

## A Multifunctional Luminescent Europium Photostabilizer based on a Novel Hindered Amine Ligand and Phenanthroline

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**ABSTRACT:** A novel hindered amine ligand, mono-2,2,6,6-tetramethyl-4-piperidyl-succinate (MTPS), has been designed to chelate europium(III) ion with 1,10-phenanthroline (Phen) as a coligand to prepare polymer photostabilizer. The luminescent property of the stabilizer and its efficiency of protecting polymer matrix from photodegradation have also been investigated. Under UV excitation, the stabilizer has red light emission in both ethanol solution and polypropylene (PP) matrix. The PP sheets containing the stabilizer display significantly improved photostability, which may be attributed to MTPS which scavenges radical, as well as Phen which makes the complex dissipate the absorbed ultraviolet light in a harmless manner. These preliminary results demonstrate that the introduction of the stabilizer can endow polymer matrices not only excellent photoluminescent properties but also improved photostability.

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### INTRODUCTION

Materials based on lanthanide ions have drawn great interests because of their applications as tunable lasers, optical amplifiers, luminescent probes, and light conversion molecular devices.<sup>1–4</sup> Among all of the trivalent lanthanide ions, Eu (III) ion is of particular interest because of its narrow emission bands and long luminescence lifetime. Because the electric dipole (ED) *f*–*f* transitions are forbidden by Laporte's rule while the much less intense magnetic dipole (MD) transitions are allowed, Eu (III) ion emits weak luminescence until it is sensitized by suitable antenna ligands. Generally, aromatic acid,  $\beta$ -diketone, 1,10-phenanthroline and bipyridine are the common antenna ligands which can effectively increase the fluorescence intensity of Eu complexes.<sup>5–7</sup> However, Eu complexes have some serious drawbacks, such as their brittleness, poor crack resistance and harsh processability. Therefore, Eu complexes are commonly incorporated into matrices such as thermoplastic polymers like poly (methyl methacrylate) (PMMA) and polycarbonate (PC). The resulting composites combine the good luminescent properties of lanthanide complexes, excellent processability and the promising mechanical properties of polymers.<sup>8–10</sup>

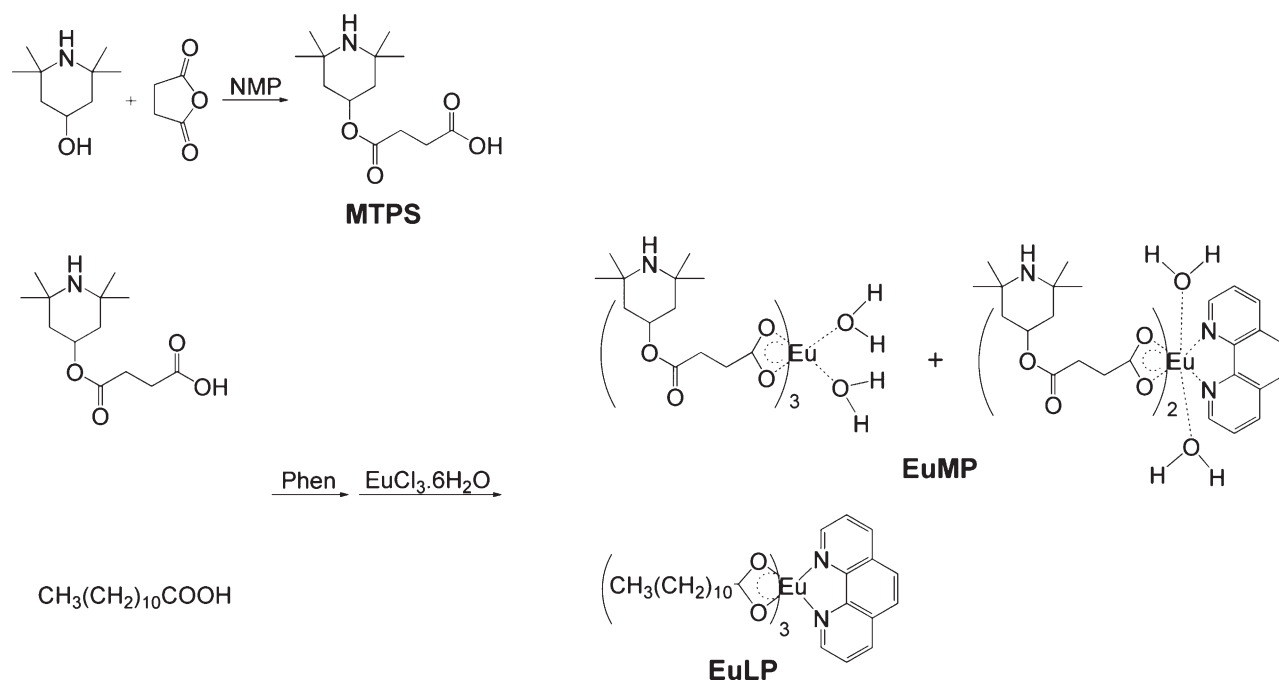
Most of the polymer products, which are used extensively outdoors, are considered to get weathered due to the direct or

