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A red-emitting copolymer phosphors based on bimetallic Eu-Ir complex for Near-UV chip-based LEDs

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Abstract: In this paper, a new Eu-Ir bimetallic complex $\text{Eu}(\text{FIRPic})_2(\text{Phen})\text{UA}$ is synthesized using the Ir complex FIRPic as ligands for Eu ions and red-emitting phosphorescent copolymer PM-Eu-Ir is successfully prepared via radical polymerization for commercial near UV chip-based LEDs. The Eu^{3+} ions were found to be effectively sensitizable by adding Ir-complex with enhanced ultra-violet light absorption at around 400 nm without affecting the fluorescence emission characteristic of the Eu^{3+} ions. The proposed copolymer PM-Eu-Ir exhibits the strongest emission peak at 612 nm with the CIE coordinates (0.461, 0.254) under 365 nm ultra-violet light excitation, which matches well with the 365 nm near-UV chip. The micro-morphology of the red copolymer phosphor PM-Eu-Ir is a typical multilayer spatial network structure; as well as having appreciable red emission and the corresponding fluorescence lifetime of 634.54 μs , it also has excellent thermal stability in a wide range of 25 ~ 250 °C. The LEDs fabricated by the copolymer PM-Eu-Ir display red light emission with a 149800 cd/m^2 luminance. The results support the potential utilization of prepared copolymer phosphor as a red component in the fabrication of near UV chip-based white LEDs.

Key words: rare-earth luminescent ions; bimetallic complexes; copolymer phosphors; NUV LED chips

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可用于近紫外 LED 芯片的铈-铱双金属配合物红光共聚荧光粉

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摘要:本研究以 Ir 配合物 FIrPic 作为 Eu 离子的配体, 合成了一种新的 Eu-Ir 双金属配合物 Eu(FIrPic)₂(Phen)UA, 并通过自由基聚合成功制备了红色发光荧光共聚物 PM-Eu-Ir, 适用于商用近紫外芯片型 LED。在不影响 Eu³⁺ 离子的荧光发射特性的前提下, 加入 Ir-配合物可以有效地敏化 Eu³⁺ 离子, 增强其对 400 nm 紫外光的吸收。在 365 nm 紫外光激发下, 共聚物 PM-Eu-Ir 在 612 nm 处显示出最强的发射峰, 其 CIE 坐标为(0.461, 0.254), 这与 365 nm 近紫外芯片非常吻合。红色共聚荧光粉 PM-Eu-Ir 的微观形貌为典型的多层空间网络结构, 除了表现出明显的红光发射和 634.54 μs 的荧光寿命外, 还在 25 ~ 250 °C 的宽温范围内具有优异的热稳定性。使用共聚物 PM-Eu-Ir 制作的 LED 发出的红光亮度为 149 800 cd/m²。研究表明, 所制备的共聚荧光粉可作为红光元件用于制造近紫外芯片白光 LED。

关键词: 稀土发光离子; 双金属配合物; 共聚型高分子荧光粉; 近紫外 LED

中图分类号: TQ422

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1 Introduction

White LEDs are known as the fourth generation of light sources after incandescent bulbs, fluorescent, and high-pressure gas discharge lamps. They offer high luminous efficiency, low energy consumption, long service life, low weight, environmental friendliness, and anti-vibration advantages^[1-3]. White LEDs are achieved mainly through light-converting techniques, which are low-cost and easy to realize industrially. One current production technology is to excite the yellow phosphor using an LED blue chip such that the two mixed radiations generate white light^[4-6]. However, the scarcity of red emission in the visible spectrum of artificial light leads to the white LED devices' low color rendering index^[7]. Furthermore, human eyes are especially sensitive to blue light, with excessive blue light stimulation causing visual fatigue and disorders of the circadian rhythm^[8]. To overcome the above drawbacks and improve the light color stability,

Jung Han *et al.*^[9] proposed an alternative solution for manufacturing white light in September 1998, namely the “ultraviolet chip + red/green/blue tricolor phosphors” mode. In this mode, the luminous performance of white light depends strongly on the ratios of three primary color phosphors. At the same time, red emission plays a role in adjusting the color temperature and color rendering index. Near-ultraviolet (N-UV) chip-based white LEDs have received considerable attention regarding many applications, such as operating theatres, museums, health lighting, and plant-growth lighting, because of their more optimal color stability and fluorescence, as well as their better user experience and eye friendliness^[10-12].

Red light is vital in determining the color temperature and color rendering performance of white LED devices. Thus, new red phosphors have become one of the research hotspots in the white LEDs industry. Many scholars have developed Eu³⁺ and Tb³⁺ doped inorganic phosphors, which exhibit excellent luminous properties^[13-16]. Numerous re-

searchers are committed to introducing rare earth complexes into polymer matrix composites in order to obtain rare-earth-doped polymer phosphors with high luminous efficiency because rare earth ions exhibit excellent luminescence properties^[17], and polymer materials have significant advantages in machine-shaping, for example, lightweight, and low-cost^[18-19]. At present, Eu^{3+} ion is often used as a red-light activator because of the $5D_0/7F_J$ transitions ($J = 0-4$) of Eu^{3+} ion that leads to a characteristic red emission band around 610 nm^[20-22]. For example, Chang C H *et al.*^[23] designed and synthesized the complexes $\text{Eu}(\text{pzc})_3(\text{phen})$ and $\text{Eu}(\text{mpzc})_3(\text{phen})$ with an excitation band between 250 and 350 nm, the most intense emission band being a narrow peak centered at 614 nm. Matsushita A F Y *et al.*^[24] prepared a red light-emitting macromolecular composite $\text{Eu}(\text{PSA})\text{Phen}$, which produced an excitation band between 275 nm and 375 nm and a main emission band of 610–630 nm (red emission) when excited at 348 nm.

