Luminescence properties of tricellulose acetate composites emitting blue light

1 Di Peng MSc

Lecturer, Chongqing University, Chongqing, China

2 Mengjun Huang PhD

Lecturer, Chongqing University of Arts and Sciences, Chongqing, China

3 Xiangwei Sun PhD

Lecturer, Chongqing University of Arts and Sciences, Chongqing, China

4 Xiang Liu MSc

Lecturer, Chongqing University of Arts and Sciences, Chongqing, China

5 Renlong Liu PhD*

Professor, Chongqing University, Chongqing, China

A series of dinuclear complexes with molar ratios of cerium to lanthanum of 1:0, 1:1, 1:2, 1:4, 1:7, 1:9 and 0:1 was synthesized using 5-sulfosalicylic acid (SSA) as the first ligand and 1,10-phenanthroline (Phen) as the second ligand, recorded as $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ ($x = 0, 0.5, 0.67, 0.8, 0.875, 0.9, 1$), and the complexes were blended with tricellulose acetate (TCA) to obtain luminescent polymer materials. The compositions and structures of the rare earth complexes were determined through elemental analysis, energy-dispersive X-ray analysis, infrared spectroscopy and thermogravimetric analysis. Under the optimum excitation wavelengths, all dinuclear complexes emitting blue light displayed the characteristic emission of the cerium (Ce^{3+}) ion. The fluorescence spectra showed that the 85:15 TCA/ $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ composite showed the strongest fluorescence among all composites and the quantum efficiency was calculated as 30.6%. The introduction of the lanthanum (La^{3+}) ion into the cerium ion complex can effectively reinforce the luminescence intensity of the complex and be favorable for retaining the excellent fluorescence in the TCA matrix. The 85:15 TCA/ $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ composite possesses fine luminescence properties and thermal stability for potential usage as a blue fluorescent material.

1. Introduction

There has been considerable interest in polymer/rare earth (RE) composites, since the composites maintain the features of RE compounds, such as excellent electrical, optical and magnetic properties, and also possess the advantages of polymer matrices, including good processability and excellent flexibility. Various lanthanide complexes were incorporated into polymers to form bonding-type/doping-type RE polymers.^{1–6} In the bonded polymers, RE compounds, regarded as monomers, should participate in polymerization or polycondensation, or the compounds would coordinate in the side-chains of polymers through chemical bonding between the RE compounds and polymers.^{5–10} Generally, the preparation process of these RE polymers is comparatively complicated and costly, which limits the extensive applications of the polymers.⁵ Nevertheless, the doped polymers can be obtained through a simple, convenient and highly efficient blending method, demanding the uniform dispersion of RE compounds in polymers, including solution blending and melt blending. Meanwhile, in order to prepare polymer hybrid materials with strong luminescence properties, it is of great importance to enhance significantly the fluorescence intensity of the incorporated RE compounds.^{6–10}

Besides choosing appropriate ligands in RE complexes, the addition of other RE ions is one of the most effective approaches to improving the luminescence intensity of the complexes.^{11–20} The incorporated metal ion can be an RE ion with strong fluorescence or non-fluorescence – for example, the introduction of terbium (Tb^{3+}) ions^{11–13} or samarium (III) (Sm^{3+}) ions¹⁴ into europium (III) (Eu^{3+}) complexes results in the fluorescence enhancement of the complexes, since the added metal ions can be favorable for improving efficiency of energy transfer from ligands to the central RE ion. Gadolinium (Gd^{3+}) ions,¹⁴ non-fluorescent lanthanum (La^{3+}) ions^{15,16} and yttrium (Y^{3+}) ions¹⁷ with inert structures have been shown to have a sensitization effect on europium (III) ions. The reason for this sensitization effect can be probably explained as follows: as for lanthanum and yttrium ions, they possess stable electronic structures and no 4f electrons, leading to the very high energy level of excited states, so that lanthanum or yttrium ions will not consume the energy absorbed by organic ligands and the energy may be concentratedly transferred to the central RE ion to reinforce the luminescence intensity of the complexes.^{15–17} In the authors' previous work, it was found that the introduction of other RE ions into the