indirect impact of ultraviolet (UV) light, which is so-called photodegradation and causes many problems such as cracking, chalking, discoloration, and the failure of physical properties.<sup>11</sup> Various light stabilizers are commonly added into polymers to minimize these unfavorable effects of the photodegradation. Among the commercial light stabilizers, tetramethyl-piperidine-containing hindered amine light stabilizers (HALS) are considered as one of the most important because of their excellent photostabilizing efficiency, which may be attributed to the formation of stabilizing species, nitroxyl radical, and related amino ether, as well as their cyclic regeneration during scavenging superoxide species.<sup>12–14</sup> For some outdoor applications including solar energy concentrator and agricultural light conversion film,<sup>15,16</sup> both excellent luminescence and good light stability are high desirable properties, which may extend their useful life greatly. A multifunctional additive combining these two properties may avoid the disadvantages of using mixtures of low molecular weight agents, such as physical loss, uneven distribution in the polymer matrix and poor compatibility.<sup>17</sup> However, no work has been dedicated to synthesizing such luminescent lanthanide additives which also have good photostabilizing function.

In this work, a novel hindered amine ligand, mono-2,2,6,6-tetramethyl-4-piperidyl-succinate (MTPS), and corresponding europium (III) complex were synthesized. The luminescent

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**Scheme 1.** Synthesis of the ligand MTPS and the complexes of EuMP and EuLP.

properties and the photo-stabilizing efficiency of the complex were investigated. Our results demonstrate that the complex may be used as a bifunctional photostabilizer. The introduction of the complex stabilizer can endow polymer matrices not only excellent photoluminescent properties but also improved photostability.

## EXPERIMENTAL

### Materials and Instrumentation

The 2,2,6,6-tetramethylpiperidinol was purchased from TCI Chemicals (Shanghai, China). Succinic anhydride and 1,10-phenanthroline monohydrate were purchased from Aladdin (Shanghai, China). Europium (III) oxide and lauric acid were purchased from Sinopharm Chemical Reagent (Shanghai, China). Isotactic polypropylene (iPP) F401 is a product of the Yangzi Petrochemical, SINOPEC (Nanjing, China) with the melt flow rate of  $0.25 \text{ g min}^{-1}$  ( $230^\circ\text{C}$ , 2.160 kg), a density of  $0.91 \text{ g mL}^{-1}$ , a tacticity of 96.5%. According to the product description, it contains a small amount of antioxidant (Antioxidant 1010).

The FTIR spectra were collected by a Nicolet Nexus 470 Infrared Spectrometer from 4000 to  $1000 \text{ cm}^{-1}$ . All spectra were averages of 32 scans with a  $4 \text{ cm}^{-1}$  resolution. The NMR data were collected on a Varian Mercury plus 400 spectrometer with  $\text{D}_2\text{O}$  as solvent. Thermogravimetric analysis (TGA) was performed using a Perkin Elmer Pyris 1 thermogravimetric analyzer under air atmosphere. The amounts of C, N, and H of the complexes were determined with an Elementar Vario El III Elemental analyzer (EA). The UV absorption of the samples in ethanol solution was measured with UV-vis spectrophotometer Lambda 35 from Perkin Elmer. Photoluminescence (PL) spectra were recorded using an FLS 920 spectrofluorometer from Edinburgh Instruments.

