

Research Article

Thermal Stability and Luminescent Properties of Tri-cellulose Acetate Composites Containing Dy(SSA)₃Phen Complex

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Dysprosium (Dy) ternary complex was prepared using 5-sulfosalicylic acid (SSA) as the first ligand and 1,10-phenanthroline (Phen) as the second ligand, denoted as Dy(SSA)₃Phen. The complex was blended with tri-cellulose acetate (TCA) via a cosolvent method to obtain polymer luminescent materials. The composition and structure of the rare-earth complex were characterized by means of elemental analysis, infrared (IR) spectra, and thermogravimetric analysis (TGA). The fluorescence spectra displayed this pure Dy(SSA)₃Phen complex, and the TCA/Dy(SSA)₃Phen composites all emit blue light. The (90/10) composite possesses fine luminescent properties with quantum yield of 33.5% and thermal stability for potential usage as blue fluorescent materials.

1. Introduction

Polymer/rare earth (RE) composites possess excellent optical, electrical, and spectroscopic properties stemming from the additive rare-earth compounds and meantime have fine processability and flexibility arising from polymer materials, which can be potentially applied in light-emitting diodes, detector systems, X-ray phosphors, solid-state lasers and bioinorganic sensors, etc. [1–5]. Considerable attention has been paid to design and synthesize polymer/RE luminescent materials with good luminescent properties and high internal quantum efficiencies [6–8]. RE-based emitters which are usually doped or bonded with macromolecules can generate characteristically sharp and narrow emissions, because of the distinctive excitation mechanism of antenna effect and f-f radiative transition [9–14]. A considerable number of research reports have focused on four kinds of RE metals, i.e., europium (Eu), terbium (Tb), samarium (Sm), and dysprosium (Dy), especially for the Eu or Tb ions based complexes, because their resonance energy levels are close to the triplet levels of organic ligands, and so the RE ions could emit strong luminescent properties via the efficient energy transfer between ligands and RE ions [15–19].

Notably, doping luminescent RE organic complexes into polymer matrices is one of the most effective approaches to obtain the polymer luminescent materials via a simple, convenient, and high efficient blending method. However, some doped-polymer/RE composites exhibited poor luminescent properties and poor mechanical properties, mainly owing to the nonuniform dispersion of RE complexes in polymer matrices and the poor chemical affinity between the doped complex and polymer matrix [9, 20]. In order to solve these problems, organic ligands of RE complexes play a significant role in boosting the chemical affinity between the added complexes and macromolecules, and especially the organic compounds possessing multifunctional groups which could be potential hydrogen-bonding acceptors or donors are primarily selected as ligands for RE complexes [21–23]. Conjugated acids were usually used as the first ligand as a result of their strong coordination ability with RE ions and the potential hydrogen-bonding acceptors from carbonyl groups, e.g., salicylic acid [13], phthalic acid [24], benzoic acid and its derivatives [25], and acrylic acid [26]. It is worthwhile pointing out that the molecular structure of polymer matrices is another significant factor for

promoting the chemical affinity between the added RE complexes and polymer chains.

In this paper, tri-cellulose acetate (TCA) was selected as the polymer matrix, because of the potential hydrogen-bonding donors from the substantial hydroxyl groups. Furthermore, as a result of good filming performance, excellent transparency, fine glossiness, well solubility, and good processability of TCA, it had been widely used in the protective film of the polarizing film of the liquid-crystal display (LCD) which required a high transparency [27]. TCA could be easily soluble in a variety of solvents, favorable to prepare polymer/RE composites by means of solution blending. Additionally, sulfosalicylic acid (SSA) was chosen as the first ligand, not only because it could sensitize the luminescent property of Dy ions but also since its oxygen of carbonyl groups provides hydrogen-bonding acceptors [13, 19]. Therefore, the hydrogen bonding is most probably formed between the ligands of the added RE complex and the TCA matrix, favorable to improve the uniform dispersion of the complex in the matrix. As a series of studies on polymer luminescent materials emitting three-color light (red, green, and blue) [10, 28], Dy-based complexes blended with TCA have been highly concerned. There are few reports of Dy³⁺ complex-doped polymer materials with fine luminescence, and thus, we synthesized Dy³⁺ ternary complexes using SSA and 1,10-phenanthroline (Phen) as the first and second ligands, respectively. The Dy(SSA)₃Phen complex can retain fine luminescent properties dispersing into the TCA matrix, and finally, the TCA/Dy(SSA)₃Phen composites emitting blue light with good thermal stability were obtained.

