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# An investigation of the effect of ligands on thermal stability of luminescent samarium complexes

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#### Abstract

Three kinds of  $Sm(L)_3Phen \cdot nH_2O$  complexes (L:  $\alpha$ -thenoyltrifluoroacetone (HTTA), 4-fluorobenzoicacid (p-FBA) and 4-aminobenzoicacid (p-ABA)) were designed and synthesized by the wet chemical method. Their thermal stabilities were

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compared through thermogravimetric analysis (TGA) and high temperature photoluminescence measurements. The results indicated that  $[Sm(p-FBA)_3Phen]_2$  presented the best thermal stability, and the photoluminescence intensity could remain 50% even after being heat-treated at 280 °C for 20 min. Not only the rigidity of the organic ligand and complexes structures, but also the coordinating ability between rare earth ions and ligand played a crucial role in the stability of the complexes. In this article, p-fluorobenzoicacid has been proven to be a promising ligand for the preparation of highly luminescent and stable rare earth complexes.

#### Keywords

Effect of ligands; Samarium complexes; Luminescent thermal stability; Substituent

#### **1. Introduction**

The interest in the development of highly luminescent polymer-based rare earth complexes has continuously grown in the last decades [1-4]. This type of complex can provide both advantages of polymers, such as molding and shaping capability, excellent UV absorption, mechanical strength and flexibility, and the luminescence characteristics of rare earth complexes [5, 6], including sharp emission bands, large Stokes shift, high quantum yields [7-10], temperature-sensitivity [11] and general versatility [12-16]. However, it is difficult to uniformly incorporate particles of rare earth compounds into a polymer matrix, which typically results in inhomogeneous dispersion and poor mechanical strength of polymer phosphors. Therefore, work in this area has focused on the development of various rare earth complexes [17], where the organic ligand promotes the compatibility between the rare earth element and the

polymer [18]. In order to improve dispersion capability of fluorescent particles into polycarbonate (PC), twin-screw extruding accompanied by a high temperature blending above 280 °C is normally used. However, it should be noted that some of the rare earth complexes may be phase transformed or decomposed during the blending process. In this case, the enhancement of the thermal resistance of the complexes becomes very critical [19,20]. Constable *et al.*[5] pointed out that ligand configuration plays a fundamental role on the thermal resistance and luminescent properties of rare earth complexes [21-23].

Based on our previous study and understanding of thermal resistance and luminescent properties of samarium complexes [24], this article extensively focuses on the design and synthesis of highly thermo-stable fluorescent complexes using different kinds of ligands and substituents. Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O (L: HTTA, p-FBA, p-ABA) complexes were prepared in this article. The effects of different ligand configurations and substituents in the benzoic acid ring on the photoluminescence and thermal resistance of samarium complexes were also compared in this study. Characterization techniques including infrared (FT-IR) spectroscopy, elemental analysis (EA), X-ray fluorescence (XRF), and photoluminescence (PL) spectroscopy were used to analyze and confirm the synthesis of these complexes. Through thermogravimetric analyses (TGA) and high temperature photoluminescence experiments, the thermal resistance and luminescence stability of these complexes were investigated and compared.

#### **2.** Experimental section

#### 2.1. Materials and reagents

SmCl<sub>3</sub>· $6H_2O$  (99.9%) was purchased from Funing Rare Earth Industrial Company Ltd.  $\alpha$ -thenoyltrifluoroacetone (HTTA) (99.00%), 4-Fluorobenzoicacid (p-FBA) (99.00%), 4-aminobenzoic acid (p-ABA) (99.00%) and 1,10-phenanthroline (Phen) (99.00%) were obtained from Sinopharm Chemical Reagent Company Ltd.