*Corresponding author e-mail address: lrl@cqu.edu.com

europium (III) complex can not only enhance the luminescence intensity of the complex but can also take advantage of keeping excellent fluorescence in polymer host matrices.¹² Polymer/RE composites emitting bright green or red light have been successfully prepared.^{12,21}

In a series of studies on polymer materials emitting three-color light (red, green and blue), blending a cerium (Ce^{3+}) ion complex with tricellulose acetate (TCA) to emit blue light has attracted more attention. The cerium ion, one of the fluorescent RE ions, has only one 4f electron, so the fluorescent emission belonging to the $f \rightarrow f^*$ transition is weak; however, when the cerium ion coordinates with nitrogen (N), the oxygen or sulfur of the side-group from aromatic compounds and the formed cerium complex are excited at the optimum excitation wavelengths. The $5d \rightarrow 4f$ transition of the cerium ion from the lowest 5d excited state to the 4f ground state is accompanied by the occurrence of the fluorescence process of the cerium ion.^{22–26} There are few reports of polymer materials doped with the cerium ion complex that have excellent fluorescence.²⁷ In this work, by introducing lanthanum ions into the cerium ion complex and using 5-sulfosalicylic acid (SSA) as the first ligand and 1,10-phenanthroline (Phen) as the second ligand, the complex can retain strong luminescence intensity, dispersing into the TCA host matrix, and, finally, TCA/ $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ composites with good luminescence properties and thermal stability were obtained.

2. Experimental

2.1 Materials

TCA, with a weight-average molecular weight of 200 000, was supplied by the authors' collaborating laboratory (Xiang Liu's research group, Chongqing University of Arts and Sciences) and was purified by acetone. Cerium (III) oxide (Ce_2O_3) and lanthanum (III) oxide (La_2O_3), at 99.99% purity, were supplied by Shanghai Yuelong Rare Earth New Materials Co., Ltd, China. SSA analytical reagent (AR), Phen (AR), dimethyl sulfoxide (DMSO; AR), acetone (AR) and absolute ethyl alcohol (AR) were purchased from Chengdu Kelong Chemical Reagent Factory, China. Sodium hydroxide (NaOH; AR) was provided by Chongqing Chuandong Chemical Co., Ltd, China. Concentrated hydrochloric acid (HCl; AR) was obtained from Chongqing Inorganic Chemical Reagent Factory, China.

2.2 Preparation of $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ complexes

The chlorination process of cerium (III) oxide and lanthanum (III) oxide was accomplished on the basis of the method described in the literature.¹² The detailed preparation steps are given in the online supplementary material. The prepared dinuclear complexes are denoted as $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ ($x = 0.5, 0.67, 0.8, 0.875, 0.9$).

2.3 Preparation of TCA/ $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ composites

Solid mixtures (1.00 g) of the purified TCA and as-prepared $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ complex powders and 40.0 ml DMSO were added to a 100 ml flat-bottom beaker immersed in an oil bath with

stirring, heated to 60°C and stirred to dissolve the complex powders and TCA completely, then cooled to room temperature and kept in this condition until much of the DMSO was evaporated. The prepared semisolid samples were transferred to an evaporating dish with a flat bottom and dried in a vacuum oven at 60°C for 10 h. Finally, thin filmlike products, the TCA/ $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ composites, were obtained and stored in a damp-proof cabinet. The weight ratios of TCA to $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ ($x = 0.8, 0.875$) complexes were 100:0, 95:5, 90:10 and 85:15.