2. Materials and Methods

2.1. Materials. Tri-cellulose acetate (TCA), with the weight-average molecular weight of 200,000, was supplied by our collaborating laboratory (Xiuli Wang's Research Group, Sichuan University) and purified by acetone. Dysprosium oxide (Dy₂O₃) at 99.99% purity was provided by Shanghai Yuelong Rare Earth New Materials Co., Ltd., China. 5-sulfosalicylic acid (SSA, AR), 1,10-phenanthroline (Phen, AR), dimethyl sulfoxide (DMSO, AR), acetone (EA, AR), and absolute ethyl alcohol (AR) were purchased from Chengdu Kelong Chemical Reagent Factory, China. Sodium hydroxide (NaOH, AR) was purchased from Chongqing Chuandong Chemical Co., Ltd., China. Concentrated hydrochloric acid (HCl, AR) was supplied by Chongqing Inorganic Chemical Reagent Factory, China.

2.2. Preparation of Dy(SSA)₃Phen Complex. Weighed 3 mmol Dy₂O₃ and 80 ml concentrated hydrochloric acid in a 100 ml bottom beaker immersed in an oil bath with magnetic stirrer, heated to 100°C to dissolve Dy₂O₃ powders absolutely, kept at the temperature for 10 hours to evaporate the solution to dryness and then cooled to room temperature. Then dissolved the remains using absolute EA in a 250 ml volumetric flask, added absolute EA to the mark, and finally got 0.1 mol/L DyCl₃ ethanol solution. About

15 mmol SSA, 5 mmol Phen, and 30 ml absolute EA were successively added in 100 ml beaker immersed in an oil bath with a magnetic stirrer to dissolve all components absolutely, and then, 5 mmol Dy³⁺ ethanol solution was added in dropwise, keeping the reaction temperature at 80°C. The pH value of the mixture was adjusted to about 6.5 with NaOH aqueous solution (6 mol/L), and the mixed solution was kept at 80°C, stirred for 4 hours, and cooled to room temperature. The precipitates were repeatedly washed with EA and deionized water to remove chloride ions, dried in a vacuum oven at 60°C for 24 hours, and then stored in a damp-proof cabinet. The ternary complex, Dy(SSA)₃Phen, was prepared.

2.3. Preparation of TCA/Dy(SSA)₃Phen Composites. Dissolved 0.50 g solid mixtures of the purified TCA and Dy(SSA)₃Phen complex powders using 30.0 ml DMSO in a 100 ml flat bottom beaker immersed in an oil bath with stirring, heated the mixed solution to 60°C with stirring, then cooled to room temperature, and underwent a natural evaporation process until the solution became semisolid samples. The prepared semisolid samples were transferred to an evaporating dish with flat bottom and dried in a vacuum oven at 60°C for 10 hours. Finally thin film-like TCA/Dy(SSA)₃Phen composites were obtained and stored in a damp-proof cabinet. The weight ratios of TCA to Dy(SSA)₃Phen were 100/0, 96/4, 93/7, 90/10, and 87/13.

2.4. Characterization. Elemental analysis of C, H, and N in the pure Dy(SSA)₃Phen complex was conducted on an Elemental analyzer (Vario EL III, Elementar Co., Germany).

Infrared transmittance spectrum was recorded on a Nicolet 6670 FTIR spectrophotometer (Thermo Fisher Corp., USA). Infrared attenuated total reflection (IRATR) was implemented and measured by averaging 32 scans at a resolution of 4 cm⁻¹ over the range 4000–450 cm⁻¹.