#### 2.2. Instruments and methods

Infrared (IR) spectra were measured at room temperature between 4000 and 400 cm<sup>-1</sup> using a Nexus 670 FT-IR spectrophotometer with KBr pellet technique. The photoluminescence (PL) spectra were recorded by a Horiba Jobin-Yvon FL3-221 spectrofluorometer with the band pass for the excitation and emission monochromators setting at 2.0 nm. A TAP-02 instrument with a temperature controlled sample holder was used to heat products from room temperature to 300 °C while high temperature photoluminescence spectra of the complexes were measured with a FL3-221 spectrofluorometer. Thermogravimetric analyses (TGA) of the samples were performed by a STA 449C/6F analyzer from room temperature to 900 °C at a heating rate of 20 °C/min in air. Elements (C, H and N) analysis was conducted by an Elementar Vario EL III (Elementar Analyzer, Germany). Elements of O, F, S and Sm were detected by X-ray fluorescence spectrometry (XRF, Thermo ARL Advant XP', America).

#### 2.3. Syntheses of Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O complexes

Three Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O (L: p-FBA, HTTA, p-ABA) complexes were synthesized

according to the previously reported procedure with minor modifications [24]. They were obtained in the following steps. First,  $SmCl_3 \cdot 6H_2O$  (2.0 mmol), L (6.0 mmol) and Phen (2.0 mmol) were dissolved by stirring in 40, 70 and 30 ml ethanol, respectively. Subsequently, the ethanol solution of  $SmCl_3$  was added dropwise into L ethanol solution within 3 min, with the molar ratio (L to Sm ion) of 3:1. An ethanol solution of Phen with the molar ratio of Phen to Sm ion being 1:1 was slowly added to the mixture within 5 min. The pH value of the mixture was adjusted between 5 and 6 by adding sodium hydroxide solution (1 mol/L). Then the mixture was stirred and refluxed at 60 °C in a water bath until an orange precipitate appeared. Finally, a suction filter was used to take a sample from the precipitation, which was then washed with water and ethanol. Powders of these complexes were stored in a silica-gel dryer after drying in a vacuum oven at 50 °C.

A comprehensive elemental analysis was carried out to evaluate the complex structure. Anal. Calc. for Sm(TTA)<sub>3</sub>Phen (C<sub>36</sub>H<sub>20</sub>N<sub>2</sub>F<sub>9</sub>O<sub>6</sub>S<sub>3</sub>Sm): N, 2.82; C, 43.49; H, 2.03; O, 9.66; S, 9.67; F, 17.20; Sm, 15.13%; Found: N, 2.80; C, 43.07; H, 1.93; O, 10.53; S, 11.04; F, 15.78; Sm, 14.77%; Anal. Calc. for  $[Sm(p-FBA)_3Phen]_2$  (C<sub>66</sub>H<sub>40</sub>N<sub>4</sub>F<sub>6</sub>O<sub>12</sub>Sm<sub>2</sub>): N, 3.75; C, 52.99; H, 2.69; O, 12.83; F, 7.62; Sm, 20.11%; Found: N, 3.68; C, 52.74; H, 2.69; O, 11.52; F, 6.73; Sm, 22.24%; Anal. Calc. for Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen•H<sub>2</sub>O (C<sub>33</sub>H<sub>30</sub>N<sub>5</sub>O<sub>8</sub>Sm): N, 9.04; C, 51.14; H, 3.90; O, 12.99; Sm, 20.35%; Found: N, 8.57; C, 49.22; H, 4.00; O, 12.72; Sm, 22.39%.

The molecular structure and synthetic route of the  $Sm(TTA)_3Phen$  [25], [ $Sm(p-FBA)_3Phen$ ]<sub>2</sub> [26], and  $Sm(p-ABA)_3H_2OPhen \cdot H_2O$  [27] complexes are shown

in Fig.1. Unlike ligand HTTA with a thiophene structure, p-FBA and p-ABA have a benzene ring structure.