The steady-state excitation and emission spectra for red-emitting europium (Eu) complexes tend to be narrow-band spectra with weak emission intensities. Their characteristic absorption peaks mainly concentrate around 340 nm, and they exhibit weak absorption of violet light at 400 nm, which does not match well with the output wavelength of commercial N-UV LED chips (350–420 nm)^[25-26]. In contrast, the excitation spectrum of iridium (Ir) complexes has a broadband structure, which can be effectively excited by UV and blue light, corresponding to a wide coverage of the emission spectrum. By synthesizing specially designed ligands for Ir complexes and modulating the coordination pattern, broadband emission spectra can be obtained in any range from the N-UV to the N-IR region, thus enabling sensitization of lanthanide ions^[27], including Eu ions.

This paper proposes a simple and practical solution to achieve broadband excitation of $\text{Eu}(\text{III})$

ion-doped polymer phosphors and broaden the application scope of red fluorescent polymeric materials. The proposed method involves synthesizing the Eu-Ir bimetallic complex using Ir complexes as the ligand for Eu ions, then preparing a red copolymer phosphor through free-radical polymerization. The paper then evaluates the material's optical and thermal properties for potential application in N-UV LEDs.

2 Experiments

2.1 Materials

Europium chloride (EuCl_3 , 99.99%), 1,10-phenanthroline (Phen, 99%), bis[2-(4,6-difluorophenyl)pyridinato-C2,N] (picolinato)iridium(III) (FIrPic >99%, Luminescence Technology Corp.), and undecylenic acid (UA, 99%), ethanol $\geq 99.7\%$, methanol $\geq 99.5\%$, methyl-methacrylate (MMA $\geq 99\%$), dimethyl sulfoxide (DMSO, AR), azodiisobutyronitrile (AIBN $\geq 98\%$).

2.2 Experiments

2.2.1 Synthesis of bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$

1 mmol EuCl_3 , 2 mmol FIrPic, 1 mmol Phen, and 1 mmol UA, according to the substance content of 1:2:1:1, were separately dissolved in 5 mL anhydrous ethanol for use. The UA ethanol solution was then injected into a 100 mL three-neck flask and stirred for about 10 minutes at 50 °C. Subsequently, the EuCl_3 ethanol solution was added drop by drop to the mix, which was neutralized to pH 4.5 with 1 mol/L NaOH ethanol solution. After further stirring for 30 minutes at 50 °C, the FIrPic ethanol solution was added to the blend, and a large amount of white precipitate became visible during the neutralization of the blended solution to pH 7 with 1 mol/L NaOH ethanol solution. Finally, the Phen ethanol solution was added to the reaction mixture via a dropper and then stirred for three more hours at 50 °C. At the

end of the experiment, the precipitate was washed several times with ethanol and dried in an oven at 55 °C until a constant weight was reached. The white powder resulting from this process was $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$. The synthesis route of the proposed Eu-Ir bimetallic complex is shown in Figure 1.

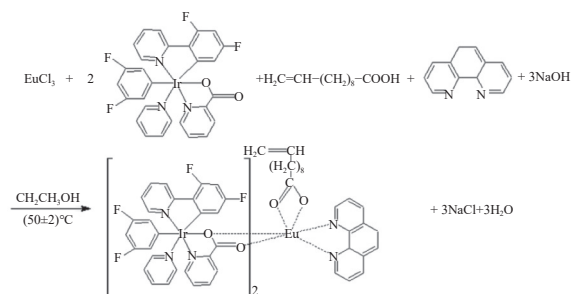


Fig. 1 Synthetic route of the bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$

2.2.2 Synthesis of copolymer phosphor PM-Eu-Ir

The reactive complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ (0.05 g) and MMA (1.28 g) were completely dissolved in the DMSO solution (10 mL) using an ultrasonic bath. The resulting mixture was then poured into a 100 mL three-neck flask, where the reaction was carried out under a nitrogen atmosphere. Subsequently, 2 mL of AIBN ethanol solution (pure AIBN is 0.04 g) was added dropwise to the mixing solutions placed in the water bath at $(78 \pm 2)^\circ\text{C}$, and deoxygenation by nitrogen gas stopped when the reactive system became very viscous. After that, the closed system remained at 78 °C for 48 hours to ensure a complete reaction, and all reactants were immersed in 100 mL methanol at room temperature. After two hours, the white flocculent precipitate started to generate. Finally, the collected precipitate was filtered through three-layer filter paper and washed with DMSO solution three times to remove unreacted monomers and impurities. Then, the resulting products were dried in an oven at 60 °C for 48 hours until a constant weight was reached. After grinding the substance thoroughly, a white powder called poly(MAA-co- $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$), abbreviated as PM-Eu-Ir, was obtained. Figure 2 shows the specific synthesis route.