### Synthesis of the Ligand and the Complexes

The ligand MTPS was synthesized as shown in Scheme 1, according to Ref. 18. An *N*-methyl-2-pyrrolidinone (NMP) solution of 2,2,6,6-tetramethylpiperidinol (20 mmol, 30 mL) was added dropwise into a solution of succinic anhydride (22 mmol) in 20 mL of NMP and the mixture was stirred at  $60^\circ\text{C}$  for 1 h. After the mixture was cooled at room temperature, the precipitate was filtered and washed with a small amount of NMP and then with warm ethanol. The product was dried under vacuum and stored without further purification.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ ): 1.49 (s, 6H,  $\text{CH}_3$ ), 1.53 (s, 6H,  $\text{CH}_3$ ), 1.75 (dd, 2H, ring  $\text{CH}_2$ ), 2.19 (dd, 2H, ring  $\text{CH}_2$ ), 2.49 (t, 2H,  $\text{CH}_2$ ), 2.60 (t, 2H,  $\text{CH}_2$ ), 5.29 (m, 1H, CH).  $^{13}\text{C}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ ): 25.3 ( $\text{CH}_3$ ), 29.1 ( $\text{CH}_3$ ), 30.8 ( $\text{CH}_2$ ), 32.0 ( $\text{CH}_2$ ), 39.1 (ring  $\text{CH}_2$ ), 57.5 (C–N), 65.9 (CH), 175.1 (C=O, carbonyl), 180.9 (C=O, carboxylic). FTIR ( $\text{cm}^{-1}$ , KBr): 3432 ( $\nu\text{OH}$ ), 3316 ( $\nu\text{NH}$ ), 2976 and 2949 ( $\nu\text{CH}_3$  and  $\nu\text{CH}_2$ ), 1731 ( $\nu\text{C=O}$ , ester), 1435 ( $\nu\text{C=O}$ , carboxylic), 1165, ( $\nu\text{C-O}$ ).

To synthesize the target Eu complex (EuMP) which contains both MTPS and 1,10-phenanthroline (Phen) as ligands,  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  was first prepared according to Ref. 19. MTPS (1.5 mmol) and Phen (0.5 mmol) were dissolved into 100 mL chloroform and an ethanol solution of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.5 mmol, 5 mL) was added dropwise afterwards. The reaction mixture was stirred at room temperature for 12 h. The product was filtered, washed with a small amount of ethanol and then chloroform, dried at  $90^\circ\text{C}$  under vacuum and stored in a desiccator. Anal. calcd for EuMP: C 51.49, H 6.84, N 5.32; found: C 51.99, H 6.50, N 5.49.  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ ): 0.92 (b, MTPS), 1.30 (b, MTPS), 1.87 (b, MTPS), 6.63 (b, Phen), 6.85 (b, Phen), 7.88 (t, 2H,  $\text{CH}_2$ ).  $^{13}\text{C}$  NMR (400 MHz,  $\text{D}_2\text{O}$ ,  $\delta$ ): 24.9, 29.1,

38.8, 57.2, 65.5, 123.7, 173.8. FTIR ( $\text{cm}^{-1}$ , KBr): 3427 ( $\nu\text{OH}$ ), 3320 ( $\nu\text{NH}$ ), 2971 and 2931 ( $\nu\text{CH}_3$  and  $\nu\text{CH}_2$ ), 1731 ( $\nu\text{C}=\text{O}$ , ester), 1604 ( $\nu\text{C}=\text{N}$ ), 1429 ( $\nu\text{C}=\text{O}$ , carboxylic), 1165, ( $\nu\text{C}-\text{O}$ ).

To investigate the effect of MTPS on the photostabilizing efficiency of EuMP, another complex, using lauric acid (LA) in place of MTPS, was synthesized and marked as EuLP. First  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.5 mmol) was dissolved into 5 mL water and an ethanol solution of Phen (0.5 mmol, 5 mL) was added dropwise. After the solution was stirred for 5 min a solution of LA (1.5 mmol) and NaOH (1.5 mmol) in 30 mL of water was added. The mixture was stirred for another 12 h and then the precipitate was filtered and washed with a large amount of water. Finally the product was dried at  $90^\circ\text{C}$  under vacuum and stored in a desiccator. Anal. calcd for EuLP: C 59.30, H 8.55, N 2.88; found: C 60.52, H 7.90, N 3.12.

