

A series of highly quantum efficiency PMMA luminescent films doped with Eu-complex as promising light-conversion molecular devices

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Abstract In this paper, a series of Eu/PMMA and Eu/PMMA/SiO₂ luminescent films have been designed, fabricated and characterized. Thermo-gravimetric analysis and photo-luminescence results indicated the Eu-complex precursor was successfully immobilized in PMMA matrix through the interaction between the Eu-complex and the –C=O groups of the PMMA matrix. The emission spectra of the Eu-complex and Eu/PMMA films recorded at 25 °C exhibited the characteristic bands arising from the ⁵D₀/⁷F_J. The fact that the quantum efficiencies (η) of the doped film increased significantly indicated that PMMA matrix acted as an efficient co-sensitizer for Eu³⁺ ions luminescent center, and therefore enhanced the η of the emitter ⁵D₀ level. Especially, with the doping nano-SiO₂ into Eu/PMMA-5 % system, the T_d -5 % of Eu/PMMA/SiO₂ has obviously improved. Due to the carrying effect of nano-SiO₂ and interaction between –C=O of PMMA chain and Eu³⁺ ions, the η of Eu/PMMA/SiO₂ films have been greatly enhanced. To the best of our knowledge, the η of Eu/PMMA/SiO₂-3 % film (78.57 %) is found to be the

highest so far reported in the literature. These Eu/PMMA/SiO₂ luminescent films show excellent luminescent properties and therefore have potential applications in light-conversion molecular device.

1 Introduction

Eu-complexes have significant technological applications in optoelectronic, biological labeling, O/PLED, sensors and sensing applications due to their intense, narrow emission bands that show little dependence on the coordinated ligands [1–5]. Unfortunately, the absorption coefficient of an europium ions very low. To overcome the problem, organic ligands, which have much larger absorption coefficients, are usually coordinated to sensitize the europium complexes. The intramolecular transfer of optical excitation energy from organic ligands results in emission bands due to electronic transitions between the 4f energy levels of the lanthanide. Such Eu-complexes display large Stokes shifts and long luminescence lifetimes in the millisecond range [6–10].

Meanwhile, the Eu-complexes generally present low thermal stability, limited photostability and poor mechanical properties. Another parallel challenge is that most of these compounds are usually achieved as hydrates, consequently the luminescence intensity is suppressed due to the activation of non-radiative channels [11–14]. In order to overcome simultaneously these deficiencies and improve the characteristics of quantum efficiencies and lifetimes, Eu-complexes have been incorporated into polymers matrix, liquid crystals and sol–gel derived organic–inorganic hybrids [15–17]. Polymer matrixes offer several advantages for the development of materials, e.g.,

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flexibility, versatility, optical quality and moderate processing conditions. By doping the Eu-complexes into the polymer matrix, compared with corresponding precursor, the luminescent properties of Eu-complex/Polymer matrix films were effectively enhanced, but the thermal resistance of Eu-complex/Polymer films gradually decreased with the increase of Eu-complexes [18, 19]. Recently, there has been considerable interest in the optical properties of luminescent species in sol–gel derived siloxane hybrid materials [20–23]. The lanthanide complexes were incorporated into the silica matrix, the thermal stability of the complexes was improved, and the mechanical properties of the hybrid materials were also strengthened after the incorporation. However, these hybrid luminescent materials was prepared through sol–gel method, and remaining a lot of solvents molecules such as water and alcohols in resulting materials if expensive and complicated thermal treatment process without use, this phenomenon will hugely decreased the thermal and photophysical properties of hybrid luminescent materials.

Therefore, in this work, firstly, we designed and synthesized an unsaturated Eu-complex based on terpyridyl(Tpy-OCH₃) as ancillary ligand, Eu(TTA)₂Tpy-OCH₃·2H₂O; Secondly, in order to study the role of PMMA matrix in doped films, the unsaturated Eu-complex was doped into the PMMA matrix forming Eu/PMMA luminescent films; Lastly, to further improve the thermal stability and luminescent properties of Eu/PMMA films, we have fabricated Eu/PMMA/SiO₂ luminescent films through using simple dispersion and solvent evaporation processes-doping the Eu-complex and nano-SiO₂ into the PMMA matrix. Whether in Eu/PMMA films or Eu/PMMA/SiO₂ films, thermogravimetric analysis (TGA) and Photo-luminescence(PL) results indicated carbonyl groups in PMMA successfully replaced the water molecules and coordinated with Eu³⁺ ions, and the thermal stability and luminescent properties of complexes were obviously enhanced compared with the Eu-complex precursor. In particular, the thermal and luminescent properties of Eu/PMMA composite films were greatly improved with the introduction of nano-SiO₂. To the best of our knowledge, this is the first report which studies in detail the effect of nano-SiO₂ on photophysical and thermal properties of Eu/PMMA luminescent films.