Thermogravimetric analysis (TGA) was implemented by a thermogravimeter (Q500, TA Instruments Co., USA) in the nitrogen atmosphere using a heating rate of 10°C/min from room temperature to 1000°C.

The luminescent properties of the pure Dy(SSA)₃Phen complex and all TCA/Dy(SSA)₃Phen composites were characterized by a fluorescence spectrophotometer (Hitachi F-7000, Hitachi High-Technologies Corp., Japan). The adopted mode was luminescence. The supplied PMT voltage and scan speed were set to 400 V and 1200 nm/min, respectively. The excitation (EX) and emission (EM) slit widths were fixed at 2.5 and 5.0 nm.

3. Results and Discussion

3.1. Elemental Analysis. The results of elemental analysis for the Dy(SSA)₃Phen complex are, respectively, listed as follows: measured value (theoretical value) C 41.6% (40.7%), H 2.3% (2.5%), N 4.8% (5.0%), and S 6.5% (5.7%). These results suggest that the molar ratio of Dy³⁺ to SSA to Phen is 1 : 3 : 1 in the prepared Dy(SSA)₃Phen complex.

3.2. FTIR Analysis. Figure 1 shows infrared spectra of the two ligands and the Dy(SSA)₃Phen complex, in the wavelength range of 3550 to 450 cm⁻¹. As for the spectrum of Phen, the peak at 1561 cm⁻¹ is assigned to the stretching vibration of -N=C group, and the peaks at 852 cm⁻¹ and 739 cm⁻¹ are ascribed to the out-of-plane bending vibration of -C-H group, and for the spectrum of SSA, the peak at 1656 cm⁻¹ belongs to the stretching vibration of the carbonyl group. Obviously, compared with the spectrum of Phen, the peak of the spectrum of the Dy(SSA)₃Phen complex corresponding to the $\nu_{\text{N=C}}$ vibration shifts from 1561 cm⁻¹ to 1536 cm⁻¹, and the peaks belonging to the $\nu_{\text{C-H}}$ vibration shift from 852 cm⁻¹ and 739 cm⁻¹ to 843 cm⁻¹ and 719 cm⁻¹, respectively, which indicates that there are coordination bonds between two nitrogen atoms from Phen ligand and the central ion (Dy³⁺ ion) in the complex [29]. Moreover, by comparison with the spectrum of SSA ligand, the peak of the spectrum of the complex assigned to the $\nu_{\text{C=O}}$ vibration shifts from 1656 cm⁻¹ to 1621 cm⁻¹, indicative of the formation of the coordination bonds between carbonyl group from SSA ligand and Dy³⁺ ion [13, 30]. Furthermore, it is worth noting that as for the spectrum of the complex two new absorption peaks appearing at 549 cm⁻¹ and 461 cm⁻¹ are attributed to the stretching vibration of O → RE and N → RE, respectively [31].

Infrared spectra of TCA and the TCA/Dy(SSA)₃Phen (95/5) and (90/10) composites are displayed in Figure 2, ranging from 4000 cm⁻¹ to 450 cm⁻¹. It can be seen that the two peaks of the spectrum of TCA occurring at 3480 cm⁻¹ and 1740 cm⁻¹ are assigned to the $\nu_{\text{O-H}}$ and $\nu_{\text{C=O}}$ vibrations, respectively. Clearly, the spectrum of the (95/5) composite is similar to that of the pure TCA except that the peak corresponding to the $\nu_{\text{O-H}}$ vibration of the composite shifts from 3480 cm⁻¹ to 3415 cm⁻¹. The possible reason is that the amount of the added Dy(SSA)₃Phen complex is comparatively low so that the characteristic peaks of the complex are almost covered by the strong peaks of TCA matrix. Nevertheless, as for the spectrum of the (90/10) composite, the peaks at 3393 cm⁻¹ and 1740 cm⁻¹ are, respectively, attributed to the $\nu_{\text{O-H}}$ and $\nu_{\text{C=O}}$ vibrations of the TCA matrix, and the peak at 1625 cm⁻¹ is assigned to the $\nu_{\text{C=O}}$ vibration of SSA from the added complex. Furthermore, the main characteristic peaks of Dy(SSA)₃Phen complex at 846 cm⁻¹, 717 cm⁻¹, and 470 cm⁻¹ also appear in the spectrum of the (90/10) composite. Compared with the spectra of the pure TCA and Dy(SSA)₃Phen complex as shown in Figures 1 and 2, it can be found that the $\nu_{\text{O-H}}$ peak for the (90/10) composite is red-shifted about 90 cm⁻¹ and the $\nu_{\text{C=O}}$ peak for the composite is red-shifted 4 cm⁻¹ from the 1621 cm⁻¹, indicative of the existence of hydrogen bonds between the oxygen atom from carbonyl groups from SSA and the hydroxyl groups from TCA.