2.4 Characterization

Elemental analysis of carbon (C), hydrogen (H) and nitrogen in $\text{Ce}(\text{SSA})_3\text{Phen}$ and $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ complexes was conducted on an elemental analyzer (Vario EL III, Elementar Co., Germany). The relative contents of cerium and lanthanum ions in $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ complexes were determined by way of energy-dispersive X-ray analysis (Edax) (Quanta 250, FEI Co., USA) at 15 kV. The infrared (IR) transmittance spectrum was recorded on a Nicolett 6670 Fourier transform infrared (FTIR) spectrophotometer (Thermo Fisher Corp., USA). The disk samples were obtained by pressing potassium bromide (KBr) with the powders of the chosen original samples and measured by averaging 32 scans at a resolution of 2 cm^{-1} over the range of $4000\text{--}450\text{ cm}^{-1}$. Thermogravimetric analysis (TGA) was performed by using a thermogravimeter (Q500, TA Instruments Co., USA) in a nitrogen atmosphere at a $10^\circ\text{C}/\text{min}$ heating rate from room temperature to 900°C . The luminescence properties of all complexes and TCA/ $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ ($x = 0.8, 0.875$) composites were characterized by using a fluorescence spectrophotometer (Hitachi F-7000, Hitachi High-Technologies Corp., Japan). The adopted mode was luminescence. The supplied photomultiplier voltage and scan speed were set to 400 V and 1200 nm/min, respectively. The excitation slit (EX slit) width was fixed at 2.5 nm, but the emission slit (EM slit) width was adjusted to 2.5 or 5.0 nm based on the luminescence intensity of various samples.

3. Experimental results and discussion

The results of elemental analysis for the $\text{Ce}(\text{SSA})_3\text{Phen}$ and $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ complexes are respectively listed as follows: measured value/wt% (calculated value/wt%) – carbon 39.46% (39.75%), hydrogen 3.06% (3.14%), nitrogen 4.53% (4.88%); carbon 39.54% (39.68%), hydrogen 3.10% (3.13%), nitrogen 4.98% (4.87%). These experimental results indicate that the molar ratio of RE^{3+} to SSA to Phen is 1:3:1 in the prepared complexes. In addition, the relative weight ratios of cerium (Ce) to lanthanum (La) of all dinuclear complexes were measured by Edax. From the relative values, the molar ratios of cerium to lanthanum ions in the complexes can still be determined, as shown in Table 1.

The IR spectra of the two ligands and the $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ complex are shown in Figure 1, ranging from 4000 to 450 cm^{-1} . The wavenumbers of the main FTIR bands of the three samples are listed in Table 2. Compared with the Phen ligand, the peak corresponding to the stretching vibration of the $-\text{N}=\text{C}$ group of

Table 1. The relative amounts of cerium and lanthanum in $Ce_{1-x}La_x(SSA)_3Phen$ complexes from Edax

Complex	Cerium: wt%	Lanthanum: wt%	Cerium/lanthanum molar ratio
$Ce_{0.5}La_{0.5}(SSA)_3Phen$	19.7	21.0	1:1
$Ce_{0.33}La_{0.67}(SSA)_3Phen$	13.6	27.2	1:2
$Ce_{0.2}La_{0.8}(SSA)_3Phen$	8.5	31.9	1:4
$Ce_{0.125}La_{0.875}(SSA)_3Phen$	5.3	44.8	1:7
$Ce_{0.1}La_{0.9}(SSA)_3Phen$	3.9	46.3	1:9

Figure 1. FTIR spectra ((a) $\lambda = 4000\text{--}450\text{ cm}^{-1}$, (b) $\lambda = 1900\text{--}450\text{ cm}^{-1}$) of ligands and the complexes: A, Phen; B, $Ce_{0.2}La_{0.8}(SSA)_3Phen$; C, SSA

Table 2. Wavenumbers of main peaks of FTIR spectra of the three samples

	$\nu_{N=C}: \text{cm}^{-1}$	$r_{C-H}: \text{cm}^{-1}$	$\nu_{C=O}: \text{cm}^{-1}$	$\nu_{C=C}: \text{cm}^{-1}$	$\nu_{O-RE}: \text{cm}^{-1}$	$\nu_{N-RE}: \text{cm}^{-1}$
Phen	1563	854, 737	—	—	—	—
SSA	—	—	1660	1607, 1479	—	—
$Ce_{0.2}La_{0.8}(SSA)_3Phen$	1541	845, 715	1630	1606, 1479	592	464