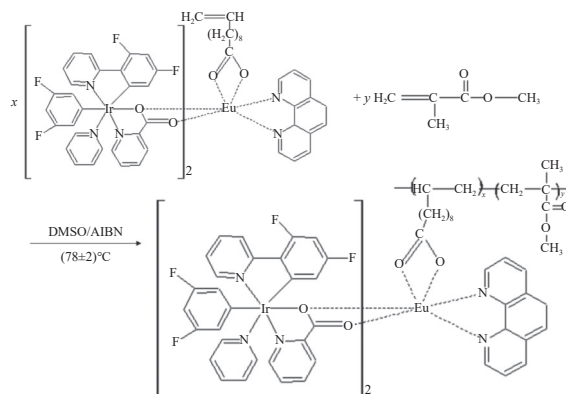


Fig. 2 Synthesis route of the copolymer PM-Eu-Ir

2.3 Characteristics

FT-IR spectra in the 4000~500 cm^{-1} range were recorded in a KBr pellet using a Fourier transform infrared spectrometer (FTIR, Tensor 27, Bruker). The UV-vis absorption spectra were taken in methylene chloride (CH_2Cl_2 , 10^{-4} mol/L) using a Hitachi-U3900 spectrometer. Fluorescence spectra were measured by a full-function steady-state fluorescence spectrometer (Fluoromax-4, Horiba) with a slit width of 5 nm, and the prepared phosphor was dissolved in 10^{-4} mol/L methylene chloride. Thermogravimetric Derivative thermogravimetry (TG-DTG) analysis and differential scanning calorimetry (DSC) curves on phosphorescent copolymer were conducted using a thermal analysis instrument (209F3, NETZSCH) with a heating rate of 10 °C/min under N_2 . The fluorescence lifetime of the phosphorescent copolymer was measured in the solid state using a fluorescence spectrometer (FLS980, Edinburgh). The quantum efficiency (QE) was measured by an FLS-980 fluorescence spectrophotometer equipped with a 450 W Xe light source in integrating sphere mode. The morphology of the synthetic complex and prepared phosphorescent copolymer was observed using FE-SEM (JSM-6700F, JEOL). The ST-900 M photometer and Keithley 2400 digital source meter measured electroluminescence spectra. All measurements were made at room temperature unless otherwise stated.

3 Results and discussion

3.1 Solubility

The bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$

synthesized in this paper exhibits good solubility in some highly and moderately polar solvents, such as DMSO, DMF, CH_2Cl_2 , CHCl_3 , and THF, but poor solubility in water, methanol, and acetone. Furthermore, because of the linear macromolecule structure of the prepared PM-Eu-Ir, the red phosphorescent copolymer has excellent solubility in most polar solvents containing acetone, THF, CH_2Cl_2 , CHCl_3 , DMSO, and DMF at room temperature, which significantly improves the film-forming performance of organic phosphors.

3.2 FT-IR spectra

The FT-IR spectra of the Ir complex FIrPic, synthetic $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$, and copolymer PM-Eu-Ir recorded by KBr tablets in the range 4000~

400 cm^{-1} are given in Figure 3 (color online). The corresponding characteristic peaks thereof are illustrated in Table 1. In Figure 3 (a), FIrPic as the first ligand shows two C-C stretching vibrations of the aromatic ring at 1346 and 1292 cm^{-1} and the C-F stretching vibration at 1246 cm^{-1} . Besides, the C=N stretching vibration of FIrPic occurs at 1477 cm^{-1} , and two C-N stretching vibrations are found at 1165 and 1107 cm^{-1} . In addition, the absorption band at 1051 cm^{-1} is ascribed to the in-plane CH bending vibration of the aromatic ring, and the absorption bands at 833, 762 and 700 cm^{-1} are attributed to the out-of-plane CH bending vibrations in the 900–670 cm^{-1} region.

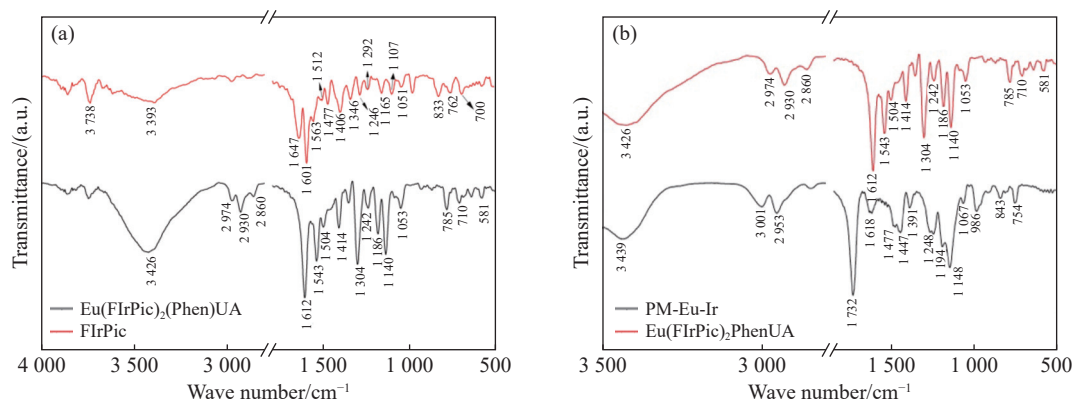


Fig. 3 FT-IR spectra of the FIrPic, $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$, and PM-Eu-Ir