### Sample Preparation for Accelerated Weathering and Evaluation of Photostabilization

Polypropylene (PP) was chosen as the polymer matrix since it is one of the most important and widely used polymer material. It is susceptible to degradation under UV light, and is generally used as a matrix to estimate the photostabilizing efficiency of light stabilizers.<sup>20</sup> To prepare PP/EuMP samples, 0.5 wt % EuMP was compounded with PP using a XSS-300 torque rheometer at  $180^\circ\text{C}$  for 7 min and the rotation speed was set at 60 rpm. Subsequently, the mixture was compression molded into 0.25 or 0.40-mm-thick sheets at  $190^\circ\text{C}$  in a press under a pressure of 15 MPa for 5 min. The PP samples containing MTPS and EuLP were also prepared respectively in an identical procedure for comparison. Here we mark the PP samples containing ligand MTPS, complexes EuMP and EuLP as PP/M, PP/EuMP and PP/EuLP, respectively.

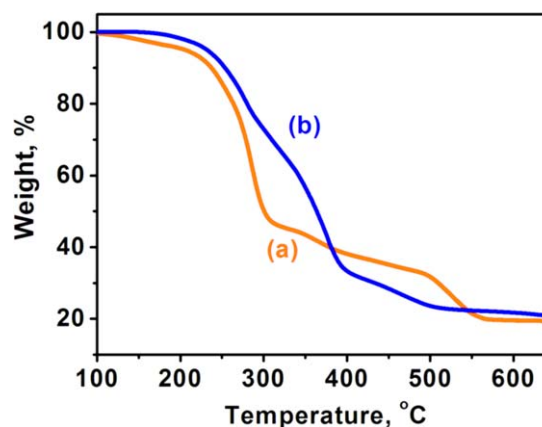
To evaluate the photostabilizing efficiency of the complex and the fluorescence fading rate of the Eu/PP sheets, accelerated photodegradation of various PP samples was carried out in a UV Test Chamber in which a 300-W high pressure mercury lamp with a wavelength range of 315–400 nm were used as the UV source. Specimens cut from 0.25 or 0.40-mm-thick sheets were exposed to UV light at a distance of about 30 cm from the lamp. The sample sheets were placed between two quartz glasses to keep them flat.

The structural changes of the PP samples were investigated using FTIR spectroscopy. Carbonyl index (CI) determined from FTIR spectra was used to evaluate the degree of degradation of PP samples. It is defined as the area of carbonyl absorption band related to the area of a reference band:  $\text{CI} = A_C/A_R$ , where  $A_C$  is the area of the carbonyl absorption band in the range from 1700 to  $1800\text{ cm}^{-1}$ , and  $A_R$  is the area of reference band in the range from 2700 to  $2750\text{ cm}^{-1}$  (CH bending and  $\text{CH}_3$  stretching band).  $A_R$  used as reference is constant during the degradation processes.<sup>21</sup>

## RESULTS AND DISCUSSION

### Synthesis and Structural Characterization of the Complexes

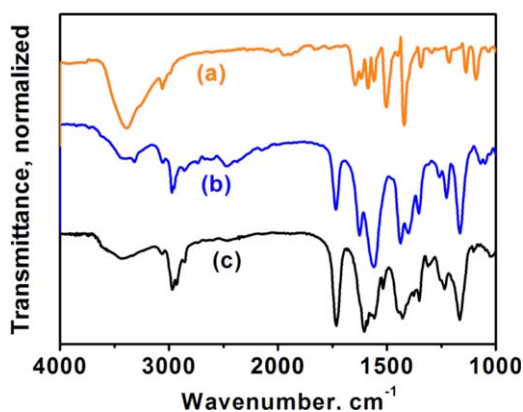
The complexes were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, EA, FTIR, TGA, and UV-visible absorption spectra. Compared to the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of MTPS (Supporting