Phen in the complex shifted from 1563 cm^{-1} and the peaks assigned to the r_{C-H} vibration of Phen also shifted from 854 and 737 to 845 and 715 cm^{-1} , respectively, indicative of the coordination between the two nitrogen atoms with lone electron pairs of Phen and the RE (III) ion.¹³ In addition, the comparison of the spectra of the SSA ligand and the complex shows that the peak assigned to the stretching vibration of the carbonyl group of SSA in the complex shifted from 1660 to 1630 cm^{-1} , but the peaks at 1607 and 1479 cm^{-1} attributed to the $\nu_{C=C}$ vibration are observed not only in the spectrum of SSA but also in the curve of the $Ce_{0.2}La_{0.8}(SSA)_3Phen$ complex, which suggests that the coordination bonds were formed between the carbonyl group of SSA and the RE (III) ion.²⁸ Meanwhile, two new absorption peaks are observed at 592 and 464 cm^{-1} , corresponding to the stretching vibrations of $O \rightarrow RE$ and $N \rightarrow RE$, respectively, which cannot be observed in the ligands.²⁰ Furthermore, the band at 3370 cm^{-1} in the spectrum of Phen and the broad band at

around 3034 cm^{-1} in the spectrum of SSA, which both belong to the O–H stretching absorption, cannot be found in the spectrum of the complex, indicating that there are no coordinated water (H_2O) molecules in the complexes, consistent with the result of the elemental analysis.

Thermal properties were evaluated by means of TGA. Figure 2 presents the TGA thermograms of the $Ce_{0.2}La_{0.8}(SSA)_3Phen$ complex, TCA and the TCA/ $Ce_{0.2}La_{0.8}(SSA)_3Phen$ (85:15) composite. Obviously, there is a two-stage decomposition process in the TGA curve of the $Ce_{0.2}La_{0.8}(SSA)_3Phen$ complex. In the first step of decomposition, the extrapolated onset (T_e) and final (T_c) temperatures are about 324 and 370°C , respectively, and similarly in the second stage, the T_e and T_c values are about 567 and 653°C , respectively. Therefore, the decomposition temperatures for the two stages are estimated to be about 324 and 567°C , respectively. In addition, the weight losses of the two stages are

Figure 2. TGA plots of $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ complex, TCA and 85:15 TCA/ $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ composite

49.8 and 36.7 wt%, which can be attributed to the decomposition of SSA and the removal process of Phen, respectively. So the mass loss of the $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$ complex is 86.5 wt%, which is in accordance with the calculated mass loss (87.1 wt%) when the ligands in the complex are absolutely removed and the residues are deemed as RE oxide. These results prove that the complexes are thermostable and can be used as luminescent materials. On the basis of the elemental analysis, Edax analysis, FTIR analysis and TGA results presented earlier, the molecular structure of the complexes can be concluded as shown in Figure 3.

As for TCA and the composite, the TGA curves present only one-stage decomposition, which suggests that each chain scission

Figure 3. Molecular structure of the $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ complexes

reaction has a similar energy barrier.²⁹ The degradation process mainly involves rupture of the anhydroglucose ring – that is, backbone rupture of TCA – and the carbonization process.³⁰ The T_d and T_c values for the TCA are about 350 and 385°C, and for 85:15 TCA/ $\text{Ce}_{0.2}\text{La}_{0.8}(\text{SSA})_3\text{Phen}$, the two temperatures are about 317 and 373°C. Thus, the decomposition temperatures for the two samples are estimated to be about 350 and 317°C, respectively. This indicates that the thermal stability of the composite is comparatively weaker than that of the pure TCA, probably because the volatile substances of organic ligands from the added complex would accelerate the rupture process of polymer chains to a certain extent. Nevertheless, it is worth noting that the composite still possesses practicable thermal properties for materials based on the decomposition temperature (over 300°C).

