

An efficient bonding-type Eu-containing copolymer as red phosphor applied in LED

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ABSTRACT

A luminescent europium-containing copolymer, poly(MMA- UA -co-Eu (DBM)₂ (TOPO)₂) was synthesized. The copolymer was characterized by FT-IR, UV-vis, gel permeation chromatograph (GPC), ICP, thermogravimetric analysis (TGA), derivative thermal gravimetric analysis (DTG) and differential scanning calorimetry (DSC). The Eu-copolymer phosphor exhibited high thermal stability, high glass transition, excellent photoluminescence properties (PL), appropriate CIE chromaticity coordinates for red and good quantum yield (18%) under near-UV light excitation. An intense red-emitting light-emitting diode (LED) was fabricated by combining poly[UA-MMA-co-Eu (DBM)₂(TOPO)₂] with a 395 nm-emitting InGaN chip. The results indicate that the Eu-copolymer phosphor may act as a red component for fabrication of white LEDs.

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LEDs offer benefits of high luminous efficiency, low energy consumption, long lifetime and friendship to environment, and are considered as a new generation solid-state lighting devices. With the development of LED chip technology, the emission bands of LED chips shifted from blue light (around 460 nm) to near-UV (NUV) range (350 to 400 nm), and the NUV light can offer higher energy to pump phosphors [1]. However, the commonly used red-emitting phosphor (Y₂O₂S:Eu³⁺) for NUV InGaN-based white LEDs exhibits a lower efficiency compared with that of the blue (e.g., BaMgAl₁₀O₁₇:Eu²⁺) and the green (e.g., ZnS:Cu⁺, Al³⁺) phosphors and a short working lifetime under UV irradiation. Therefore, it is urgent to develop a new kind of red phosphors that can be efficiently excited by NUV around 350–400 nm light (Fig. 1).

In recent years, europium (III) β-diketonate complexes as a red phosphor in the fabrication of white LEDs have been reported [2–5] because of their wide excitation band, high internal quantum yields, and good color purity [6,7]. However, a main drawback of this technique is the photodecomposition of the rare earth organic complexes under NUV irradiation from the chip.

In comparison to rare earth organic complexes with small molecular weight, besides the advantage of the desired mechanical flexibility, rare earth luminescent polymers show excellent electroluminescence capability and can be processable in solution or fused state, which is more attractive for optical and electronic applications. Okamoto and his coworkers synthesized a series of rare earth metal-containing polymers, studied their luminescence properties, and indicated the potential for laser application [8–10].

In this paper, using dibenzoyl methane (DBM) as the principal ligand and trioctylphosphine oxide (TOPO) as the secondary ligand, undecylenic acid (UA) as the linking ligand, and methyl methacrylate (MMA) for building the copolymer backbone, we report synthesis of a new luminescent bonding-type europium-containing copolymer, poly[MMA-UA-co-Eu(DBM)₂(TOPO)₂] and its photoluminescent properties. A red LED was fabricated with this copolymer and an NUV chip.

Poly(UA-MMA) was prepared by reversed emulsion polymerization. 42 mL of cyclohexane, 8 mL of H₂O, 1 mL of Span 80 and 1 mL of Tween 80 as emulsifier were added in a 250 mL four neck bottle. The mixture was stirred and heated at 80 °C. Undecylenic acid (UA) (20 mmol) solution and methyl methacrylate (MMA) (80 mmol) was added into a dropping funnel, 0.48 g of K₂S₂O₈ as initiator was mixed with 20 mL H₂O and added into another dropping funnel. At the same time, comonomer UA, MMA and initiator K₂S₂O₈ were slowly added dropwise into the four neck bottle under constant stirring in an hour. The polymerization was carried out by heating and stirred at 82 °C for 6 h. Azeotrope of cyclohexane and H₂O was evaporated and retrieved into a reagent bottle at 85 °C. The viscous homogeneous solution in the four neck bottle was then dissolved in 60 mL of acetone and poured into 200 mL of H₂O with stirring. The resulting precipitate was washed with ethanol and H₂O for three times, respectively, finally dried under vacuum at 40 °C for 48 h to give a polymer powder.

FT-IR (cm⁻¹): 3444, 2957, 1733, 1453, 1246, 1153, 986, 750, 563 and 483.