Tab. 1 FT-IR characteristic peaks of the ligands, complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$

Complex	$\nu_{\text{C=O}}(\text{-COOH})$	$\nu_{\text{as}}(\text{CH}_2)$	$\nu_{\text{s}}(\text{CH}_2)$	$\nu_{\text{C-OH}}$	$\delta_{\text{C-H}}$	$\nu_{\text{Eu-N}}$	$\nu_{\text{C=N}}$
FIrPic	1647, 1406	-	-	-	833, 762, 700	-	1477
Phen	-	-	-	-	864, 739	-	1493
UA	1711	2925	2855	910	-	-	-
$\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$	-	2930	2860	-	785, 710	581	1414

Since the C=O and C-O in carboxyl ion (-COO-) are two essentially equivalent C=O bonds and are strongly coupled to each other, the corresponding absorption band of the -COO- group in FIrPic is split into two parts: the asymmetrical stretching vibration $\nu_{\text{as}}(\text{COO})$ at 1647 cm^{-1} and the symmetrical stretching vibration $\nu_{\text{s}}(\text{COO})$ at 1406 cm^{-1} . The $\Delta\nu(\text{as-s})(\text{COO})$ of 241 cm^{-1} is lar-

ger than 200 cm^{-1} [28] because FIrPic is a mono-coordinate complex. However, the bimodal characteristic absorption bands are almost invisible when the coupling between two CO bonds in carboxylate (-COO-) is weak. This suggests successful coordination between the first ligand FIrPic and $\text{Eu}(\text{III})$ ions.

The overall vibration mode of the aromatic ring skeleton in the chosen complex FIrPic presents a

series of sharp absorption peaks at 1601, 1563, and 1512 cm^{-1} with different intensities. According to the hard/soft acid/base principle^[29], the rare-earth Eu ion is a classic hard acid with a coordination number of 8, which makes it easier to form stable complexes with hard-base ligands containing oxygen or nitrogen atoms. Therefore, compared with the original complex FIrPic, the vibration bands of the aromatic ring skeleton of the bimetallic Eu-Ir complex shift to lower frequencies (1612, 1543, and 1504 cm^{-1}) as the degree of conjugation increases. The absorption band at 1053 cm^{-1} is caused by the in-plane CH bending vibration of the aromatic ring in the Eu-Ir complex.

Compared with the second ligand Phen, the out-of-plane C-H bending vibrations of the aromatic ring of the Eu-Ir complex are shifted from 864 and 739 cm^{-1} to 785 and 710 cm^{-1} , respectively. The -C=N stretching vibration shifts from 1493 cm^{-1} to 1414 cm^{-1} because two Eu-N coordination bonds formed in the coordination of the Eu(III) ion with the second ligand, Phen, resulting in a reduced force constant of C=N^[30]. Hence, the corresponding absorption peak shifts to lower frequencies, indicating that the coordination between the second ligand Phen and Eu(III) ions is successful.

The absorption peaks at 2925 and 2855 cm^{-1} are related to the asymmetric CH_2 stretching vibration and symmetric CH_2 stretching vibration in the active ligand UA, respectively. When Eu(III) ions form a stable complex with UA, the relevant vibration peaks will shift towards higher frequencies because of the hyperconjugation effect; for example, the asymmetrical stretching vibration $\nu_{\text{as}}(\text{CH}_2)$ and symmetrical stretching vibration $\nu_{\text{s}}(\text{CH}_2)$ of $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ are shifted to 2930 and 2860 cm^{-1} .

The absorption band observed at 1711 cm^{-1} is attributed to the C=O stretching vibration of carboxylic acid in UA. However, no C=O stretching vibration band is found in the FT-IR spectrum of $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ because the carboxyl group

(COOH) reacts with the Eu ion to generate a carboxylate. Similarly, the C-OH out-of-plane bending vibration of carboxylic acid in UA is at 910 cm^{-1} while the corresponding C-OH vibration of $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ is invisible due to the Eu-O bond formed in the coordination between C-OH group and the Eu ion, indicating that the active ligand UA is successfully coordinated with the Eu(III) ion. Finally, the vibration frequency of 2974 cm^{-1} is assigned to the = CH_2 symmetric stretching at the end of the double bond, and further polymerization can take place because of the C=C double bond of $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$.

As can be seen in Figure 3(b), the band shape of phosphorescent copolymer PM-Eu-Ir accords with that of complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$. The characteristic absorption peak at 1732 cm^{-1} in copolymer PM-Eu-Ir is associated with the C=O stretching vibration mode in PMMA. Compared with the absorption peak at 2974 cm^{-1} for $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$, there is no absorption peak corresponding to the C=C double bond in the FT-IR spectrum of PM-Eu-Ir as a result of successful copolymerization. Besides, the Eu-N stretching vibration band at 581 cm^{-1} in PM-Eu-Ir is much weaker than that in $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$; this is because the Eu-Ir complex accounts for a smaller proportion of whole block copolymer macromolecules after the occurrence of copolymerization.