3.3. Thermal Analysis. Thermal properties of pure Dy(SSA)₃Phen complex and TCA/Dy(SSA)₃Phen composites were characterized via TG analysis, and the TGA curves are shown in Figure 3. As for the plot of the Dy(SSA)₃Phen complex, there is a two-stage decomposition process,

corresponding to the removal processes of two ligands. The total mass loss of the complex is 79.2%, which is in good agreement with the calculated value (80.9%) when the ligands of the Dy(SSA)₃Phen complex are completely decomposed and the final residues are rare-earth oxide [32]. The weight loss of the first stage is 58.6% which is considered as the removal process of SSA ligand, and that of the second stage is 20.4% belonging to the decomposition process of Phen ligand. Furthermore, at the first decomposition stage of the complex, the extrapolated onset (T_e) and final (T_c) temperatures are about 273°C and 325°C, and at the second stage, the T_e and T_c are about 557°C and 669°C, suggesting that the Dy(SSA)₃Phen complex possesses fitting thermal stabilities for the usage of luminescent materials. Based on the above-mentioned elemental analysis, FTIR analysis, and TGA results, the molecular structure of the Dy(SSA)₃Phen complex can be ascertained, as shown in Figure 4.

As for TCA and the TCA composites, the TGA thermograms are displayed in Figure 3, and the T_e and T_c values as well as the mass-loss values are listed in Table 1. Obviously, there is only one stage of decomposition occurring on the TGA curves of TCA and the composites, which suggests that the decomposition process of the composites is similar to that of the pure TCA, and during the processes, each chain scission reaction has an analogous energy barrier [33]. It can be seen that with the increase of the content of the added complex, the T_e , T_i , and T_c values show a descending trend. This is probably caused by the fact that the degradation process of TCA macromolecules is related to the rupture of the anhydroglucose ring, i.e., the backbone rupture as well as the carbonization process and the volatile substances released from organic ligands of the added complex are probably favorable to boost the rupture process of TCA macromolecular chains [34]. The more the additive content of the complex, the more the released substances and the faster the degradation processes of the TCA composites. However, it is particularly worth pointing out that the T_e and T_i values of all composites are nearly over 300°C, much higher than the onset temperature. As a consequence, the TCA/Dy(SSA)₃Phen composites still possess practicable thermal properties for materials.

3.4. Photoluminescent Properties. Figures 5 and 6 show the excitation and emission spectra of pure Dy(SSA)₃Phen complex and all TCA/Dy(SSA)₃Phen composites, respectively. It is obvious that the profile of the spectra of all composites is similar to that of the pure complex, i.e., there are broad and strong bands ranging from 260 nm to 360 nm in all excitation spectra, which suggests that the pure complex and the TCA composites can be well excited in the given wavelength range, as shown in Figure 5. The maximal values of the excitation spectra are the optimum excitation wavelengths for emission spectra, i.e., 326 nm is the optimum excitation wavelength for the pure Dy(SSA)₃Phen complex; 309 nm, 309 nm, 312 nm, and 312 nm are corresponding to the TCA/Dy(SSA)₃Phen (96/4, 93/7, 90/10, and 87/13) composites, respectively. Meanwhile, it can be seen that the excitation spectra of the composites represent