Poly(MMA-UA-co-Eu(DBM)₂(TOPO)₂) Poly (UA-MMA) (2.0 g) sample was dissolved in 50 mL of acetone by heating in a 150 mL three neck bottle and stirred at 40 °C. Europium chloride (0.263 g, 1.0 mmol), which was prepared from Eu₂O₃ and hydrochloric acid, was dissolved in 20 mL of ethanol and acetone (1:1). Then, the EuCl₃

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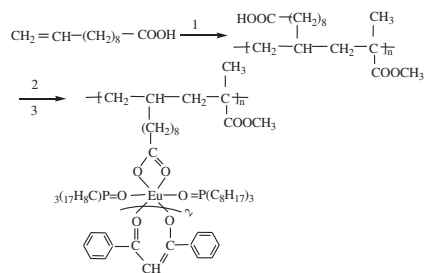


Fig. 1. Synthetic route for the Eu-containing copolymer. Reagents and conditions: 1. MMA/K₂S₂O₈/cyclohexane; 2. EuCl₃/KOH/ethanol/acetone; 3. DBM/TOPO/acetone.

mixture solution was slowly added dropwise into the three neck bottle and the mixture solution was adjusted to pH 6.5 using ethanol solution of KOH (2 mol/L) under constant stirring at 45 °C for 10 h. At last, 20 mL of DBM (0.45 g, 2 mmol) and TOPO (0.77 g, 2 mmol) acetone solution (pH 6.5) was slowly added. The reactive mixture was refluxed for another 12 h and cooled after evaporating a most part of acetone. Much deposition was obtained from the filtrate after 60 mL H₂O was added. The deposition was washed with anhydrous ethanol and distilled water three times, respectively, and dried under vacuum at 50 °C for 48 h to give 2.74 g of a flavous product with a yield of 85%.

FT-IR (cm⁻¹) (KBr): 3437, 2919, 1733, 1604, 1555, 1518, 1462, 1411, 1246, 1144, 995, 837, 750, 606, 563 and 483.

In comparison with synthetic method, in which polymers are synthesized by copolymerization of rare earth metal-containing monomers and organic monomers, our synthesis routine is more simple, and gives a higher yield.

The number-average molecular weights (*M_n*), the polydispersity indexes (PDI) of the obtained polymers, as shown in Table 1, were measured by gel permeation chromatography (GPC) using polystyrene as standard and THF as the eluent.

FT-IR analysis confirmed the coordination of Eu(III) with the groups DBM, TOPO and UA in the copolymer. The FT-IR spectrum of poly(UA-MMA) shows that the C=O and C-O stretching vibrations of COOH in UA appear at 1733 cm⁻¹ and 1144 cm⁻¹. The FT-IR spectrum of poly[MMA-UA-co-Eu(DBM)₂(TOPO)₂] shows that the bands at 1604 cm⁻¹ and 1462 cm⁻¹ correspond to the typical antisymmetric and symmetric stretching vibrations of carboxylate, which confirms that the carboxyl of UA has coordinated with the Eu(III) ion. The C=O and C=C stretching vibrations of DBM in the copolymer shifted to lower frequencies, from 1540 cm⁻¹ and 1460 cm⁻¹ of the free DBM to 1518 cm⁻¹ and 1411 cm⁻¹ of the coordinated DBM, respectively. The P=O stretching vibrations of the free TOPO at 1149 cm⁻¹ were shifted to lower frequencies at 995 cm⁻¹ in polymer. These results suggest that the coordination bonds formed between the Eu(III) ion and the ligands DBM and TOPO in the copolymer.

Fig. 2 displays the UV-vis absorption spectra of EuCl₃, DBM, TOPO, poly(UA-MMA) and poly[MMA-UA-co-(DBM)₂(TOPO)₂] in THF solution (1.0 × 10⁻⁵ mol·dm⁻³). The maximum absorption in the absorption spectrum of free DBM appears at 344 nm, which is assigned to the π → π* transitions of ketonic form and enol form of DBM in THF. In comparison with DBM, EuCl₃, TOPO and poly(UA-MMA) almost shows no absorption in near UV-visible region, so the main absorption band at 344 nm of poly[MMA-UA-co-(DBM)₂(TOPO)₂] is attributed to the enol form of the coordinated DBM, indicating the

Table 1
Properties of poly[MMA-UA-co-(DBM)₂(TOPO)₂] and poly(UA-MMA).