3.3 UV-visible absorption spectra

Figure 4 (color online) displays the UV-vis absorption spectra of Ir complex FIrPic, bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$, and phosphorescent copolymer PM-Eu-Ir dissolved in CH_2Cl_2 solution (1×10^{-4} mol/L) at room temperature. The spectrum of complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ has two absorption bands at 275 nm and 344 nm in the near-UV region, which can be assigned to the absorption from the ligand Phen and the conjugated structures formed in the complex, respectively. Compared to Ir complex FIrPic, the highest absorption peak occurs at a longer wavelength (344 nm), and the corres-

ponding absorption intensity is stronger than that of the peak at around 378 nm for FIrPic, which matches well with commercial 365 nm UV-LED chips.

The absorption spectrum for copolymer PM-Eu-Ir displays three clear absorption bands centered at 229, 269, and 340 nm. This demonstrates that the prepared copolymer-based red phosphor can be excited by UV light, such as commercial 365 nm chips. The absorption peak located at 229 nm is primarily attributed to the π - π^* interactions between UA and Phen ligands in complex Eu(FIrPic)₂(Phen)UA. Moreover, the absorption bands around 269 and 340 nm are mainly ascribed to the conjugated double bonds in the benzene ring of the ligands. It can be concluded that little or no dissociation occurs during the polymerization between MMA and Eu(FIrPic)₂(Phen)UA, which remain a stable bimetallic ligand system. Thus, central Eu³⁺ ions can emit the characteristic fluorescence after absorbing the UV light^[31].

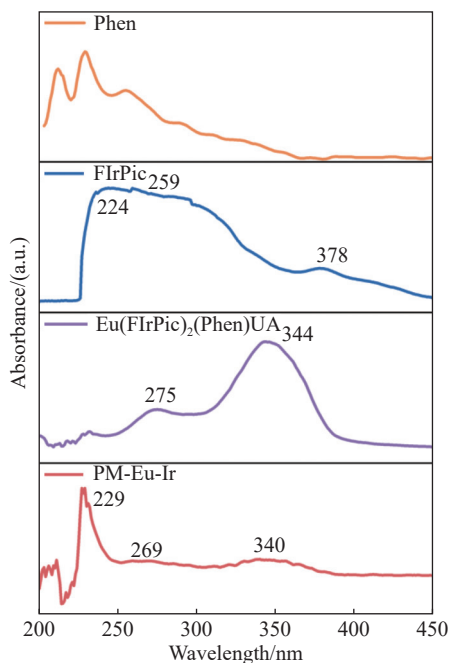


Fig. 4 UV-vis absorption spectra of the Ir complex FIrPic, bimetallic complex Eu(FIrPic)₂(Phen)UA, and phosphorescent copolymer PM-Eu-Ir

3.4 Micro-morphology

The FE-SEM micrographs of synthetic bimet-

allic complex Eu(FIrPic)₂(Phen)UA and the phosphorescent copolymer PM-Eu-Ir can be seen in Figure 5. There are significant differences between them: the Eu(FIrPic)₂(Phen)UA presents a long laminated structure with an average width of about 1 μ m, while the micro-morphology of PM-Eu-Ir is a typical multilayer spatial network structure consisting of micro-size spherical aggregates, and the interior of each aggregate is composed of intertwined molecular chains, suggesting that the polymerization reaction is complete in this experiment, not a simple mixture of Eu-Ir complex monomers and linear polymer PMMA.

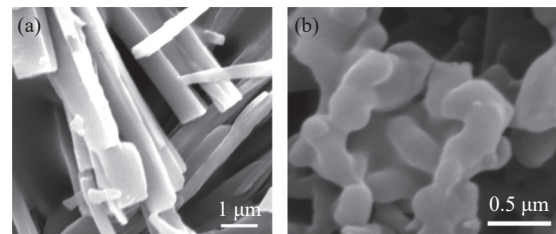


Fig. 5 FE-SEM images of the bimetallic complex Eu(FIrPic)₂(Phen)UA (a) and phosphorescent copolymer PM-Eu-Ir (b)

3.5 Thermal performance of phosphorescent copolymer

The thermal properties of the copolymer PM-Eu-Ir were investigated by differential scanning calorimetry (DSC), thermogravimetric (TG), and differential thermal gravimetric (DTG) analysis at a heating rate of 10 °C/min under N₂ atmosphere. As shown in Figure 6 (color online), the glass transition temperature (T_g) of copolymer PM-Eu-Ir was found to be 134 °C; a high T_g value is essential for maintaining good thermal stability of phosphors when encapsulated into LED devices. According to the ASTM E1641-2007 (Standard Test Method for Decomposition Kinetics by Thermogravimetric)^[32], the intersection of an extended baseline and line composed of a point of 5% weight loss and a point of 50% weight loss is defined as the onset decomposition temperature (T_{onset}), as illustrated in Figure 6(b), the T_{onset} of synthetic PM-Eu-Ir is 257 °C.