Figure 4 shows the excitation and emission spectra of the $\text{Ce}(\text{SSA})_3\text{Phen}$, $\text{La}(\text{SSA})_3\text{Phen}$ and $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ complexes ($x = 0.5, 0.67, 0.8, 0.875, 0.9$). Obviously, broad and strong bands ranging from 270 to 340 nm appear in the excitation spectra of all complexes, with a given maximum for each sample as shown in Figure 4(a). Each excitation spectrum was obtained by monitoring a given emission wavelength stemming from the peak

Figure 4. (a) Excitation and (b) emission spectra of $\text{Ce}_{1-x}\text{La}_x(\text{SSA})_3\text{Phen}$ complexes at different EM and EX slit widths: A, $\text{Ce}(\text{SSA})_3\text{Phen}$ (5.0, 2.5 nm); B, $\text{La}(\text{SSA})_3\text{Phen}$ (5.0, 2.5 nm); C, $x = 0.5$ (5.0, 2.5 nm); D, $x = 0.67$ (5.0, 2.5 nm); E, $x = 0.8$ (2.5, 2.5 nm); F, $x = 0.875$ (2.5, 2.5 nm); G, $x = 0.9$ (5.0, 2.5 nm)

value of the emission spectrum of each complex in Figure 4(b). From the excitation spectra, it is seen that all complexes can be well excited in the 300–330 nm wavelength range, and the optimum excitation wavelengths for emission spectra were 318, 320, 320, 321, 321, 313 and 311 nm, corresponding to the $Ce_{1-x}La_x(SSA)_3Phen$ complexes with $x = 0, 0.5, 0.67, 0.8, 0.875$ and 1, respectively. From the emission spectra, all complexes exhibit intense broad emission bands with the maxima at 437, 434, 434, 437, 436, 426 and 424 nm, belonging to the $Ce_{1-x}La_x(SSA)_3Phen$ complexes with $x = 0, 0.5, 0.67, 0.8, 0.875$ and 1, respectively, on the optimum excitation wavelengths. No doubt that for the $Ce(SSA)_3Phen$ complex, the strong emission band with a maximum at 437 nm is mainly caused by the $5d \rightarrow 4f$ transition of the cerium ion from the lowest $5d$ excited state to the $4f$ ground-state levels $^2F_{5/2}$ and $^2F_{7/2}$.^{22,24} Theoretically, the $^2D \rightarrow ^2F_{5/2}$ and $^2D \rightarrow ^2F_{7/2}$ transitions of the cerium ion can cause the appearance of two emission peaks, but actually the spectral signature of the cerium complex may be influenced by crystal field effects and the introduction of the first as well as the second ligand, which probably induces the two peaks to overlap to form one intense and broad emission band in the 420–460 nm wavelength range for the $Ce(SSA)_3Phen$ complex, emitting blue light.²⁴

Interestingly, the excitation and emission peak values of the $Ce_{1-x}La_x(SSA)_3Phen$ complexes ($x = 0.5, 0.67, 0.8, 0.875$) are close to those of the mononuclear $Ce(SSA)_3Phen$ complex, and the values for the $Ce_{0.1}La_{0.9}(SSA)_3Phen$ and $La(SSA)_3Phen$ complexes are similar. This indicates that when the molar ratios of cerium to lanthanum ions are 1:1, 1:2, 1:4 and 1:7, the dinuclear complexes exhibit the characteristic emission of the cerium ion. It should be pointed out that the excitation and emission spectra of the $Ce_{0.2}La_{0.8}(SSA)_3Phen$ and $Ce_{0.125}La_{0.875}(SSA)_3Phen$ complexes were obtained by setting both the EM and EX slit widths as 2.5 nm, dissimilar to the condition of other complexes; when the EM and EX slit widths were fixed at 5.0 and 2.5 nm, the relative intensity of the excitation and emission bands of the two complexes could exceed 10 000, and the exceeded band became irregular and invalid so that the EM slit width was reduced to 2.5 nm. This suggests that the spectral intensities of the $Ce_{0.2}La_{0.8}(SSA)_3Phen$ and $Ce_{0.125}La_{0.875}(SSA)_3Phen$ complexes are completely stronger than those of all the other complexes. Many papers have reported that the introduction of inert RE ions can greatly improve the emission intensity of central RE ions – for example, the emission intensity of the europium ion was obviously sensitized by yttrium, lanthanum and gadolinium ions in the given complexes.^{14,17} As for the $Ce_{1-x}La_x(SSA)_3Phen$ system, the spectral intensity displays a non-linear relationship with increase in the concentration of lanthanum ions; when molar ratios of cerium to lanthanum ions are 1:4 and 1:7, the luminescence intensity of the complexes can be evidently enhanced by lanthanum ions, particularly for the $Ce_{0.125}La_{0.875}(SSA)_3Phen$ complex, which has the strongest intensity. With continually increasing content of lanthanum ions (cerium/lanthanum = 1:9), the spectral intensity drops to a minimum value and the peak wavelength is close to that of the uninuclear $La(SSA)_3Phen$ complex as displayed in Figure 4.