Polymer	Eu (%)	<i>M_n</i>	PDI	<i>T_d</i> (°C)	<i>T_g</i> (°C)
Poly(UA-MMA)	0	23355	3.45	344	106
Poly[MMA-UA-co-Eu(DBM) ₂ (TOPO) ₂]	4.05	38559	1.70	342	92

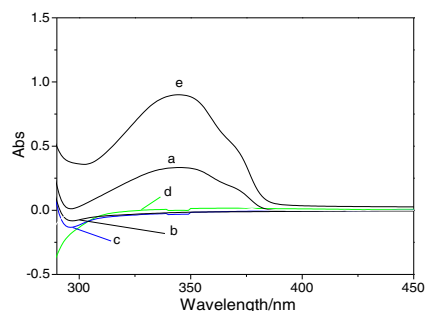


Fig. 2. UV-visible absorption spectra of the ligands, EuCl₃ and the Eu-containing copolymer in THF solution (1.0 × 10⁻⁵ mol·dm⁻³): a. DBM; b. TOPO; c. EuCl₃; d. poly(UA-MMA); e. poly[UA-MMA-Eu-(DBM)₂(TOPO)₂].

formation of a Eu(III)-DBM coordination structure though the dehydrogenation of DBM. The wide and strong absorption band of the Eu-complex and the Eu-containing copolymer in 300–400 nm range mainly originates from the absorption of the first ligand DBM, and this absorption range is fit for being excited by the NUV light emitted from an InGaN chip. TOPO, as the secondary ligand, plays a role that satisfies the high coordination number of 8 for the central Eu³⁺ ion and is involved in the absorption and transfer of intramolecular energy [11], therefore improves the fluorescence efficiency, the coordination stability and the thermal stability [12–14] of the polymer, though it does not have obvious absorption in above 300 nm region.

Eu content of the copolymer was measured by ICP. The thermal stability of the Eu-copolymers was evaluated by means of thermogravimetric analysis (TGA) and derivative thermal gravimetric analysis (DTG) under nitrogen atmosphere, and the data are presented in Table 1. poly[MMA-UA-co-(DBM)₂(TOPO)₂] keeps high thermal stability compared as that of poly(UA-MMA).

The glass transition temperatures (*T_g*) and the starting temperatures of decomposition (*T_d*) of the Eu-copolymer with Eu content of 4.05% are lower only by 14 °C and 3 °C than that of poly(UA-MMA). This result indicates that the thermal stability and the *T_g* of the Eu-copolymer can be weakened a little because of introducing TOPO group into the polymer chains. Since TOPO has a long chain and is a flexible group, this leads to the freedom of chain mobility of the polymers, and reduces the *T_g* value. TGA and DTG measurements illustrate that the Eu-containing copolymer is stable up to 340 °C, which meets the requirement in thermal stability for fabrication of LEDs.

The photoluminescence excitation (PLE) and emission (PL) spectra of the Eu-copolymer sample were measured at room temperature and are shown in Fig. 3. Emission of the Eu(III) ions was monitored at 617 nm, the Eu-copolymer shows wide and strong excitation bands in

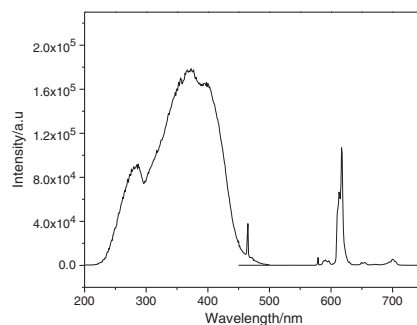


Fig. 3. PLE (λ_{em} = 617 nm) and PL (λ_{ex} = 395 nm) spectra of poly[MMA-UA-co-Eu(DBM)₂(TOPO)₂].

a range of 230–495 nm. The strongest excitation peak is located at 373 nm, and the excitation intensity at 395 nm keeps on being high, so it matches to the emission wavelength of a 395 nm-emitting InGaN chip, indicating that the Eu-copolymer is suitable to fabrication of the NUV-emitting InGaN-based LED. Excited by 395 nm-light, the Eu-copolymer exhibits five narrow emission peaks centered at 579, 592, 617, 652, and 700 nm, assigned ${}^5D_0 \rightarrow {}^7F_J$ ($J=0-4$) transition of Eu^{3+} ion, respectively. The most strong fluorescence emission peak is located at 617 nm, which is attributed to the ${}^5D_0 \rightarrow {}^7F_2$ electro-dipole transition of the central Eu^{3+} ion, revealing that Eu^{3+} ions in the copolymer occupied sites without inversion parity. Because the forbidden ${}^5D_0 \rightarrow {}^7F_2$ electro-dipole transition is sensitive to the coordinative environment of Eu^{3+} ion [15,16], the asymmetric microenvironment leads to the polarization of the Eu^{3+} ion under the influence of the electric field of the surrounding ligands, which increases the probability for the electro-dipole transition. The luminescence quantum yield of poly[MMA-UA-co-Eu(DBM) $_2$ (TOPO) $_2$] was measured to be 0.18 according to the reported method by Lin [17] using an integrate sphere at room temperature. The 5D_0 lifetime of Eu^{3+} ion for poly[MMA-UA-co-Eu(DBM) $_2$ (TOPO) $_2$] was 373 μs by measuring the decay curve of ${}^5D_0 \rightarrow {}^7F_2$ (617 nm) of the Eu^{3+} , and the curves were fitted with a single-exponential function, confirming that the Eu^{3+} ions in the Eu-copolymer molecule occupied the same parity sites.