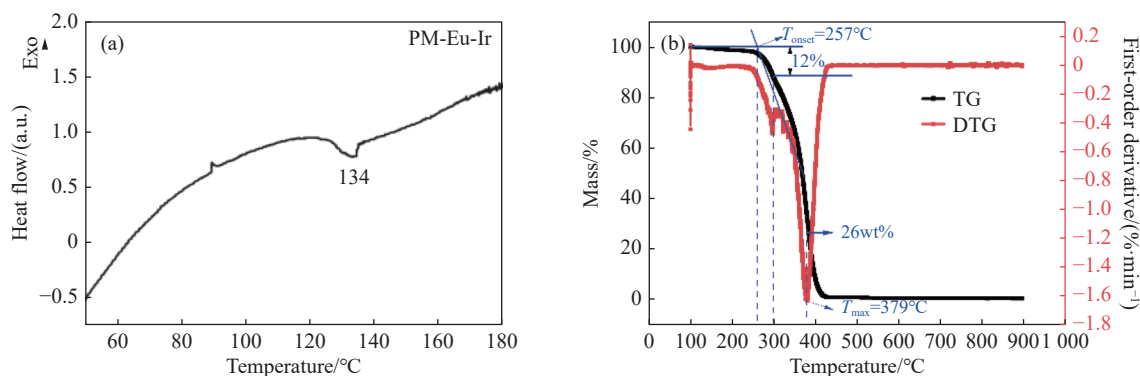


Fig. 6 (a) DSC curves and (b) TG-DTG curves of copolymer PM-Eu-Ir

It seems obvious that no weight loss occurs between 100 °C and T_{onset} because there is no coordination water in copolymer PM-Eu-Ir. Then, the maximum decomposition rate of $-1.7\%/min$ appears at 379 °C with a weight loss of 74%. Eventually, complete decomposition of the sample is reached at 419 °C with a residue of 1.4wt%. More specifically, the TG curve of PM-Eu-Ir displays two weight loss steps. The first step in the range of 257~300 °C changes gently, and the weight loss of 12% is primarily related to the decomposition of small molecule ligands and precursor complexes from the copolymer side chain. The second step (310~410 °C) changes sharply, the maximum weight loss of 86% in this step is due to the pyrolysis of the main chain of the copolymer and the complete decomposition of complexes at higher temperatures. Besides, the above results illustrate that the prepared red-phosphorescent copolymer remains stable up to 257 °C, indicating PM-Eu-Ir has good thermal stability in a wide range (25~250 °C) and meets the temperature requirements for the LED emitting layer, given that the operating temperature of LED is generally below 150 °C^[33-34].

3.6 Fluorescence properties

The excitation and emission spectra of synthetic bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ and phosphorescent copolymer PM-Eu-Ir dissolved in the CH_2Cl_2 solution (1×10^{-4} mol/L) at room temperature are presented in Figure 7 (a) and 7 (b) (color online). The excitation spectrum for

$\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ complex exhibits a narrow band in the 350 to 420 nm range and two excitation wavelengths at 375 and 393 nm, respectively, which match well with commercial UV-LED chips. In particular, the peak located at 393 nm indicates that adding Ir complex increases the absorption intensity of Eu ions to violet 400 nm light irradiation, extending the applicability of prepared bimetallic complexes to UV-LED chips.

When $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ is excited by 365 nm UV light, its emission spectrum shows a multi-peak structure covering the yellow to red light visible region of the spectrum, and the five sharp emission peaks at 579, 592, 613, 652 and 700 nm are attributed to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions of the Eu(III) ion, respectively^[35-37]. Specifically, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition at 592 nm is a magnetic dipole transition less affected by surroundings, while the highest peak at 613 nm caused by $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition corresponds to the electric dipole transition susceptible to external electromagnetic fields^[38], its relevant CIE chromaticity coordinates (0.581, 0.311) are shown in Figure 7(c). As the Ir complex FIrPic emits bright green fluorescence under UV light excitation (see Figure 8, color online), the synthetic bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ exhibits excellent red emission under UV light of the same wavelength, which suggests that the trivalent Eu ion can be efficiently sensitized by the addition of Ir complex, without affecting the emission characteristics of Eu^{3+} ions.