The possible reason is that the cerium ions in the complex were almost covered by quantities of lanthanum ions. So the luminescence property of the $Ce_{0.1}La_{0.9}(SSA)_3Phen$ complex is similar to that of the $La(SSA)_3Phen$ complex, but the lanthanum ion relative concentration of the former is less than that of the latter, leading to the weaker spectral intensity of the $Ce_{0.1}La_{0.9}(SSA)_3Phen$ complex.

Additionally, it is well known that lanthanum ions have no 4f electrons and the energy level of excited states exceeds the triplet levels of the ligand, so lanthanum ions theoretically do not emit in the visible region. However, the $La(SSA)_3Phen$ complex shows an emission band as exhibited in Figure 4(b), which is probably attributed to the enhanced $\pi \rightarrow \pi^*$ electron transition of the SSA ligand.³¹ In the $Ce_{1-x}La_x(SSA)_3Phen$ system, the energy absorbed by the SSA ligand, including the energy from the first excited triplet state of the ligand, cannot be consumed through radiation transition of lanthanum ions but can be transferred to cerium ions through an intramolecular transfer process, which causes the enhancement of the characteristic emission of cerium ions in the complexes.

To obtain polymer composites with excellent luminescence properties, $Ce_{0.2}La_{0.8}(SSA)_3Phen$ and $Ce_{0.125}La_{0.875}(SSA)_3Phen$ complexes were respectively added into the TCA matrix by using the solvent blending method. Figures 5 and 6 display the excitation and emission spectra of the TCA/ $Ce_{0.2}La_{0.8}(SSA)_3Phen$ and TCA/ $Ce_{0.125}La_{0.875}(SSA)_3Phen$ composites. The profile of the spectra of all composites is similar to that of the pure complexes, indicating that the doped $Ce_{0.2}La_{0.8}(SSA)_3Phen$ and $Ce_{0.125}La_{0.875}(SSA)_3Phen$ complexes in the composites can still present the characteristic emission of cerium ions. It should be noted that the spectra of the three samples – that is, the two pure complexes and the 85:15 TCA/ $Ce_{0.2}La_{0.8}(SSA)_3Phen$ composite – were obtained at the 2.5 nm EM slit width and 2.5 nm EX slit

Figure 5. Excitation and emission spectra of TCA/ $Ce_{0.2}La_{0.8}(SSA)_3Phen$ composites at different EM and EX slit widths: A, 0:100 (2.5, 2.5 nm); B, 85:15 (2.5, 2.5 nm); C, 90:10 (5.0, 2.5 nm); D, 95:5 (5.0, 2.5 nm)

Figure 6. Excitation and emission spectra of TCA/Ce_{0.125}La_{0.875}(SSA)₃Phen composites at different EM and EX slit widths: A, 0:100 (2.5, 2.5 nm); B, 85:15 (5.0, 2.5 nm); C, 90:10 (5.0, 2.5 nm); D, 95:5 (5.0, 2.5 nm)

width, and those of the other samples were achieved at 5.0 and 2.5 nm, indicative of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite having the strongest fluorescence intensity in all composites. It is obvious that the spectral intensity of the composites gradually increases with increasing content of the doped complexes, but there are still some different phenomena – for example, the excitation spectra of the composites in the two systems are blue-shifted by more than or equal to 7 nm compared with the 321 nm peak value for the two pure complexes, and the emission spectra of the composites exhibit blue shift of more than 10 nm except that the excitation and emission spectra of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite are blue-shifted by only 4 nm; the intensity and peak value of the fluorescence spectra of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite are close to those of the pure complex.