2 Experimental

2.1 Materials and instrument

Commercial PMMA powder (average molecular weight 350,000 g/mol) was provided by Alfa Aesar Company and used without any further treatment. Nano-SiO₂ (average diameter 50 ± 5 nm, directly provided by Aike Regant

Co., Chengdu, China) was used to mix with the polymer solution. EuCl₃·6H₂O was obtained by dissolving Eu₂O₃ in concentrated chlorhydric acid. Other chemicals were all commercially available and used without further purification. FT-IR spectra were carried out using a Nicolet Is-10 (Nicolet) Fourier Transform Infrared Spectrometer. TGA was made with TA Q50 at a heating rate of 15 °C/min under N₂ atmosphere and over a temperature range from 35 to 650 °C. Differential scanning calorimetry (DSC) made on TA Q20 at a heating rate of 10 °C/min under nitrogen. UV–Vis absorption spectrum was determined on a Shimadzu spectrophotometer (UV 2540). The PL measurements in solid state and THF solution were conducted in a Hitachi F-4600 fluorescence spectrophotometer. Luminescent lifetimes were obtained with the FLS920 steady state spectrometer with a pulsed xenon lamp.

2.2 Preparation of Eu/PMMA and Eu/PMMA/SiO₂ luminescent films

Synthesis of Eu-complex, the detailed process was similar to reported Ref. [16]; The Eu/PMMA luminescent films was prepared through doping the Eu-complex Eu(TTA)₂Tpy-OCH₃·2H₂O with the proportion 1, 3, 5, and 7 % (w/w) into the PMMA matrix. The PMMA was dissolved in THF, followed by addition of the required amount of Eu-complex Eu(TTA)₂Tpy-OCH₃·2H₂O in THF solution, and the resulting mixture was heated at 60 °C for 30 min. The Eu/MMA luminescent films were obtained after evaporation of excess solvent at 60 °C.

Due to the transparent, thermal and luminescent properties of Eu/PMMA-5 % system is the best among of these Eu/PMMA films, so when prepared the Eu/PMMA/SiO₂ films, we chose the Eu/PMMA-5 % system as host. And the doping percentage (w/w) of nano-SiO₂ is 1, 3, 5, 7 for Eu/PMMA/SiO₂-1, 3, 5 and 7 %, respectively. The detailed fabricated process of Eu/PMMA/SiO₂ films as follows: the PMMA and Eu(TTA)₂Tpy-OCH₃·2H₂O were dissolved in THF, followed by addition of the required amount of nano-SiO₂, and the resulting mixture was heated at 60 °C for 1.5 h under the ultrasonic. The Eu/PMMA/SiO₂ luminescent films were obtained after evaporation of excess solvent at 60 °C. The average thickness of all resulting luminescent films was estimated by optical microscopy to be of ca. 0.2 mm.

3 Results and discussion

3.1 Design and characterization

To further to improve the quantum efficiency and thermal resistance of Eu/Polymer luminescent films, an ancillary

ligand 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine (Tpy-OCH₃) and a corresponding Eu-complex based Tpy-OCH₃ as ancillary ligand have been prepared. The overall procedure was summarized in Scheme S1. The Eu-complex Eu(TTA)₂Tpy-OCH₃·2H₂O was synthesized according to the well-established procedure with a high yield of 81 %, and characterized by FT-IR, ¹H NMR, ESI-MS, and elemental analyses. The elemental analyses and ESI-MS studies indicated that the central Eu³⁺ ion is coordinated to an ancillary ligand Tpy-OCH₃, two TTA ligands, as well as two water molecules.

The fact of the –C=O stretching band from 1665 cm⁻¹ for the free ligand TTA to 1609 cm⁻¹ in the FT-IR spectra (Fig. 1) of the compounds given good evidence that the Eu³⁺ ions are coordinated with the oxygen atoms of TTA. Besides, for Eu/PMMA film systems, the band of 1609 cm⁻¹ presented increasing intensity with increased doping concentration from 1 to 7 %, the result indicated the Eu-complex precursor successfully doped into PMMA matrix. Fig. S1 showed the FT-IR spectra of Eu-complex and Eu/PMMA-5 % films, when PMMA is doped with precursor Eu(TTA)₂Tpy-OCH₃·2H₂O, the bands at 3450 cm⁻¹ disappeared, which is attributed to the coordination of the –C=O group from PMMA to Eu³⁺ ions replacing the water molecules in Eu-complex Eu(TTA)₂Tpy-OCH₃·2H₂O, this result was again in good agreement with the TG analyses of doped polymer films, where no mass loss was noted in the temperature region 30–120 °C.

The FT-IR absorption of Eu/PMMA-5 % film and Eu/PMMA/SiO₂ films displayed a very strong peak at 1730 cm⁻¹ assigned to the ν(C=O) stretching band of PMMA matrix (Fig. 2). With the increase of doping percentage nano-SiO₂, the broad band centered at 3578 cm⁻¹ and a strong peak at 1148 cm⁻¹ were gradually increased,