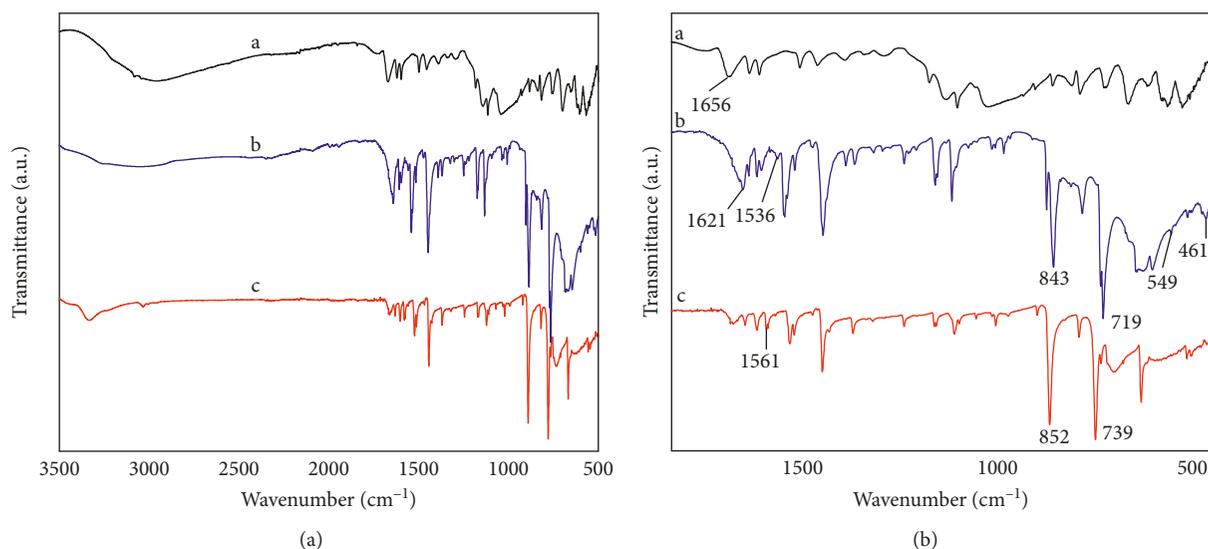


FIGURE 1: FTIR spectra ((a) 3550–450 cm^{-1} ; (b) 1800–450 cm^{-1}) of ligands and the complex: a, SSA; b, $\text{Dy}(\text{SSA})_3\text{Phen}$; c, Phen.

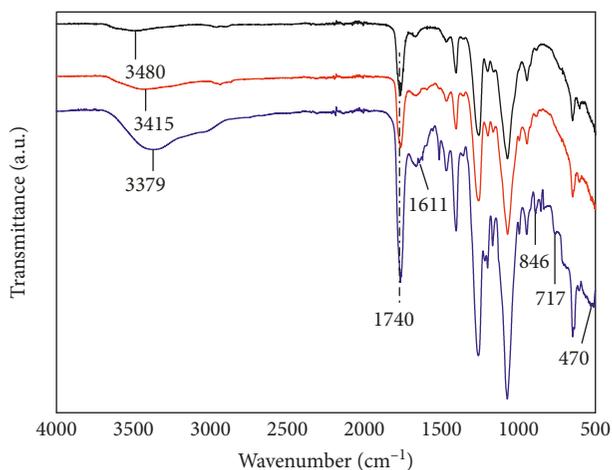


FIGURE 2: FTIR spectra of TCA and the TCA/ $\text{Dy}(\text{SSA})_3\text{Phen}$ composites: a, TCA; b, (96/4); c, (90/10).

