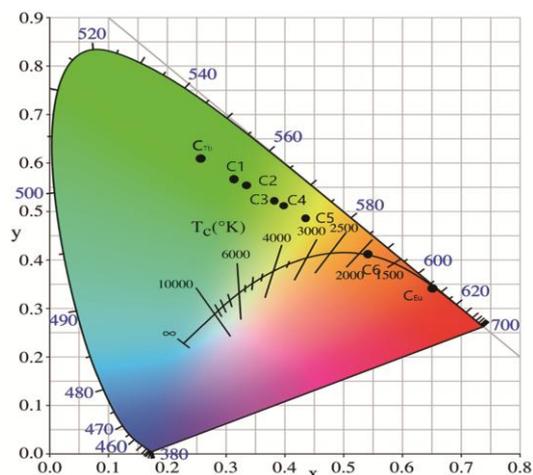


Figure 11. CIE chromaticity coordinates diagram of all the samples

4 Conclusions

In summary, in this work, the red emission of $\text{Eu}(\text{BPA})_3\text{phen}$ and the green emission of $\text{Tb}(\text{BPA})_3\text{phen}$ have been successfully synthesized, using BPA as the first ligand and phen as the cooperative ligand. Then novel color-tunable system of $[\text{Eu}(\text{BPA})_3\text{phen} + \text{Tb}(\text{BPA})_3\text{phen}]$ composite were synthesized by adjusting the mass ratio of $\text{Eu}(\text{BPA})_3\text{phen}$ to $\text{Tb}(\text{BPA})_3\text{phen}$ complexes. The morphology and properties of final products were characterized in detail by SEM, FTIR, TG-DSC and fluorescence spectral. Through a series of representations that $[\text{Eu}(\text{BPA})_3\text{phen} + \text{Tb}(\text{BPA})_3\text{phen}]$ composite, a physical blend of $\text{Eu}(\text{BPA})_3\text{phen}$ and $\text{Tb}(\text{BPA})_3\text{phen}$, can emission fluorescent from red to yellow to green under the excitation of 350-nm single-wavelength ultraviolet light. The initial decomposition temperature was 334 °C, approximately. The products after decomposition are stable oxides (Eu_2O_3 and Tb_2O_3). The color-tunable luminescent materials have potential applications in many fields, such as the lighting, fluorescent probe and biological labeling.

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