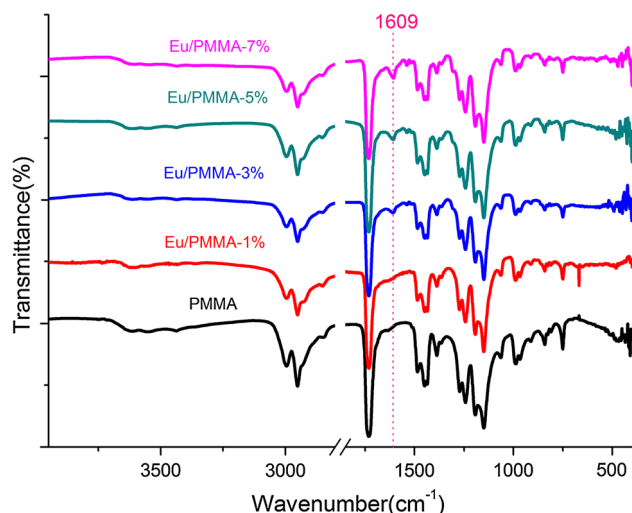


Fig. 1 The FT-IR spectra of PMMA and Eu/PMMA films

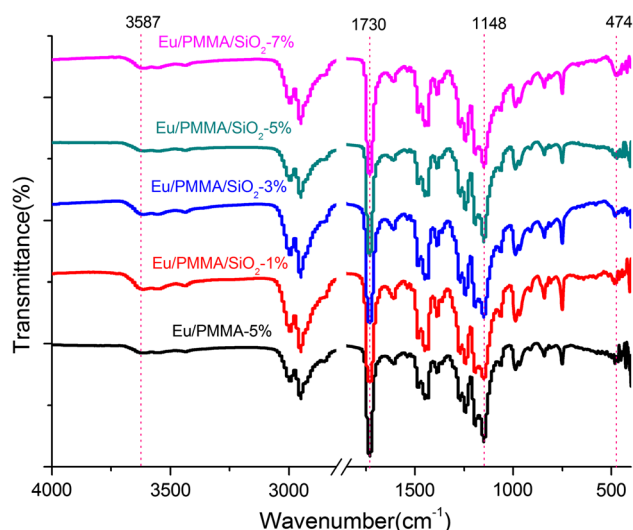


Fig. 2 The FT-IR spectra of Eu/PMMA-5 % film and Eu/PMMA/SiO₂ composite films

they are attributed the Si–OH stretching and Si–O–Si symmetric stretching vibrations of nano-SiO₂, respectively. Particularly, a new absorbance at near 474 cm⁻¹ appeared for Eu/PMMA/SiO₂ film systems, which is attributed the bending vibration of Si–O–Si of nano-SiO₂. All of the results revealed the nano-SiO₂ was successfully doping into the Eu/PMMA-5 % film system.

3.2 Thermal measurement analysis

To study the thermal behavior of the precursor Eu-complex and Eu/PMMA luminescent films, DSC and TGA measurements have been carried out. Figure 3 showed that TGA curves of Eu-complex, pure PMMA film and Eu/

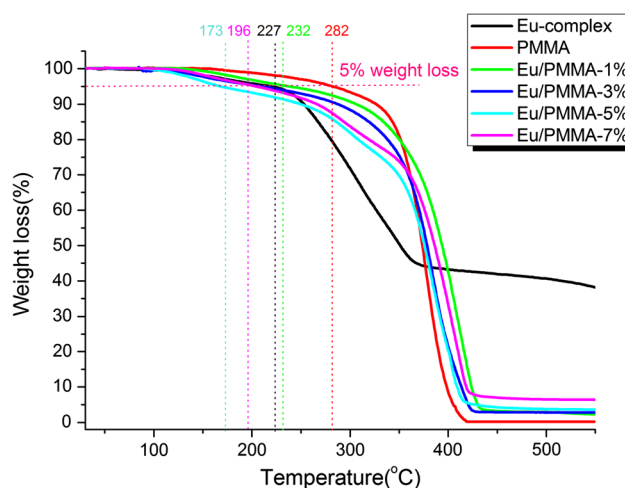


Fig. 3 TGA curves of the Eu-complex, pure PMMA, and Eu/PMMA films under an inert atmosphere of N₂

MMA-1, 3, 5, and 7 % (w/w) luminescent films recorded under an inert atmosphere of N_2 . It is clear from the TGA data that Eu-complex undergoes a mass loss of approximately 5.1 % (Calcd: 3.8 %) in the first step (103–228 °C), which corresponds to the elimination of the coordinated water and solvent molecules. The second decomposition stage occurs from 229 to 373 °C, and the mass loss is about 48.1 % (Calcd. 43.7 %), which corresponds to the degradation of first ligand TTA. The last decomposition stage occurs from 376 to 690 °C, which corresponds to the decomposition of ancillary ligand Tpy-OCH₃. The final residue is approximately 26 % of the initial mass, it correspond to formation of the non-volatile europium(III) oxyfluoride.

From the TGA data that the pure PMMA polymer film decomposes in only one step event under thermal degradation and the temperatures of the thermal decomposition $T_{d-5\%}$ was 282 °C. Similarly, these samples of PMMA polymer doped with the Eu-complex also presented curves of decomposition under an inert atmosphere with only one decomposition event. As indicated in Fig. 3, the Eu/PMMA-1, 3, 5 and 7 % luminescent films exhibited decreasing $T_{d-5\%}$ with increasing doping percentages of Eu-complex, they were 232, 227, 173, 196 °C, respectively. The maximum shift of $T_{d-5\%}$ was 109 °C for the Eu/PMMA film system in comparison to that of the pure PMMA film. Even though, the results showed the Eu/PMMA films still had a higher 5 % weight loss temperature, about 200 °C for all Eu/PMMA films, and therefore they still have potential applications in special fields.