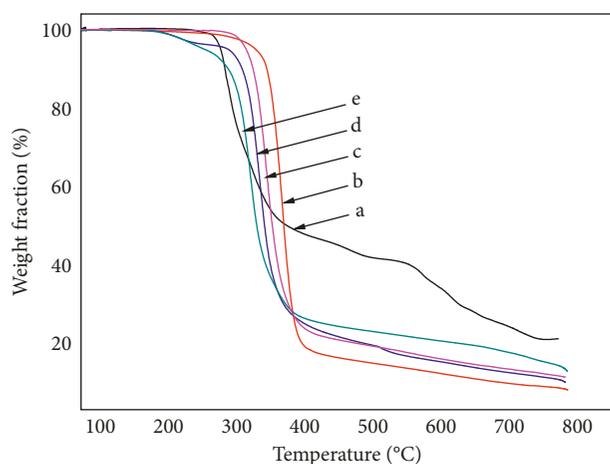


FIGURE 3: TGA thermograms of pure $\text{Dy}(\text{SSA})_3\text{Phen}$ complex and TCA/ $\text{Dy}(\text{SSA})_3\text{Phen}$ composites: a, $\text{Dy}(\text{SSA})_3\text{Phen}$; b, TCA; c, (96/4); d, (93/7); e, (90/10).

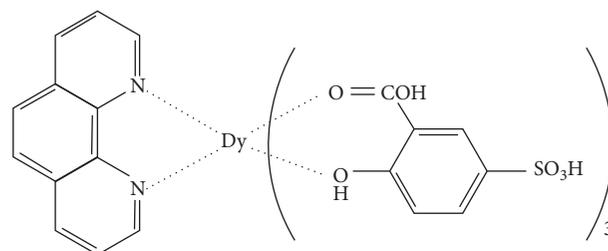


FIGURE 4: Molecular structure of the $\text{Dy}(\text{SSA})_3\text{Phen}$ complexes.

TABLE 1: The T_e , T_i , T_c , and mass-loss values of pure TCA and the TCA/ $\text{Dy}(\text{SSA})_3\text{Phen}$ composites.

TCA/ $\text{Dy}(\text{SSA})_3\text{Phen}$	T_e ($^{\circ}\text{C}$)	T_i ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	Mass loss (%)
(100/0)	347.0	366.9	380.1	92.1
(96/4)	325.9	342.1	364.3	89.9
(93/7)	313.4	331.3	355.2	88.6
(90/10)	297.7	316.9	342.6	86.6

T_e , T_i , and T_c denote extrapolated onset, onset, and final temperatures, respectively.

obvious blueshift compared with the 326 nm peak value for the pure complex, and especially for the (96/4) and (93/7) composites, the peaks are blueshifted by 17 nm, indicating that TCA macromolecules may influence the excitation process of the added complex. The main reason is that the interaction between TCA and the added $\text{Dy}(\text{SSA})_3\text{Phen}$ complex as discussed in FTIR analysis probably affects the energy transfers of the SSA ligands during the excitation process of the doped complex in TCA composites.

Emission spectra of TCA/ $\text{Dy}(\text{SSA})_3\text{Phen}$ (0/100, 96/4, 93/7, 90/10, and 87/13) composites were obtained by exciting at 326 nm, 312 nm, 312 nm, 309 nm, and 309 nm, respectively, as shown in Figure 6. For the pure $\text{Dy}(\text{SSA})_3\text{Phen}$ complex, the strong emission band with a maximum at 436 nm is assigned to $\pi \rightarrow \pi^*$ electron transition of the SSA ligands and the weak band at around

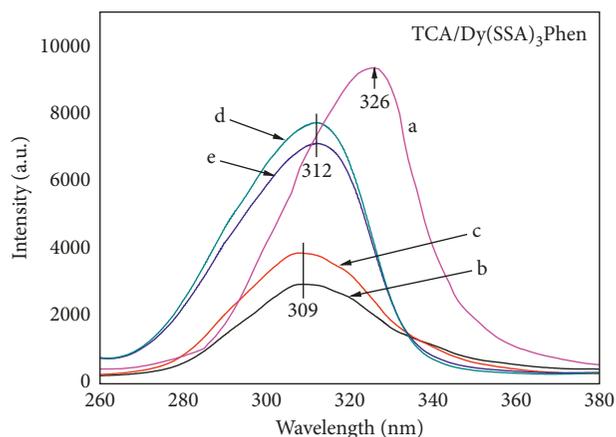


FIGURE 5: Excitation spectra of $\text{Dy}(\text{SSA})_3\text{Phen}$ complex and $\text{TCA}/\text{Dy}(\text{SSA})_3\text{Phen}$ composites: a, 0/100; b, 96/4; c, 93/7; d, 90/10; e, 87/13.