#### **3. Results and discussion**

#### 3.1. FT-IR spectra

The FT-IR spectra of Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O (L: HTTA, p-FBA, p-ABA) complexes before and after heat treatment at 280 °C for 20 min are shown in Fig. 2. The IR absorption peaks of the complexes in Fig. 2(b), can be compared with the raw material shown in Fig. 2(a). The IR absorption peaks of the Sm(TTA)<sub>3</sub>Phen complex are similar to those reported in the literature [24, 28]. The appearance of peaks at 581  $cm^{-1}$ , which corresponds to the stretching vibration of  $v_{Sm-O}$ , indicates the presence of chemical bonding between HTTA and  $\text{Sm}^{3+}$ . The stretching vibration of  $v_{C=N}$  at 1560 cm<sup>-1</sup> belongs to the second ligand of Phen as shown in Fig. 2. After forming coordination bonds with Sm<sup>3+</sup>, these peaks moved to lower frequencies of 1540 cm<sup>-1</sup> [29]. It can be observed that stretching vibration peaks of  $v_{C=N}$  in [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> and Sm(p-ABA)Phen also shifted to lower wavenumber 1539 cm<sup>-1</sup> and 1552 cm<sup>-1</sup>, respectively. The FT-IR spectra of the [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> and  $Sm(p-ABA)_3H_2OPhen \cdot H_2O$  proved intense absorption bands at 1416, 1625 cm<sup>-1</sup> and 1401, 1623 cm<sup>-1</sup>, which were attributed to the characteristics of the carboxylate group including symmetric  $v_s$  (C=O) and asymmetric  $v_{as}$  (C=O) vibrations, respectively [30]. The 3500 cm<sup>-1</sup> peak is the stretched vibration of  $v_{H-O}$  because the organic complex easily absorbs water in air.

After heat treatment at 280 °C, the spectra in Fig. 2 obviously shows that the 581 cm<sup>-1</sup> stretching vibration of  $v_{Sm-O}$  in the Sm(TTA)<sub>3</sub>Phen complex disappeared. It indicated that the Sm-O bond was unstable and the HTTA group dissociated from the center samarium ions after heat treatment, which can be further confirmed in the following discussions on DSC/TG and high temperature luminescence results. Meanwhile, the peaks of [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> and Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen • H<sub>2</sub>O exhibited no change after heat treatment at 280°C. These observations proved that complexes of [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> and Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen • H<sub>2</sub>O were more stable than Sm(TTA)<sub>3</sub>Phen.

#### **3.2.** Thermal stability

Thermogravimetric analyses (TGA) of Sm(TTA)<sub>3</sub>Phen, [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> and  $Sm(p-ABA)_3H_2OPhen \cdot H_2O$  were carried out to explore their degradation behavior and water content. As shown in Fig. 3, [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> exhibited a higher thermal stability than Sm(TTA)<sub>3</sub>Phen and Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen•H<sub>2</sub>O. The peak at 252°C corresponds to the phase transition of Sm(TTA)<sub>3</sub>Phen. Its initial decomposition temperature occurs at 318  $\pm$ 10 °C. whereas Sm(TTA)<sub>3</sub>Phen and  $Sm(p-ABA)_3H_2OPhen \cdot H_2O$  begin to lose weight at  $318 \pm 10$  °C. For  $Sm(TTA)_3Phen$ complex, there is a  $\sim 66.8\%$  mass loss between 318 $\sim 374$  °C, which corresponds to the dissociation of the TTA component. Beyond 374 °C, the SmPhen structure also decomposes. The thermal decomposition of  $[Sm(p-FBA)_3Phen]_2$  took place in almost one step at much higher temperatures from 340 to 530 °C. However, TGA themogram of Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen•H<sub>2</sub>O shows that ~5% mass loss at 100 °C is attributed to

the disassociation of physisorbed water molecules. At the end of the total decomposition of  $Sm(p-ABA)_3H_2OPhen \cdot H_2O$ , the rest of the molecules give a weight plateau at above 410 °C, which corresponds to  $Sm_2O_3$ . Herein, it is interesting to note that TGA curves of  $[Sm(p-FBA)_3Phen]_2$  and  $Sm(TTA)_3Phen$  exhibit that their anhydrous nature may lead to enhanced thermal resistance. In addition, p-FBA has a benzene ring structure, which is more stable than the thiophene ring, corresponding to its higher thermal resistance than  $Sm(TTA)_3Phen$ . The main reason for the poor stability of  $Sm(p-ABA)_3H_2OPhen \cdot H_2O$  was assigned to the  $-NH_2$  group which is a hydrophilic group as well as an electron donating group. Its hydrophilic nature makes it easy to absorb water. Moreover, its electron donating capability will activate the carboxyl group on the para position of the benzene ring, which makes the electron density of Sm-O coordinating bonds increase and the bond stability decrease.