As can be seen from the Fig. 3, the TG curves recorded in the temperature interval from room temperature to 120 °C exhibited no mass loss event. The result indicated that the water molecules coordinated with the Eu^{3+} ions in the precursor $Eu(TTA)_2Tpy-OCH_3 \cdot 2H_2O$ were absent after doping reaction process. When the Eu-complex was embedded into the PMMA matrix, the coordination of the two water molecules was successfully replaced by the interaction between the Eu-complex and the $-C=O$ groups of the PMMA matrix, in agreement with the results of other polymer systems previously analyzed [16, 24, 25].

The TGA analysis of Eu-complex and Eu/PMMA films showed the $T_{d-5\%}$ of Eu/PMMA-5 % film was 173 °C, and it was well below that of Eu-complex precursor (227 °C). Poor thermal stability of Eu/PMMA films will greatly limit their application in many fields. Nano-SiO₂ possesses excellent thermal property; we hope the introduction of nano-SiO₂ can effectively enhanced the thermal resistance of Eu/PMMA-5 % film. Figure 4 showed that with the increase of doping concentration of nano-SiO₂, the $T_{d-5\%}$ of Eu/PMMA/SiO₂ had obviously improved. They were 207, 248, 248, 235 °C for Eu/PMMA/SiO₂-1, 3, 5, and 7 %, respectively. This can be ascribed to the forming

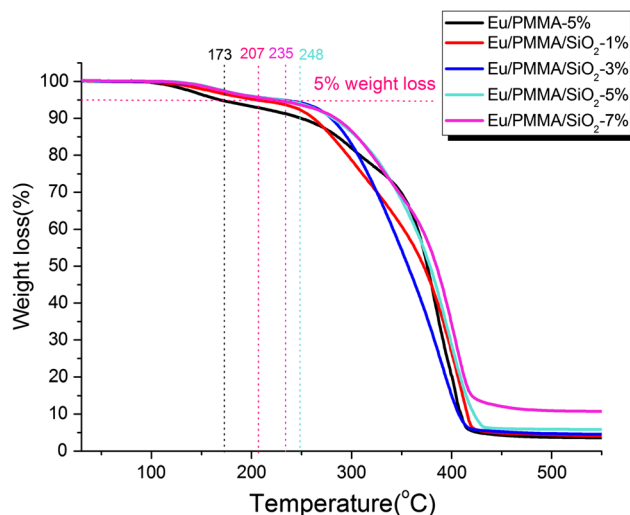


Fig. 4 TGA curves of the Eu/PMMA-5 % film and Eu/PMMA/SiO₂ films under an inert atmosphere of N_2

of cross-linked network between PMMA chains and nano-SiO₂. Compared with the Eu/PMMA-5 % film, the $T_{d-5\%}$ of Eu/PMMA/SiO₂ films had been improved maximum 75 °C. The results indicated the thermal resistance of Eu/PMMA/SiO₂ films can meet application requirement in many fields.

The differential scanning calorimetry (DSC) analysis of the PMMA matrix and Eu/PMMA films were measured to investigate their phase stability (Fig. 5). The glass transition temperature (T_g) of Eu/PMMA films which doped Eu-complex 1, 3, 5 and 7 % were 98.6, 97.1, 94.5, and 91.6 °C, respectively, which is lower than that of the pure PMMA matrix (T_g 106.2 °C). The result revealed that the rigidity of the Eu/PMMA films was reduced with increase

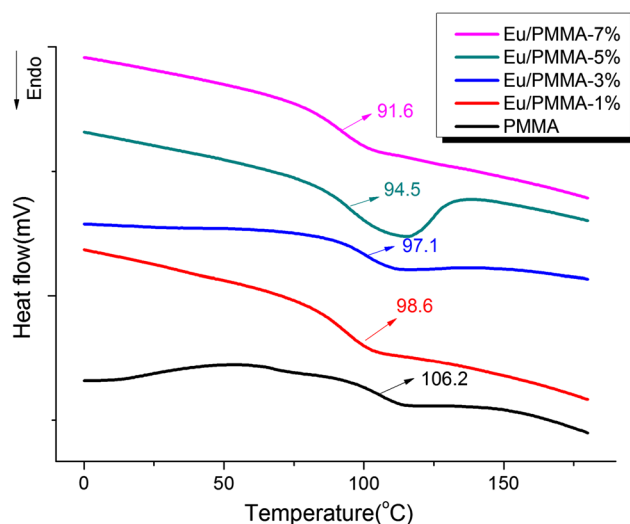


Fig. 5 DSC curves of PMMA matrix and Eu/PMMA luminescent films

of doping concentration of Eu-complex precursor. In addition, due to the forming of cross-linked network between PMMA chain and nano-SiO₂, the T_g values of Eu/PMMA/SiO₂ composite films exhibited the gradually increased tendency when the doping concentration of nano-SiO₂ from 3 to 7 % (Fig. S2), they are 96.2, 97.9 and 107.7 °C for Eu/PMMA/SiO₂-3, 5, and 7 %, respectively. However, the T_g values of Eu/PMMA/SiO₂-1 % was slightly lower than that of Eu/PMMA-5 % film, this may be attributed the introduction of 1 % nano-SiO₂ not only no forming of cross-linked network between PMMA and nano-SiO₂, but also decreasing the rigidity of PMMA molecular chain.