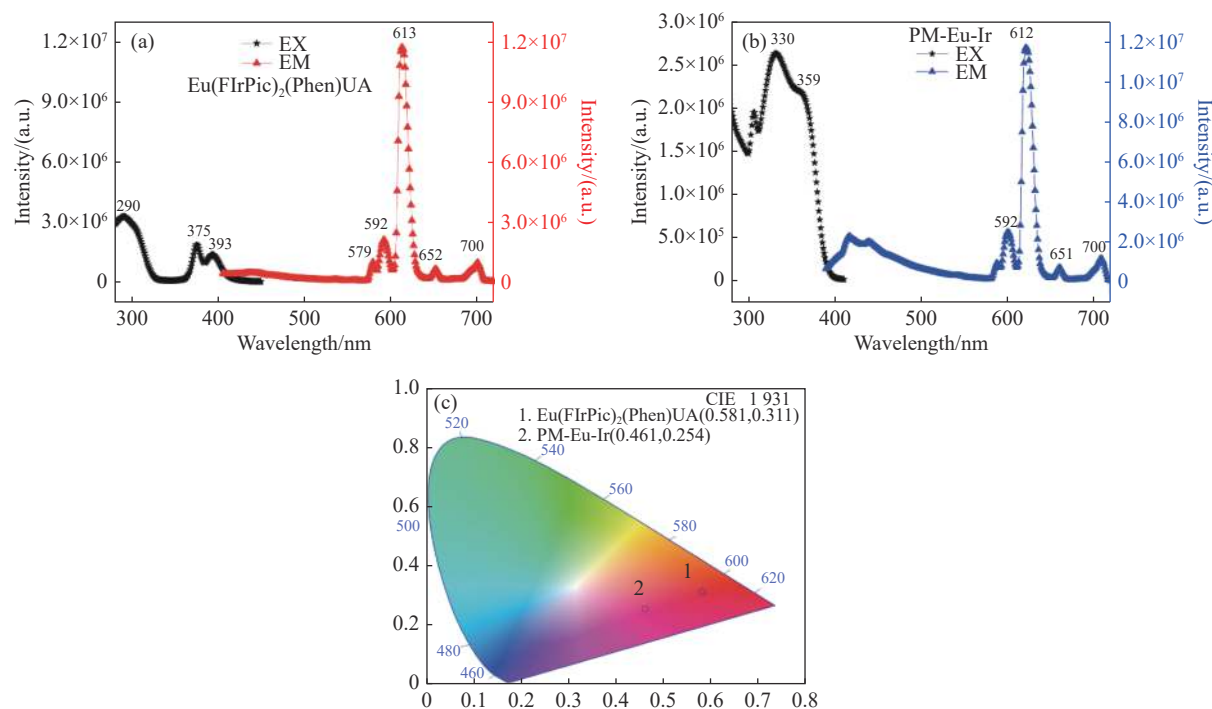


Fig. 7 Fluorescence spectra of (a) the bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$, (b) phosphorescent copolymer PM-Eu-Ir and (c) the CIE chromaticity coordinates

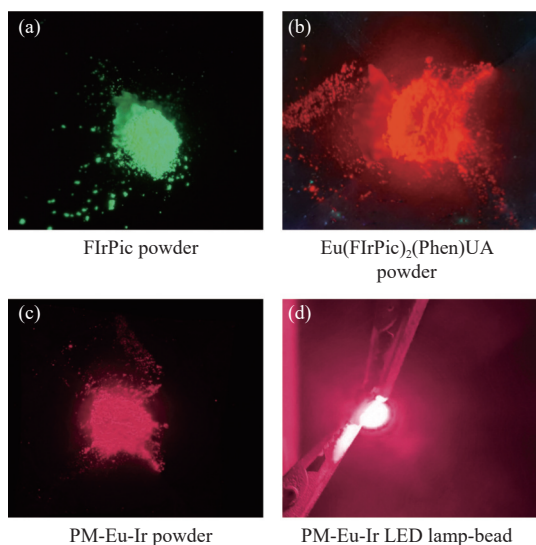


Fig. 8 Emission images of (a) Ir complex, (b) Eu-Ir bimetallic complex powder, (c) copolymer phosphors, and (d) the red LED lamp-bead under 365 nm UV irradiation

The excitation spectrum of the copolymer PM-Eu-Ir presented in Figure 7(b) displays an excitation band between 350 nm and 420 nm and a peak wavelength of 359 nm, indicating that PM-Eu-Ir can match well with 365 nm N-UV LED chips. Compared with bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$, the excitation peak of co-

polymer PM-Eu-Ir shows a blue-shift from 393 to 359 nm. This may be because the nonluminescent ground-state complex formed in copolymerization of $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ complex with MMA leads to static quenching, which typically changes the excitation wavelength for fluorescent molecules. Moreover, the PM-Eu-Ir exhibits a sharp and strong emission peak at 612 nm when excited at 365 nm, and its corresponding CIE coordinates (0.461, 0.254) are closer to the reddish-violet light region, as marked in Figure 7(c). Furthermore, five characteristic emission peaks at 583, 592, 612, 651, and 700 nm are also attributed to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, $^5\text{D}_0 \rightarrow ^7\text{F}_3$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions of Eu^{3+} ions, respectively.

3.7 Fluorescence lifetime and quantum efficiency of the copolymer PM-Eu-Ir

The fluorescence-decay curve of Eu^{3+} ions in the copolymer PM-Eu-Ir and bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ recorded at the excitation wavelength of 365 nm is displayed in Figure 9 (color online). $\text{Eu}(\text{III})$ ions show a reddish-violet emission at 612 nm due to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition,

and no emission is observed from Ir(III) ions in the copolymer after being excited.

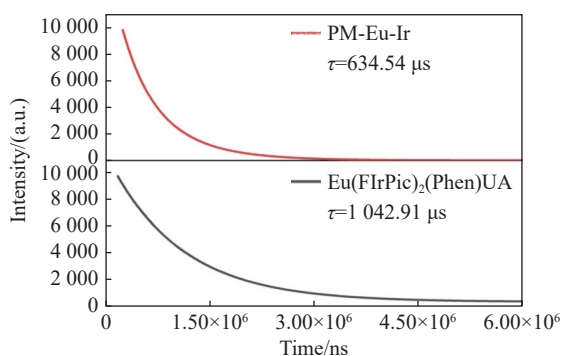


Fig. 9 Fluorescence decay curve of the copolymer PM-Eu-Ir and $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$.