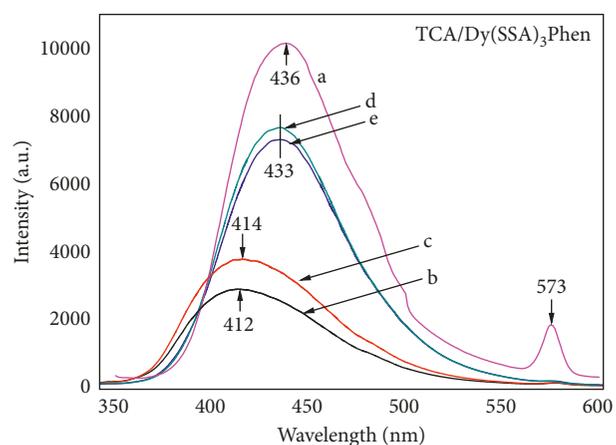


FIGURE 6: Emission spectra of $\text{Dy}(\text{SSA})_3\text{Phen}$ complex and $\text{TCA}/\text{Dy}(\text{SSA})_3\text{Phen}$ composites: a, 0/100; b, 96/4; c, 93/7; d, 90/10; e, 87/13, under excitation wavelengths at 326 nm, 312 nm, 312 nm, 309 nm, and 309 nm, respectively.

573 nm is ascribed to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition of Dy^{3+} ions [2, 35, 36]. This is probably because the introduction of the central Dy^{3+} ions is propitious to the energy transfers of the SSA ligands, due to the larger planar structure of the $\text{Dy}(\text{SSA})_3\text{Phen}$ complex (Figure 4) [36]. The Commission Internationale de L'Éclairage (CIE) coordinate of the pure complex is calculated from its emission spectrum excited at 326 nm. The coordinates (0.15, 0.09) indicate that the complex emits blue light, as shown in Figure 7. Obviously, as for the $\text{TCA}/\text{Dy}(\text{SSA})_3\text{Phen}$ composites, there are intense broad emission bands in the 360 nm–500 nm wavelength range in the emission spectra, with the maxima at 412 nm, 414 nm, 434 nm, and 434 nm corresponding to the (96/4), (93/7), (90/10), and (87/13) composites, respectively, upon the optimum excitation wavelengths. This suggests that the doped $\text{Dy}(\text{SSA})_3\text{Phen}$ complexes in the composites can still exhibit the characteristic emission of the SSA ligands similar to that of the pure complex. Dissimilarly, the weak bands at around 573 nm are absent in the emission spectra of all

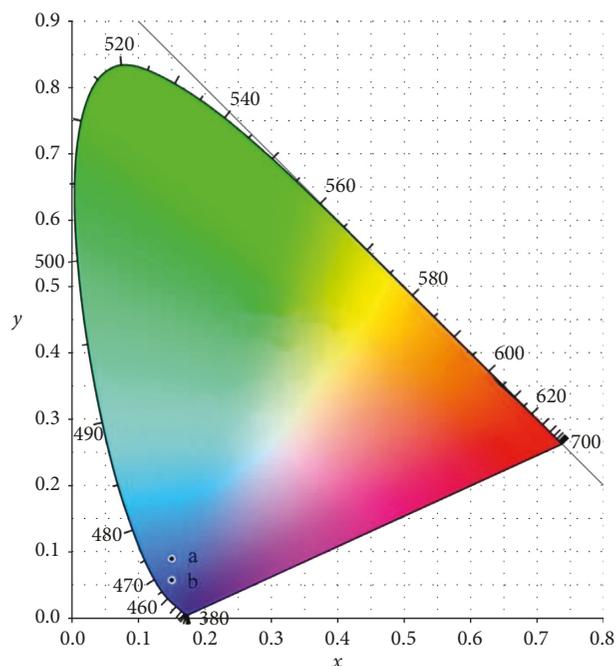


FIGURE 7: CIE coordinate photograph of the $\text{Dy}(\text{SSA})_3\text{Phen}$ complex and the $\text{TCA}/\text{Dy}(\text{SSA})_3\text{Phen}$ (95/5) composite: a, (0.15, 0.09) for the complex; b, (0.15, 0.06) for the composite.