3.3 Photophysical properties analysis

Figure 6 showed the excitation spectra of the PMMA matrix films doped with Eu-complex Eu(TTA)₂Tpy-OCH₃·2H₂O at different concentrations 1, 3, 5 and 7 % (w/w), and recorded at room temperature in the spectral range of 200–500 nm, by monitoring the emission at 617 nm. The spectral region from 200 to 400 nm was dominated by an intense broad band which was assigned to the PMMA matrix and organic ligands absorption, and subsequent efficient intramolecular energy transfer to the Eu³⁺ ion. Furthermore, the typical intraconfigurational transitions were absent in these excitation spectra, owing to efficient energy transferred from the organic moiety to the Eu³⁺ ions. All facts suggested the PMMA matrix serve as efficient co-sensitizers for the Eu³⁺ ions in this work.

The emission spectra of Eu/PMMA luminescent films (–1, 3, 5 and 7 %) excited at 330 nm demonstrated five characteristic emission bands that were assigned to the ⁵D₀ → ⁷F_J (J = 0–4) transitions of the Eu³⁺ ions. As displayed in Fig. 6 right, the emission intensity of the Eu³⁺

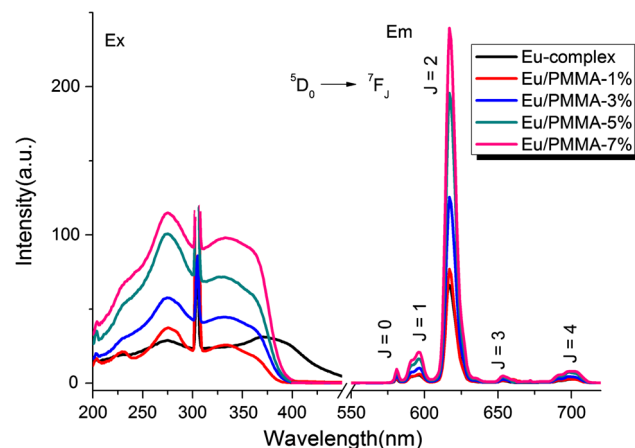


Fig. 6 The PL spectra of Eu-complex and Eu/PMMA films in solid. *Left* excitation spectra ($\lambda_{em} = 617$ nm), *right* emission spectra ($\lambda_{ex} = 330$ nm)

ions at 617 nm increased with the increasing of Eu-complex, the phenomenon of concentration quenching did not occur with the increasing Eu³⁺ ions content. The transition of highest intensity was dominated by the hypersensitive ⁵D₀ → ⁷F₂ transition at approximately 617 nm, which implies that the Eu³⁺ ions didn't occupy a site with inversion symmetry.

Moreover, the presence of only one peak in the region of the ⁵D₀ → ⁷F₀ transition at 580 nm demonstrated the occurrence of a unique chemical environment around the Eu³⁺ ions of symmetry type C_s , C_n , or C_{nv} . It was well-known that the magnetic-dipole transition ⁵D₀ → ⁷F₁ was nearly independent of the ligand field and therefore can be used as an internal standard to account for ligand differences. The intensity ratio (I_2/I_1) of the magnetic dipole transition to the electric dipole transition in the lanthanide complex measured the symmetry of the coordination sphere. The values of I_2/I_1 in the Eu/PMMA films were shown in Table 1. Compared with the Eu-complex, the I_2/I_1 of Eu/PMMA films was higher; these results suggested that, when the Eu-complex was incorporated into the PMMA matrix, the Eu³⁺ ions showed different local environments because of the influence of the surrounding polymer. The symmetry of the coordination sphere for the Eu³⁺ ions changed moderately in the Eu/PMMA films as compared to the Eu-complex. When incorporated into the PMMA matrix, however, the complexes exhibited disorder of a certain magnitude. Under the influences of the electric field of the surrounding ligands, the distortion of the symmetry around the Eu³⁺ ions by the capping PMMA results in the polarization of the Eu³⁺ ions, which increases the probability for electric dipole, allowed transition. The influences of PMMA matrix on the coordinative environment of the Eu³⁺ ions changed the energy transfer probabilities of the electric dipole transitions, accounting for the increased in luminescent intensity of the 617 peak.

In addition, the CIE chromaticity coordinates of Eu-complex, Eu/PMMA-1, 3, 5, and 7 % films from the emission spectra were near (0.66, 0.33), it revealed that all luminescent materials in this work belong pure red emission. The results were important because they indicated these materials can be used in some special fields such as O/PLEDs, optoelectric devices, sensors, etc.