These phenomena suggest that the luminescence properties of the composites are not only related to the additive amount of the complexes but also correlated with the kind of the complexes or the interaction between the TCA matrix and the additive complexes. When the content of the added complexes is low (5 and 10 wt%), the complexes are completely diluted by TCA molecules, mainly resulting in weak luminescence properties. When the content of the complexes is 15 wt%, the major factors are perhaps the molar ratio of cerium to lanthanum ions of the complexes and the interaction between TCA molecules and the organic ligands from the dinuclear complexes. It is well known that there are abundant hydroxyl groups in TCA molecules and carbonyl groups in SSA molecules, probably leading to the existence of hydrogen bonds between the oxygen atoms from the carbonyl groups and hydroxyl groups. The hydrogen bond can be proved by FTIR results, demonstrating that obvious red shift occurs in the ν_{O-H}

peak of the TCA matrix and the $\nu_{C=O}$ peak of SSA from the IR spectrum of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite (see Figure S1 in the online supplementary material). This interaction potentially disturbs the coordination between the oxygen atom from the carbonyl groups of SSA and central ions and probably reduces the energy transfers from SSA to central ions. Therefore, the TCA matrix in the composites can have an impact on the luminescence properties of the added complexes. Moreover, it is unexpected that the luminescence intensity of the 85:15 TCA/Ce_{0.125}La_{0.875}(SSA)₃Phen composite is inferior to that of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite, although the Ce_{0.125}La_{0.875}(SSA)₃Phen complex exhibits the strongest spectral intensity of all pure complexes. In pure Ce_{1-x}La_x(SSA)₃Phen complexes, when the molar ratio of cerium to lanthanum ions is 1:7, the sensitization effect of lanthanum on cerium ions is optimal, probably due to the optimum energy transfer from Phen, SSA and cerium ions to lanthanum ions. Nevertheless, in the 85:15 TCA/Ce_{0.125}La_{0.875}(SSA)₃Phen composite, the energy transfer process is more affected by TCA molecules than that in the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite. The possible reason is that due to the aforementioned interaction, the decrease in the energy absorbed by SSA causes lower energy for lanthanum ions when the content of lanthanum ions is relatively high, leading to a weaker sensitization effect of lanthanum on cerium ions.

The color coordinate of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite is displayed in Figure 7. The Commission Internationale de L'Eclairage (CIE) coordinate is calculated from

Figure 7. CIE coordinate photograph of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite

the emission spectrum of the composite excited at 317 nm. The coordinates (0.15, 0.08) show that the composite emits blue light as shown in the figure.³² The luminescence quantum efficiency of the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite reaches 30.6% (see the details in the online supplementary material). Consequently, a blue fluorescent polymer material with fine luminescence properties was successfully obtained.

4. Conclusion

All dinuclear complexes and the chosen TCA composites emitting blue light displayed the characteristic emission of the cerium ion. In pure complexes, the Ce_{0.125}La_{0.875}(SSA)₃Phen complex exhibited the strongest luminescence intensity and the Ce_{0.2}La_{0.8}(SSA)₃Phen complex took the second place. The introduction of lanthanum ions can obviously improve the luminescence intensity of the dinuclear complex and can be favorable for retaining the excellent fluorescence of the TCA matrix. In TCA composites, the 85:15 TCA/Ce_{0.2}La_{0.8}(SSA)₃Phen composite possesses fine luminescence properties and thermal stability for potential usage as blue fluorescent material.

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