**Figure 1.** TG curves of the complexes EuMP (a) and EuLA (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Information Figures S1 and S2), some of the peaks of EuMP (Supporting Information Figures S3 and S4) are observed broadened, overlapped, and shifted, indicating that both MTPS and Phen chelate Eu ion successfully.<sup>22–24</sup> However, it is difficult to determine the exact ratio of the two ligands because of the broadening and overlap of the peaks. The EA results indicate that the compositions of EuMP and EuLP conform  $\text{Eu}(\text{MTPS})_{2.5}(\text{Phen})_{0.5}(\text{H}_2\text{O})_2$  and  $\text{Eu}(\text{LA})_3(\text{Phen})$  respectively. EuMP is a mixture which may be composed of two complexes:  $\text{Eu}(\text{MTPS})_3(\text{H}_2\text{O})_2$  and  $\text{Eu}(\text{MTPS})_2(\text{Phen})(\text{H}_2\text{O})_2$ . Our efforts of removing the weakly fluorescent  $\text{Eu}(\text{MTPS})_3(\text{H}_2\text{O})_2$  were not successful due to the chemical similarity of the two complexes. For EuMP, the extra ligands in the solution failed to replace the coordinated water during the synthesis process, probably due to the steric hindrance of the hindered amine group of MTPS. It is clear from the thermogravimetric analysis data (Figure 1) that EuMP undergoes a mass loss of about 3.7% (calcd. 3.9%) at about  $140^\circ\text{C}$ , which may be assigned to the removal of coordinated water molecules.<sup>5,8,25</sup> On the contrary, EuLP has no obvious mass loss until  $190^\circ\text{C}$ , suggesting the absence of solvent molecule in the coordination sphere. Further, decomposition takes place for all these complexes in the region  $190\text{--}550^\circ\text{C}$ . The final residues are 19.2% for EuMP and 20.9% for EuLP (calcd: 19.1 and 18.9%), respectively.

As shown in Figure 2, the FTIR spectrum of EuMP shows a broad absorption in the region of  $3100\text{--}3700\text{ cm}^{-1}$ , suggesting the existence of coordinated solvent molecules. The intensive band for EuMP at  $1733\text{ cm}^{-1}$  is ascribed to the stretching vibration  $\nu(\text{C}=\text{O})$  of the ester carbonyl group, which has no shift compared to that for MTPS, indicating that this group is not coordinated onto Eu (III) ion. The symmetric stretching vibration  $\nu(\text{C}=\text{O})$  of the carboxyl group shifts from 1435 to  $1429\text{ cm}^{-1}$ , which suggests that the coordination bonds are formed between the Eu (III) ion and the carboxyl group of MTPS.<sup>26</sup> Further, the stretching vibration  $\nu(\text{C}=\text{N})$  of Phen has a red shift from 1614 to  $1604\text{ cm}^{-1}$ , showing the involvement of the nitrogen atom of Phen in the complex formation with Eu(III).<sup>5</sup>

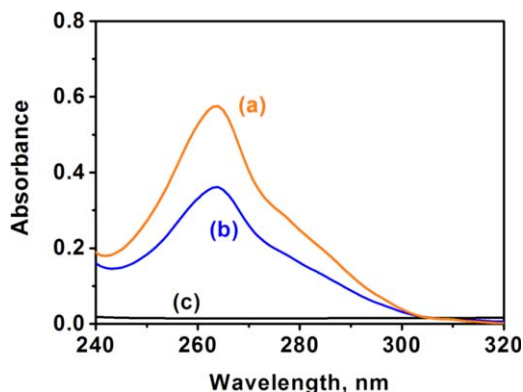


**Figure 2.** FTIR spectrum of Phen (a), MTPS (b) and EuMP (c). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

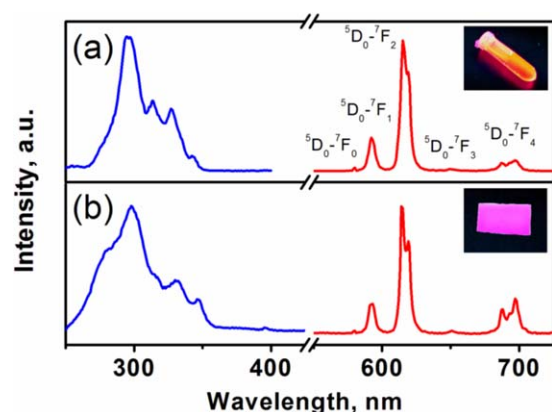
UV–visible absorbance spectra of ligand Phen, MTPS and complex EuMP in ethanol solution ( $c = 2.1 \times 10^{-5} M$ , average molecular weight of EuMP was used to calculate its concentration) were recorded at room temperature and are shown in Figure 3. The absorption maxima at 264 nm for Phen is the result of the  ${}^1\pi \rightarrow \pi^*$  absorption while MTPS has no absorption. The molar absorption coefficient value of Phen was calculated as  $2.73 \times 10^4 L M^{-1} cm^{-1}$  based on Lambert–Beer relation. The absorption spectrum of EuMP is similar to that of Phen, and the average molar absorption coefficient value of EuMP is calculated as  $1.72 \times 10^4 L M^{-1} cm^{-1}$ , about half of the coefficient value of Phen. If only one ligand absorbs UV at the absorption maxima, the ratio of the molar absorption coefficient value of the complex to that of the ligand depends on the number of the ligand in the complex.<sup>5,8,25</sup> Our result of molar absorption coefficient ratio suggests that averagely only 0.5 ligands exist in one complex molecule, which is consistent with TGA and EA results that EuMP are composed of  $1 : 1$  of  $Eu(MTPS)_3(H_2O)_2 : Eu(MTPS)_2(Phen)(H_2O)_2$ .