The luminescence decay curves of Eu/PMMA films were obtained by monitoring the emission at the hypersensitive ⁵D₀ → ⁷F₂ transition (617 nm) and excitation at the ⁷F₀ → ⁵L transition (365 nm). These data can be adjusted with a first-order exponential decay function and the lifetime values (τ) of the emitter ⁵D₀ level of the doped systems were determined and are listed in Table 1. All τ values of Eu/PMMA luminescent films were higher than that of the Eu-complex indicating that radiative processes were operative in all the doped PMMA films due to the

Table 1 Experimental intensity parameters $\Omega_{2,4}$ and luminescent parameters for Eu-complex and Eu/PMMA films doped with various amounts of the complex $\text{Eu}(\text{TTA})_2\text{Tpy-OCH}_3\cdot 2\text{H}_2\text{O}$, at room temperature(330 nm excitation)

System	Ω_2 (10^{-20} cm ²)	Ω_4 (10^{-20} cm ²)	$A_{\text{rad}}/\text{S}^{-1}$	$A_{\text{nrad}}/\text{S}^{-1}$	τ/ms	η (%)	I_2/I_1	CIE (x, y)
Eu-complex	15.12	2.84	544.70	1209.69	0.57	31.05	10.27	0.67, 0.33
Eu/PMMA-1 %	17.75	2.90	624.43	988.48	0.62	38.71	12.54	0.67, 0.33
Eu/PMMA-3 %	18.46	2.91	645.90	723.97	0.73	47.15	12.15	0.67, 0.33
Eu/PMMA-5 %	17.44	2.85	614.28	562.19	0.85	52.21	12.20	0.67, 0.33
Eu/PMMA-7 %	16.78	2.93	591.64	495.32	0.92	54.43	11.62	0.67, 0.33

absence of multiphonon relaxation by coupling with the -OH group oscillators from the $\text{Eu}(\text{TTA})_2\text{Tpy-OCH}_3\cdot 2\text{H}_2\text{O}$.

The intrinsic luminescent quantum efficiency (η) of the $^5\text{D}_0$ emission level in this Eu-complex and Eu/PMMA films at room temperature was obtained based on the luminescence data [26–29]. According to these calculated results, the radiative (A_{rad}) and non-radiative (A_{nrad}) decay rates, and η of the Eu/PMMA films doped with $\text{Eu}(\text{TTA})_2\text{Tpy-OCH}_3\cdot 2\text{H}_2\text{O}$ at different doping concentrations were presented in Table 1. Compared with the Eu-complex precursor, all the PMMA doped films exhibited higher quantum efficiency values, ranging from 38.71 to 54.43 %. These spectral data indicated that beyond immobilizing the Eu^{3+} ions among matrices, the PMMA also acted as sensitizer of the system which greatly enhanced the luminescence of the Eu^{3+} ion. It was well-known that the efficiency of the intermolecular energy transfer was strongly dependent on the distance between the donor and acceptor. According to this point, it was suggested that for the present system, the PMMA chain, because of its long chain, had the capability to enwrap the $\text{Eu}(\text{TTA})_2\text{Tpy-OCH}_3\cdot 2\text{H}_2\text{O}$ complex and keeps the acceptor and donor close. In such a case, energy can be transferred efficiently from ligand to Eu^{3+} ions, resulting in the enhancement of intrinsic Eu^{3+} ions emission of a $\text{Eu}(\text{TTA})_2\text{Tpy-OCH}_3\cdot 2\text{H}_2\text{O}$. Thus the preserved rigidity in the complex structure in PMMA could be the origin of the enhanced quantum efficiencies.

Judd–Ofelt theory is a useful tool for analyzing f–f electronic transitions. Interaction parameters of ligand fields can be given by the Judd–Ofelt parameters Ω_λ (where $\lambda = 2, 4,$ and 6) [30]. The experimental intensity parameters (Ω_2 and Ω_4) for the doped Eu/PMMA films and $\text{Eu}(\text{TTA})_2\text{Tpy-OCH}_3\cdot 2\text{H}_2\text{O}$ complex were listed in Table 1. Large values of Ω_2 were observed for all luminescent materials in this work. Especially, the values of Ω_2 of Eu/PMMA films were higher than the precursor $\text{Eu}(\text{TTA})_2\text{Tpy-OCH}_3\cdot 2\text{H}_2\text{O}$, it was attributed to the $-\text{C}=\text{O}$ groups successfully coordinated with the Eu^{3+} ions in Eu/PMMA films, and effectively increased the asymmetry around the Eu^{3+} .

To further improve the luminescent properties of Eu/PMMA composite films, the nano- SiO_2 particles was introduced into the Eu/PMMA-5 % system, and the excitation and emission spectra of obtained Eu/PMMA/ SiO_2 composite films showed in Fig. 7. Figure 7 (left) indicated that the positions and line width of excitation spectra of Eu/PMMA/ SiO_2 films were similar to those obtained from the Eu/PMMA composite films. Figure 7 (right) emission spectra showed the emission intensity at 617 nm of Eu/PMMA/ SiO_2 -1 % was slightly lower the Eu/PMMA-5 % system, this can be ascribed to the concentration quenching of Eu-complex. Some previously work conclusion indicated that the nano- SiO_2 posses carrying effect [20, 31], when doped nano- SiO_2 into the europium complex system, the europium complex can be effectively embedded the surface of nano- SiO_2 to forming a core–shell structural sphere. In our this work, when doping 1 % nano- SiO_2 into Eu/PMMA-5 % system, due to the concentration of nano- SiO_2 is too low to nano- SiO_2 can't provide enough surface to embed all Eu-complex molecules, so the concentration quenching was occurred, the detailed Schematic representation can be seen Fig. 8a. With the increase of doping concentration of nano- SiO_2 , the emission intensity at