The decay curve for sample PM-Eu-Ir is fitted to the exponential equation (1) as follows:

$$I(t) = A + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) \quad (1)$$

where τ_1 and τ_2 are the shorter and longer lifetime parameters, respectively. B_1 and B_2 are fitting constants. The average fluorescence lifetime of PM-Eu-Ir is calculated by displayed equation (2).

$$\langle \tau \rangle = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2} \quad (2)$$

The lifetime of the copolymer phosphor PM-Eu-Ir is 634.54 μs with a fitting coefficient χ^2 of 1.383. The lifetime of bimetallic complex $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ is 1042.91 μs with the fitting coefficient χ^2 of 1.120. PM-Eu-Ir has a shorter fluorescent lifetime than $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$, resulting

in a shorter copolymer response time.

In addition, the quantum efficiency (QE) of the phosphors was tested under 365 nm excitation, showing that the QE of $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$ is 22.63%, which is slightly higher than that of other reported Eu^{3+} -complex red phosphors^[39-40]. Moreover, the QE of PM-Eu-Ir is 30.68%, higher than that of $\text{Eu}(\text{FIrPic})_2(\text{Phen})\text{UA}$.

3.8 Fabricated LEDs with the copolymer PM-Eu-Ir

The electroluminescence (EL) spectra of the fabricated red LED lamp beads with PM-Eu-Ir at 3.5 V are presented in Figure 10(a) (color online). Apart from the main peak at 612 nm, we can see other characteristic peaks of Eu(III) ion emission. The EL spectral curve of the red LEDs is consistent with that of the copolymers. Besides, as shown in the subgraph of Figure 10(a), the CIE chromaticity coordinates of the tested red LEDs (0.480, 0.323) accord with that of the copolymer PM-Eu-Ir (0.461, 0.254). Figure 10(b) (color online) displays the luminance–voltage characteristics of the original LEDs (365 nm UV chip) without PM-Eu-Ir and red LEDs fabricated with PM-Eu-Ir, which shows the maximum luminance (149 800 cd/m^2) of the red LEDs increases by 2.3 times compared to that (45 920 cd/m^2) of the original LEDs. These results indicate that PM-Eu-Ir has strong application potential in red LEDs.

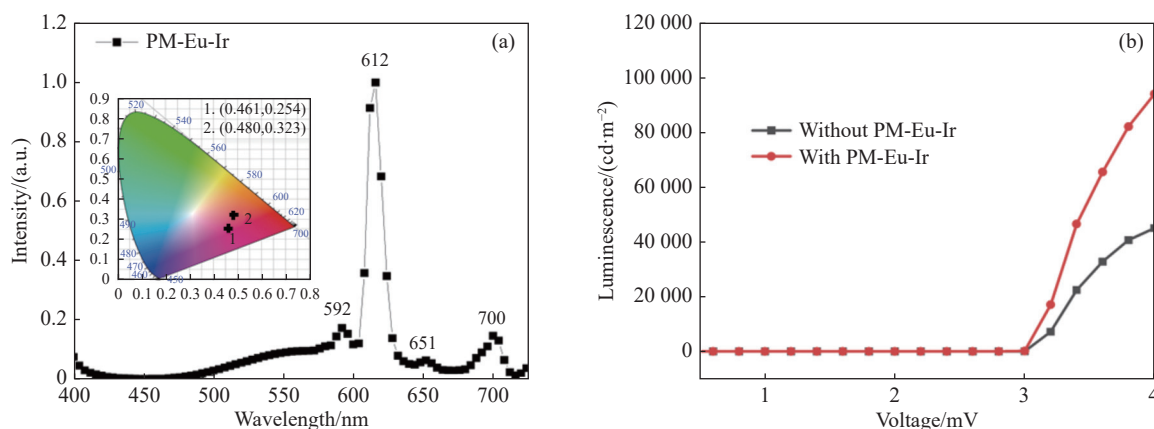


Fig. 10 (a) Electroluminescence (EL) spectra and (b) the luminance–voltage curves of the original 365 nm UV-LED chip with and without PM-Eu-Ir. The inserted photograph is the CIE chromaticity coordinates of photoluminescence

4 Conclusions

In this paper, we propose a red-emitting copolymeric phosphor PM-Eu-Ir synthesized through radical polymerization using the complex $\text{Eu}(\text{FIRPic})_2(\text{Phen})\text{UA}$ as the precursor and PMMA as the macromolecular ligand. The bimetallic Eu-Ir complex containing central Eu^{3+} ions and Ir complex FIRPic (the first ligand), Phen (the second ligand), and UA (the active ligand) were synthesized by a simple and effective method. The prepared copolymeric phosphor PM-Eu-Ir was shown to be soluble in common organic solvents at room temperature, which significantly improves the film-forming perform-

ance of phosphors used in large-area displays and the packaging of remote phosphor-converted LEDs. The micro-morphology of PM-Eu-Ir is a typical multilayer spatial network structure, indicating a complete polymerization reaction between Eu-Ir complex monomers and linear polymer PMMA. As far as prepared phosphorescent copolymer PM-Eu-Ir is concerned, it shows good thermal stability in the temperature range of 25~250 °C, a strong red emission at 612 nm when excited at 365 nm, and an average fluorescence lifetime of 634.54 μs . The fabricated LEDs with the copolymer PM-Eu-Ir display red light exhibit emission with a luminance of 149 800 cd/m^2 , meeting the requirements of commercial near-UV LED applications.

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