#### Fluorescence Properties of the Complexes

The excitation and emission spectra of EuMP in ethanol solution ( $1 mg mL^{-1}$ ) and in PP matrix (0.5 wt %, 0.25-mm-thick) were recorded at 293 K. As shown in Figure 4(a), EuMP in



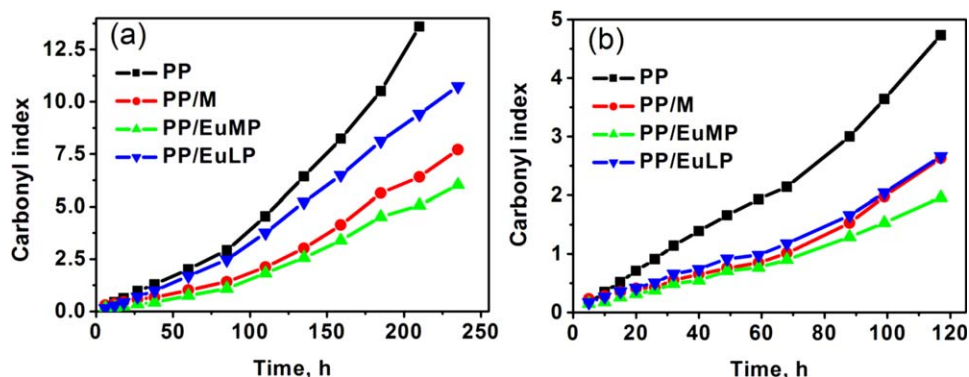
**Figure 3.** UV–visible absorption spectra of Phen (a), EuMP (b) and MTPS (c) in ethanol solution ( $c = 2.1 \times 10^{-5} M$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 4.** Excitation and emission spectra of EuMP in (a) ethanol solution ( $1 mg mL^{-1}$ ) and (b) PP matrix;  $\lambda_{ex} = 327 nm$ ,  $\lambda_{em} = 615 nm$ ; 293 K. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

solution exhibits a band between 260 and 350 nm in the excitation spectrum corresponding to the absorption of 1,10-phenanthroline,<sup>5</sup> while the sharp characteristic peak of the Eu (III) ion (395 nm) can hardly be observed, indicating that the luminescence sensitization via the excitation of the ligand is efficient.<sup>25</sup> The excitation maximum in the spectrum of EuMP in PP [Figure 4(b)] has a faint red shift compared to that in the spectrum of solution, which may be related with the weak interaction between complexes and PP. The room temperature emission spectra of EuMP in solution and in PP both display five sharp peaks between 550 and 750 nm associated with the  ${}^5D_0 \rightarrow {}^7F_j$  transitions of Eu (III) ion. The so-called hypersensitive  ${}^5D_0 \rightarrow {}^7F_2$  transition of the europium complexes is sensitive to the symmetry of the coordination sphere, which can be measured by the intensity ratio ( $A_{21}$ ) of the electric-dipole transition ( ${}^5D_0 \rightarrow {}^7F_2$ ) to the magnetic-dipole transition ( ${}^5D_0 \rightarrow {}^7F_1$ ).<sup>8</sup> The  $A_{21}$  values of EuMP in solution and in PP are 4.31 and 4.45, respectively. The slight difference of the two  $A_{21}$  values suggests that the interaction between the complex and PP is not very strong.