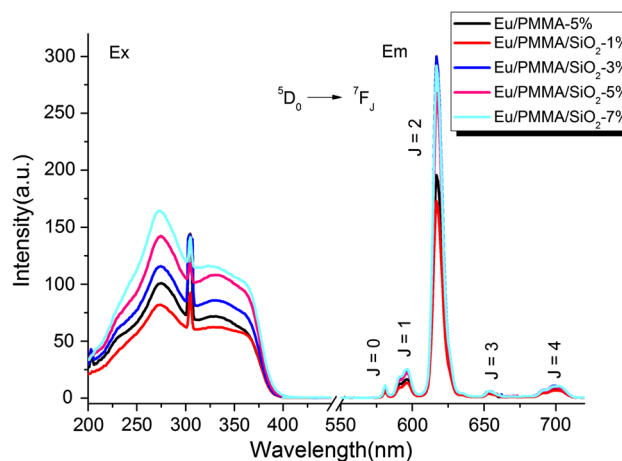


Fig. 7 The PL spectra of Eu/PMMA-5 % film and Eu/PMMA/ SiO_2 films. *Left* excitation spectra ($\lambda_{\text{em}} = 617$ nm), *right* emission spectra ($\lambda_{\text{ex}} = 330$ nm)

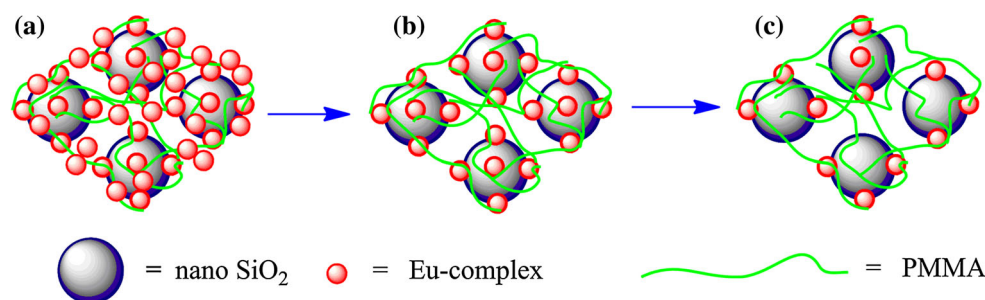


Fig. 8 Schematic representation of interaction between Eu-complex, PMMA and nano-SiO₂. **a** The doping concentration of nano-SiO₂ is low 3 %, e.g. Eu/PMMA/SiO₂-1 % film; **b** the doping concentration

of nano-SiO₂ is 3 %, e.g. Eu/PMMA/SiO₂-3 % film; **c** the doping concentration of nano-SiO₂ is more than 3 %, e.g. Eu/PMMA/SiO₂-5 and 7 % film

617 nm of Eu/PMMA/SiO₂ films have obviously enhanced, the intensity of Eu/PMMA/SiO₂-3 % film is higher 1.6-fold than the Eu/PMMA-5 % film. In this moment, 3 % nano-SiO₂ can provide enough surfaces to embed the Eu-complex to forming core-shell sphere. Furthermore, PMMA chain in system can effectively encapsulated the core-shell sphere through the coordination interaction between carbonyl groups of PMMA matrix and Eu³⁺ ions (Fig. 8b). Compared with the Eu/PMMA-5 % system, nano-SiO₂ carrying effect and interaction between -C=O and Eu³⁺ ions can more effectively remove the water molecules, so the emission intensity of Eu/PMMA/SiO₂-3 % film was obviously enhanced. However, continuously increased the doping concentration of nano-SiO₂, the emission intensity of Eu/PMMA/SiO₂-5 and 7 % film exhibited a slight decrease tendency. Fortunately, the emission intensity of Eu/PMMA/SiO₂-5 and 7 % composite films were still higher than that of Eu/PMMA-5 % film, they are 1.4 and 1.5 times as much as Eu/PMMA-5 % film, respectively. When the doping concentration of nano-SiO₂ exceeded 3 %, the Eu-complex molecules can't fully fill with the surfaces of nano-SiO₂, and the PMMA chain can't encapsulate these unsaturated core-shell sphere very well (Fig. 8c), so the emission intensity of Eu/PMMA/SiO₂-5 and 7 % composite films is slightly lower than that of Eu/PMMA/SiO₂-3 % film. These results indicated the optimum doping content of nano-SiO₂ in Eu/PMMA-5 % system is 3 %.

Table 2 revealed the change tendencies of lifetime (τ) and quantum efficiency (η) for Eu/PMMA/SiO₂ system

were similar with the change of emission intensity at 617 nm, it further confirmed that the concentration quenching was occurred when the doping concentration of nano-SiO₂ is 1 %. Most importantly, the τ of Eu/PMMA/SiO₂-3, 5 and 7 % were over 1 ms, they were 1.27, 1.15 and 1.09 respectively. The η for Eu/PMMA/SiO₂-3, 5 and 7 % were higher 1.5, 1.4 and 1.2 times than that of Eu/PMMA-5 % system, respectively. To the best of our knowledge, the quantum efficiency (η) of Eu/PMMA/SiO₂-3 % film (78.57 %) was found to be the highest so far reported in the literature based on PMMA as matrix. The η of Eu/PMMA/SiO₂-3 % film increased by about 25 % compared with the PVB system luminescent film in our previous work. In addition, the values of I_2/I_1 , Ω_2 and Ω_4 for Eu/PMMA/SiO₂ system were lower than that of Eu/PMMA-5 % system, it revealed that the coordination environment of Eu³⁺ ions have been changed with the introduction of nano-SiO₂, and the symmetry of Eu-complex was decreased. The all Eu/PMMA/SiO₂ composite films exhibited characteristic red emission of Eu³⁺ ions under UV 365 nm excitation (Fig. 9), and it was suggested that these complexes can be potential red luminescent materials.