#### 3.3. Photoluminescence properties

Fluorescence emission spectra of  $Sm(L)_3$ Phen (L: (a) HTTA, (b) p-FBA, (c)

p-ABA) complex powders were measured. It is expected that the emission peak wave lengths of samarium complexes which was tested at room temperature were the same for different ligands and did not change after heat treatment at 280 °C. As can be seen in Fig. 4, three emission peaks existed at 564, 600 and 645 nm with different intensities, which belong to the transitions of  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$ ,  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$  and  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$  of Sm<sup>3+</sup> [31]. The strongest peak near 645 nm is the characteristic red fluorescence of Sm<sup>3+</sup> resulting from  ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$  electron dipole transition. In addition,

there is a weaker wide emission band (400-480 nm) in the  $[Sm(FBA)_3Phen]_2$  complex, which belongs to the ligand of p-FBA.

The luminescent spectra of samples heat-treated at 280 °C for 20 min revealed that different samarium complex structures resulted in different thermal resistivity. It is obvious that [Sm(FBA)<sub>3</sub>Phen]<sub>2</sub> possessed the strongest thermal resistivity, which remained almost 50% of the original intensity after a heat treatment at 280 °C for 20 min, while the intensity of Sm(TTA)<sub>3</sub>Phen and Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen•H<sub>2</sub>O only preserved 39% and 16%, respectively.

To investigate the high temperature luminescence properties, the luminescence intensities of different samples as a function of testing temperature were also measured. Photoluminescence results up to 280 °C are displayed in Fig. 5 and Fig. 6. Excitation measurements were also taken to find out the pump wavelengths for maximum emission intensity and to investigate the effects of the host lattice on the orbitals of the Sm<sup>3+</sup> ion.

For all the complexes, it is clear that the luminescence intensity decreased dramatically with the increase of testing temperature. A simple relationship has been reported by Weber et al for the temperature dependency of nonradiative transition rates based on multiphonon emission (MPE) (Eq. (1)) [32]:

$$W_{\rm nr}(T) = W_{nr(T=0)} [1 - \exp(\frac{hv}{k_B T})]^{-n}$$
(1)

where  $W_{nr}(T)$  is the  $T^n$  dependence nonradiative rate,  $W_{nr(T=0)}$  is a constant nonradiative rate at low temperature, n is the number of phonons involved in the transition, hv is the photon energy,  $k_B$  is the Boltzmann constant, and T is the

temperature. As the temperature increases, more phonons become available for multiphonon relaxation of electrons to low energy levels. From Eq. (1), we can expect that increasing temperature will result in a drastically increased nonradiative rate, which depends on  $T^n$ . This dependence of fluorescence intensity on temperature for [Sm(FBA)<sub>3</sub>Phen]<sub>2</sub> and Sm(TTA)<sub>3</sub>Phen complexes is shown in Fig. 6. While Sm(ABA)<sub>3</sub>Phen makes an exception from room temperature to 100 °C before the H<sub>2</sub>O molecules dissociate away from the NH<sub>2</sub> group, the luminescence intensity increases slightly below 100 °C, then drops drastically with further increase of temperature.

As shown in Fig. 5(a) and Fig. 6, the luminescence peaks of the Sm(TTA)<sub>3</sub>Phen complex were very weak when the temperature reached 280 °C. According to the TGA testing results, Sm(TTA)<sub>3</sub>Phen complex began to transform its phase at 252 °C. Therefore, in this case we expected that not only the nonradiative effects, but also complex structure has caused a significant decrease of luminescence intensity when the Sm(TTA)<sub>3</sub>Phen complex was heated above 252 °C. The matastable crystal structure may forbid the energy transfer from the ligand to the center samarium ions.