composites. Furthermore, the emission spectra of the composites are also blueshifted, similar to the blueshift of the excitation spectra, which suggests that the TCA matrix has an impact on the excitation and emission processes of the additive $\text{Dy}(\text{SSA})_3\text{Phen}$ complex in the TCA composites.

It should be noted that a comparison of the spectral intensity of all samples indicates that the excitation and emission spectra of the pure $\text{Dy}(\text{SSA})_3\text{Phen}$ complex shows the strongest spectral intensity, and the spectral intensity of the $\text{TCA}/\text{Dy}(\text{SSA})_3\text{Phen}$ composites represents a nonlinear relationship with increasing the concentration of the added complex. When the content of $\text{Dy}(\text{SSA})_3\text{Phen}$ complex in the composites is less than 10 wt.%, the spectral intensity of the composites gradually increases with the increase of the additive content of the complex, and the intensity of the (87/13) composite is slightly lower than that of the (90/10) composite. The possible reason is that in the (96/4) and (93/7) composites, the concentration of the doped complexes is relatively low so that the complexes might be completely diluted, leading to weak spectral intensity. Nevertheless, when the additive content exceeds 10%, superfluous $\text{Dy}(\text{SSA})_3\text{Phen}$ complexes maybe aggregate in the TCA matrix, probably causing the concentration quenching existing in the (87/13) composite. Another possible reason is the inhomogeneity of the film. These caused the excitation, and emission intensity of the composite decreases. Clearly, when the concentration of the $\text{Dy}(\text{SSA})_3\text{Phen}$ complex is appropriate, namely, 10%, the spectral intensity of the composite is strong and close to that of the pure complex. The coordinates (0.15, 0.06) indicate that the (90/10) composite can also emit blue light, as shown in Figure 7.

A comparison method was adopted to calculate quantum yield (QY), and quinine sulfate (in 0.1 M H₂SO₄) was the standard with literature quantum yield 0.54 at 350 nm [37]. The QY of the TCA/Dy(SSA)₃Phen (90/10) composite in dimethyl sulfoxide was calculated by Equation (1), where subscripts “s” and “x” denote standard and test, respectively; *I* is the integrated fluorescence intensity excited at 312 nm; *A* is the absorption at 312 nm; *n* is the refractive index of the solvent. The QY of the composite was calculated to be 33.5%.

$$QY_x = QY_s \left(\frac{I_x}{I_s} \right) \left(\frac{A_s}{A_x} \right) \left(\frac{n_x}{n_s} \right). \quad (1)$$

4. Conclusion

The Dy(SSA)₃Phen complex and the TCA/Dy(SSA)₃Phen composites all emit blue light. There are hydrogen bonds between oxygen atom of carbonyl groups from SSA and hydroxyl groups from TCA, which is favorable for the added complex to retain strong luminescence in the TCA composites. When the content of the added Dy(SSA)₃Phen complex is more than 10%, the concentration quenching or the inhomogeneity of the film probably exists in the (87/13) composite. The TCA/Dy(SSA)₃Phen (90/10) composite possesses fine luminescent properties with the quantum yield of 33.5% and thermal stability for potential usage as blue fluorescent materials.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest to disclose in relation to the current research.

Authors' Contributions

Xiangwei Sun carried out the data analysis, wrote the draft, and revised the manuscript. Feiyue Wu participated in the design of the study and revised the manuscript. Yan Luo participated in the data analysis. Yuntao Li and Xiang Liu participated in the statistical analysis and revised the manuscript. Kunpeng Liu participated in the design of the study. Mengjun Huang conceived the study and revised the manuscript. All authors read and approved the final manuscript.

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