4 Conclusions

A series of novel Eu/PMMA and Eu/PMMA/SiO₂ luminescent films were designed, prepared and characterized. TGA results exhibited the thermal stability of Eu-complex

Table 2 Experimental intensity parameters $\Omega_{2,4}$ and luminescent parameters for Eu/PMMA-5 % and Eu/PMMA/SiO₂ films doped with various amounts of the nano-SiO₂, at room temperature(330 nm excitation)

System	Ω_2 (10^{-20} cm ²)	Ω_4 (10^{-20} cm ²)	A_{rad}/S^{-1}	A_{nr}/S^{-1}	τ/ms	η (%)	I_2/I_1	CIE (x, y)
Eu/PMMA-5 %	17.44	2.85	614.28	562.19	0.85	52.21	12.20	0.67, 0.33
Eu/PMMA/SiO ₂ -1 %	17.38	2.73	681.01	634.78	0.76	51.76	12.15	0.67, 0.32
Eu/PMMA/SiO ₂ -3 %	17.26	2.84	618.66	168.74	1.27	78.57	11.97	0.67, 0.33
Eu/PMMA/SiO ₂ -5 %	17.36	2.82	620.70	248.86	1.15	71.38	11.89	0.67, 0.33
Eu/PMMA/SiO ₂ -7 %	16.60	2.78	588.30	329.13	1.09	64.12	11.16	0.67, 0.33

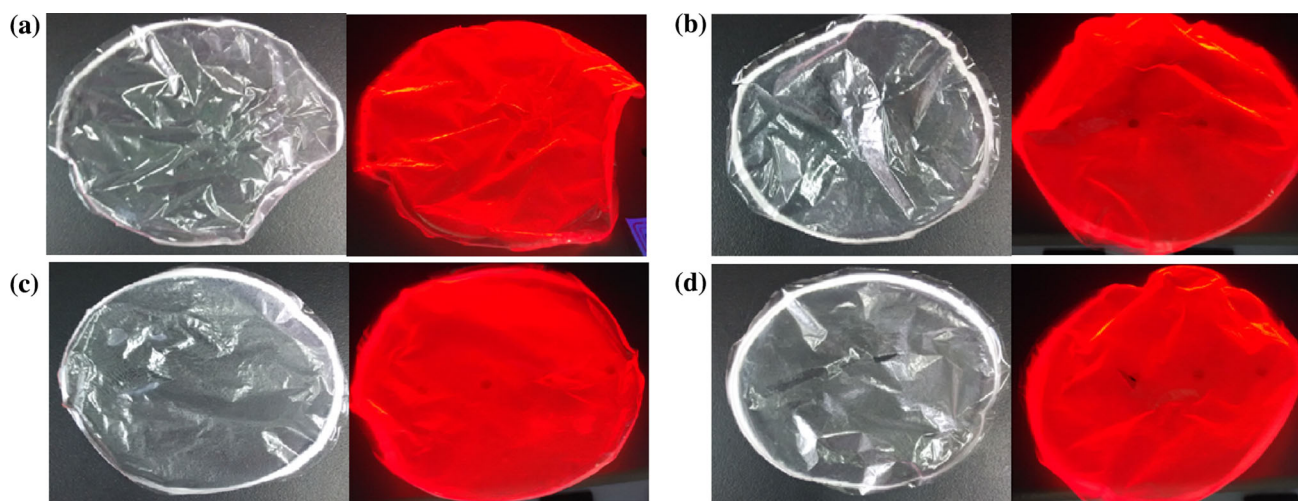


Fig. 9 Photographs of Eu/PMMA/SiO₂ composite luminescent films under normal light (*left*) and under 365 nm illumination (*right*). **a** Eu/PMMA/SiO₂-1 %; **b** Eu/PMMA/SiO₂-3 %; **c** Eu/PMMA/SiO₂-5 %; **d** Eu/PMMA/SiO₂-7 %

precursor was improved through doping it into PMMA matrix for Eu/PMMA system. PL results showed all Eu/PMMA films exhibited exceptionally high quantum efficiencies (39.71–54.43 %). Furthermore, the introduction of nano-SiO₂ can significantly improve the thermal stability of Eu/PMMA-5 % film. Most importantly, Eu/PMMA/SiO₂-3, 5 and 7 % composite luminescent films exhibited higher η and longer lifetime than that of Eu/PMMA-5 % film due to the carrying effect of nano-SiO₂ and coordination interaction of carbonyl groups and Eu³⁺ ions. Especially, the Eu/PMMA/SiO₂-3 % film exhibited the highest quantum efficiency (78.57 %) so far reported in the literature. In conclusion, these Eu/PMMA/SiO₂ luminescent films show promising PL efficiency and therefore have potential applications as polymer light-emitting diodes, optoelectronics, and supramolecular luminescent probes and active polymer optical fibers.

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