The luminescence decay curves of EuMP in ethanol solution and in PP sheets were obtained by monitoring the emission of the hypersensitive  ${}^5D_0 \rightarrow {}^7F_2$  transition at 615 nm and the excitation at 327 nm (Supporting Information Figure S5). A multiexponential decay function was used to fit the curve and the lifetime values ( $\tau$ ) of the emitter  ${}^5D_0$  level of the samples were obtained. Two lifetime values [995 and 295  $\mu s$ , corresponding to  $Eu(MTPS)_2(Phen)(H_2O)_2$  and  $Eu(MTPS)_3(H_2O)_2$  respectively] were found, which indicates the presence of two kinds of chemical environment around the Eu (III) ions, and is consistent with EA and TGA results. Because of the “antenna” effect, the complex containing Phen contributes more to the good photoluminescence. After EuMP was incorporated into PP, its lifetime values increased to 1483 and 374  $\mu s$ , which are much higher than those for solution phase, suggesting that the influence of OH oscillators is inhibited due to the water loss during the molding process or the interaction of PP matrix with the complexes.



**Figure 5.** The plots of carbonyl index versus irradiation time for various PP samples of (a) 0.25-mm-thick and (b) 0.40-mm-thick. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Photostabilizing Efficiencies of the Complexes

The photostabilizing efficiency of EuMP in PP was studied using FTIR. The main photodegradation products of PP include hydroperoxide and carbonyls such as carboxylic acids, ketones, and lactones. They show intense absorption between 1700 and 1800  $\text{cm}^{-1}$  in FTIR spectrum. CI values represent the degradation degree of aged PP, and can be calculated by the area of carbonyl absorption with a reference absorption.<sup>20</sup> The effects of irradiation time on CI values of PP, PP/M, PP/EuMP, and PP/EuLP were calculated and shown in Figure 5. From Figure 5(a), we can see that the CI values for all 0.25-mm-thick samples have a similar change tendency that they are gradually enhanced with the increased exposure time. For the pristine PP sample, the CI values increase much faster. Among the other samples, PP/EuMP shows the best photostability and following by PP/M and PP/EuLP. For PP/EuMP and PP/M, the improved photostabilizing effects may be attributed to the existence of the tetramethyl piperidine group (hindered amine) in MTPS, which is a long term radical scavenger and plays an important role in anti-aging action.

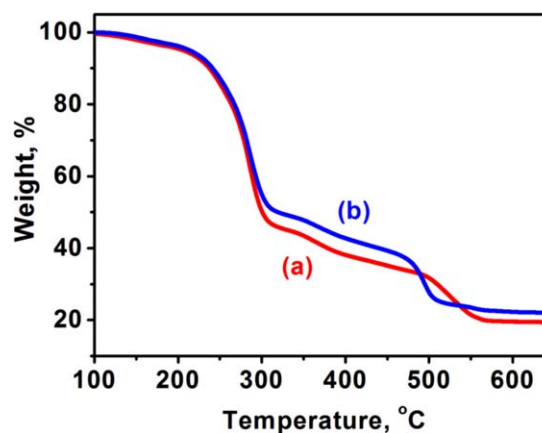
Compared to MTPS, EuMP has a higher photostabilizing efficiency even if it has a lower proportion of tetramethyl piperidine group. This may be attributed to the fact that EuMP absorbs UV and then emits red–orange light effectively because of the “antenna” effect of Phen, which makes the complex simultaneously play a role as UV absorber that dissipates the absorbed UV light into a harmless manner.<sup>12,27</sup> This is also the reason why EuLP still displays some photostabilizing effect without tetramethyl piperidine group in its molecule. However, the CI values of PP/EuLP are higher than those of PP/M and PP/EuMP after the same irradiation time, indicating that the UV absorbance effect of the complexes in our work contributes less to the photostabilizing efficiency than the radical scavenging effect of the tetramethyl piperidine in MTPS does. The EuMP in PP acts as both radical scavenger and UV absorber, which hence leading to the best photostabilizing efficiency.