In the case of the  $[Sm(FBA)_3Phen]_2$  complex vs. the  $Sm(p-ABA)_3H_2OPhen \cdot H_2O$  complex, different para substituents were used on the phenyls of benzoic acid. The results exhibit that para electron withdrawing groups (as -F in FBA) deactivate phenyls' rings as their  $\pi^*$  electron density decreases [33], and make the carboxyl oxygen become reduction potentials [34], which leads to a stronger coordinate ability of  $Sm^{3+}$  [35]. The  $Sm^{3+}$  are bridged by four p-FBA ligands [26], making  $[Sm(FBA)_3Phen]_2$  become ultra-stable. In contrast to the case of electron withdrawing

substituents, para electron donating groups (as  $-NH_2$  in ABA) activate the carboxyl oxygen and weaken the combination with samarium ions, which results in an unstable complex.

#### **4.** Conclusions

The main objective of this work was to find out whether the category of ligand itself or the type of substituent on the benzene ring will significantly affect the complex luminescent properties and their thermal resistance. The results demonstrated that both of these would happen. Three interesting conclusions were made: First, the [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> complex presented the best thermal resistance in comparison to the Sm(p-TTA)<sub>3</sub>Phen complex and the Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen•H<sub>2</sub>O complex. Second, although the Sm(TTA)<sub>3</sub>Phen complex showed the strongest luminescence intensity, phase transition begins at 252 °C, which makes it unsuitable to be dispersed into PC, while [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> presents a promising thermo stable complex. Finally, the type of substituent on the benzene ring plays an important role in the complex stability. Owing to the electron withdrawing group of -F, which deactivates carboxyl at the para position of the beneze ring, the substituent leads to the stable luminescent properties observed from the dinuclear [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> complex, and vice versa, for the Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen•H<sub>2</sub>O complex. With a stable p-fluorobenzoicacid, together with the down conversion capability of the Sm<sup>3+</sup> ion, [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> shows potential applications in photovoltaic devices or light emitting fields as a thermally stable phosphor material.

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#### Figure captions

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**Fig. 1.** Molecular structure and synthetic route of the Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O (L: (a) HTTA, (b) p-FBA, (c) p-ABA) complexes.

**Fig. 2.** The FT-IR spectra of (a) Raw materials (SmCl<sub>3</sub>·6H<sub>2</sub>O, Phen, HTTA, p-FBA, p-ABA), (b) Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O (L: HTTA, p-FBA, p-ABA) complexes before and after heat treatment at 280°C for 20 min.

**Fig. 3.** DSC/TG curves of (a) Sm(TTA)Phen, (b) [Sm(p-FBA) Phen]<sub>2</sub> and (c) Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen•H<sub>2</sub>O.

**Fig. 4.** Fluorescence excition ( $\lambda_{em}$ =647nm) and emission ( $\lambda_{ex}$ =360nm) spectra of Sm(L)<sub>3</sub>Phen• nH<sub>2</sub>O (L: (a), (b) HTTA; (c), (d) p-FBA; (e), (f) p-ABA) complex before and after 280 °C heat treatment (holding 0 min, 10 min, 20 min).

**Fig. 5.** High temperature photoluminescence spectra of  $Sm(L)_3Phen \cdot nH_2O$  complexes. (a) Sm(TTA)<sub>3</sub>Phen ( $\lambda_{ex}$ =380nm), (b) [Sm(FBA)<sub>3</sub>Phen]<sub>2</sub> ( $\lambda_{ex}$ =360nm), (c) Sm(p-ABA)<sub>3</sub>H<sub>2</sub>OPhen \cdot H<sub>2</sub>O ( $\lambda_{ex}$ =360nm).

Fig. 6. Emission intensity as a function of testing temperature for Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O complexes



(b)



(c)













Highlight:

- Designed classical complexes of Sm(L)<sub>3</sub>Phen•nH<sub>2</sub>O have been synthesized by wet chemical method to compare their thermal and photoluminescent stability.
- Substitutes on ligands play a crucial role on the stability of the complexes.
- p-fluorobenzoicacid works well as a superior thermal stability ligand because of Sm<sup>3+</sup> were bridged by four p-FBA during the synthesis process.
- [Sm(p-FBA)<sub>3</sub>Phen]<sub>2</sub> complex can well serve as a thermally stable down-converting phosphor.