Poly[MMA-UA-co-Eu(DBM) $_2$ (TOPO) $_2$] was used as a phosphor in a mass ratio of 1:10 of phosphor to silica gel to fabricate an LED with a ~ 395 nm-emitting InGaN chip. As a comparison, most inorganic phosphors are applied in a 1:1 or 1:2 mass ratio for the fabrication of LEDs. The emission spectra of the original chip (dash line) and the LED with the Eu-copolymer (solid line) under 20 mA forward bias are shown in Fig. 4. The most emission from the chip was absorbed by the Eu-copolymer, confirming that the copolymer was efficiently excited by the NUV light emitted from the chip. The emission peaks at 580, 592, 617, 654, and 702 nm for the Eu-copolymer-LED were due to the $\text{Eu}^{3+} {}^5D_0 \rightarrow {}^7F_J$ ($J=0-4$) transitions. The CIE chromaticity coordinates of the fabricated LEDs with an ~ 395 nm-emitting InGaN chip in a mass ratio of copolymer to the silicone of 1:2 and 1:10, were ($x=0.4271$, $y=0.1936$) and ($x=0.5870$, $y=0.2848$), respectively. The remained NUV emission peak of the copolymer-LED depends on the mass ratio of the copolymer to the silicone. The fabricated LED with a 395 nm-emitting InGaN chip in a mass ratio of 1:10 of the copolymer to silica gel exhibited the strongest red emission and the lowest remained NUV emission and the efficiency of the LED achieved 1.17 lm/W while as a comparison, the efficiency of the original LED

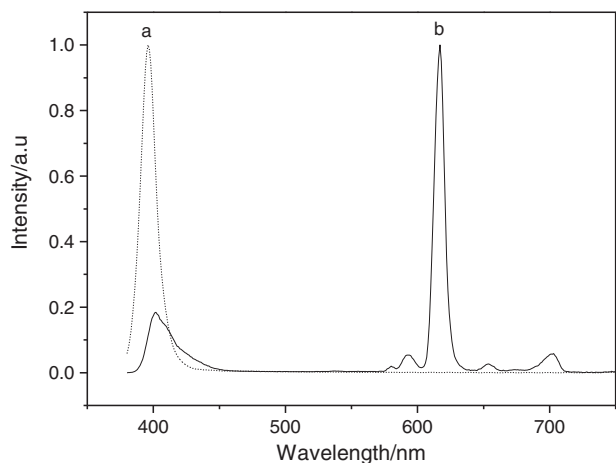


Fig. 4. Emission spectra of the original InGaN LED without phosphor (a, dash line) and the LED with the Eu-copolymer (b, solid line) under 20 mA forward bias.

without phosphor was only 0.77 lm/W. The CIE chromaticity ordinates of poly[MMA-UA-co-Eu(DBM) $_2$ (TOPO) $_2$]-LED ($x=0.59$, $y=0.28$) were close to National Television Standard Committee standard CIE values for red ($x=0.67$, $y=0.33$) [18]. The remained ~ 395 nm emission from the InGaN chip in the copolymer-LED can be used to excite a blue and a green phosphor to generate white light. This result indicates that poly[MMA-UA-co-Eu(DBM) $_2$ (TOPO) $_2$] is a good candidate as a red component in the fabrication of white LED with a high color-rendering index.

In summary, a bonding-type europium-containing copolymer, poly[MMA-UA-co-Eu(DBM) $_2$ (TOPO) $_2$], was synthesized. The copolymer exhibits high thermal stability, good PL properties, and excellent CIE chromaticity coordinates. A bright red LED was fabricated by coating the copolymer phosphor onto a 395 nm-emitting InGaN chip. All the results indicate that the Eu-copolymer is a good candidate as a red component in fabrication of white LEDs with high color-rendering index, and may provide a new application field for europium-containing copolymers.

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Hai gang Yan got Master's degree at Guangxi Normal University in 2002. Research area is in bioinorganic chemistry. Since 2002, I have worked in Chemistry and environmental sciences at the Department of Zhangzhou Normal University, water treatment and chemicals were my main research contents. I went into the School of Chemistry and Chemical Engineering, Sun Yat-sen University to study for a doctorate in 2008. Professor Menglian Gong is my tutor, research areas are material physics and chemistry. I mainly researched Bonding-type europium-containing copolymer and applied it in LED.