It is generally accepted that the protection mechanism of UV absorbers is related to the absorption of harmful UV light and the sample thickness usually has an essential effect on the photostabilizing efficiency.<sup>28</sup> Therefore, the effect of Eu complex as a

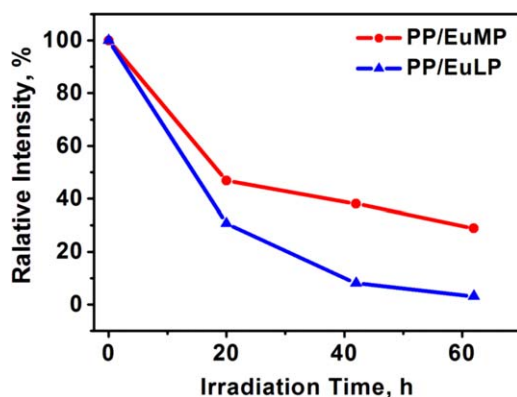
UV absorber may be further confirmed by comparing the CI values of samples with various thicknesses. As shown in Figure 5, the PP/EuMP or PP/EuLP with thickness of 0.4 mm [Figure 5(b)] has smaller CI values at the same aging durations and shows a slower growth rate compared to the thinner ones [0.25 mm, Figure 5(a)], indicating that thicker samples have better photostability. On the contrary, for MTPS, which acts as a radical scavenger alone, its photostabilizing efficiency is relatively independent of sample thickness.

### Fluorescence Fading of PP/Complex Sheets

The maintenance of fluorescence of the complex is also an important factor for its long term application. Therefore, thermogravimetric analysis was performed to measure the decomposition temperature of EuMP powder undergone UV irradiation. As shown in Figure 6, after the powder was exposed to UV for 2 h, the weight loss which is at about 500°C for the nonirradiated EuMP takes place at about 480°C. The irradiated sample has a lower decomposition temperature, indicating that the structure of the complex has changed after UV irradiation, which consequentially causes some loss of physical properties. In our investigation, we found that the fluorescence intensity of the complex in PP matrix gradually faded upon UV exposure.



**Figure 6.** TG curves of EuMP before (a) and after (b) UV irradiation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 7.** Fluorescence fading comparison of PP/EuMP and PP/EuLP by monitoring the peak intensity of  ${}^5D_0 \rightarrow {}^7F_2$  (615 nm); 293 K. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Bojinov et al. once reported that tetramethyl piperidine may protect some fluorophores from photodegradation.<sup>29</sup> In this work, to examine the influence of MTPS on the fluorescence stability of the resulting complexes, the intensity fading rate of PP/EuMP is compared with PP/EuLP by photoluminescence spectra. As shown in Figure 7, the intensities of the emission maximum (615 nm) for both samples of PP/EuMP and PP/EuLP faded under UV irradiation. After the samples were exposed to UV for 60 h, the fluorescence intensity of PP/EuMP decreases to 29 %, while that of PP/EuLP to 3%. This fluorescence fade may be associated with the structural change of the complexes. The complexes containing MTPS have a lower fading rate, suggesting that MTPS protects them from structural change in some degree. Furthermore, we used a multiexponential decay function to fit the luminescence decay curve of PP/EuMP, and found that after UV irradiation, the lifetime values of PP/EuMP decreased from 1483 and 347 to 529 and 107  $\mu$ s, respectively (Supporting Information Figure S6). For unexposed PP/EuLP, its luminescence decay curve was fitted using a monoexponential decay function and a lifetime value of 1590  $\mu$ s was obtained, indicating the presence of only one emissive Eu(III) center. However, the decay curve for PP/EuLP after photooxidation was fitted by a multiexponential function and two lifetime values of 465 and 82  $\mu$ s were obtained, attributed to the presence of two emissive Eu(III) center. The increase of the emissive center may be ascribed to the fact that some of the complexes decomposed almost completely. Compared to PP/EuMP, the decrease in lifetime value of PP/EuLP is more quickly. This result suggests that the fluorescence of PP/EuMP is damaged less than that of PP/EuLP under UV light. Obviously, MTPS in EuMP plays an important role in maintaining the fluorescence of the complexes.

## CONCLUSIONS

A novel hindered amine ligand and the corresponding multifunctional complex EuMP were synthesized. Under UV excitation, the complex has red fluorescence. After incorporating EuMP into the PP matrix, the EuMP/PP sheets are also able to emit bright red light and have better photostability. The

improved photo-stability is due to hindered amine which scavenges radical, as well as Phen which enables the complex to dissipate the absorbed ultraviolet light in a harmless manner. Moreover, the fluorescence of the PP sheets containing MTPS complex also faded slowly under long-term UV exposure.

## ACKNOWLEDGMENTS

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