

# Synthesis and investigation of a photosensitive, europium-containing polymer



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## ABSTRACT

A series of europium complexes containing polymeric reactivity groups have been successfully synthesized using a simple method. Among them,  $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$ , which has the best fluorescence properties and solubility, was polymerized with glycidyl methacrylate (GMA) for use as a novel UV-written polymer material. The Poly (GMA-co- $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$ ) containing different proportions of europium were prepared, and their spectroscopic properties were investigated in detail. Polymer films with optimum proportions (a molar ratio between GMA and  $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$  of 15) exhibited good UV light lithograph sensitivities, strong visible fluorescence intensities, high glass transition temperatures ( $T_g$ :  $>170^\circ\text{C}$ ), good thermal stabilities ( $T_d$ : up to  $295^\circ\text{C}$ ) and solvent resistances after crosslinking. Micro patterns with smooth top surfaces were fabricated from the resulting polymer by using direct UV exposure and chemical development.

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## 1. Introduction

Rare earth Europium ions ( $\text{Eu}^{3+}$ ) have been extensively studied with regards to their superior photophysical and coordination properties in a variety of photoluminescent materials. Europium complexes are unique and attractive because among other benefits, they possess the advantages of a large Stokes shift, narrow red light emissions and long fluorescence lifetimes. They have previously been applied to red organic light-emitting diodes [1–9], lasers [10], biosensors and optoelectronics [11–19].

The various europium complexes were synthesized by combining  $\text{Eu}^{3+}$  with selected organic ligands, such as  $\beta$ -diketones [20] and synergistic ligands (1,10-phenanthroline [21], dipyrindine [22]). These ligands all have low molecular weights and can form a high degree of  $\pi$ -electron delocalization to improve energy transfer effectiveness from the ligands to the central  $\text{Eu}^{3+}$ , thereby increasing luminescence efficiency [23–25].

One of the most promising and effective applications of europium complexes is that of Eu-doped polymers [26–32], which possess the advantages of europium complexes and of polymer matrixes. Despite the obvious advantages in such physical

blending-type polymers, europium complexes are difficult to disperse in polymers, which usually leads to phase separation [33]. This problem could greatly influence the resulting fluorescence properties of Eu-doped polymers. To solve the problem, we attempt to introduce an organic ligand with excellent polymerization activity, namely methacrylic acid, which can provide carboxyl groups as the coordinating groups for  $\text{Eu}^{3+}$ . In general, methacrylic acid plays a dual role as an organic ligand and compatibilizer so that the europium chelates can utilize the olefinic double bonds to copolymerize with other monomers. At the same time, epoxy resins possess high versatility because of their low shrinkage by UV curing with cationic initiators, good adhesion and excellent mechanical properties [34]. Direct-write UV lithography in cationically polymerized epoxy resins is one of the most promising technologies for fabricating patterns [35].

In this paper,  $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$ ,  $\text{Eu}(\text{DBM})_3(\text{MA})$ ,  $\text{Eu}(\text{TTA})_2(\text{Phen})(\text{MA})$ , and  $\text{Eu}(\text{TTA})_3(\text{MA})$  were synthesized and the photoluminescence properties were investigated. The complex  $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$  was polymerized with glycidyl methacrylate (GMA). The transparent polymer films were then formed by coating the cross-linkable copolymers (Poly (GMA-co- $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$ ) with diphenyliodonium hexafluorophosphate (PI) as a photo initiator onto a substrate. After being exposed to UV light (365 nm), the polymer formed a highly cross-linked matrix structure. It exhibited good chemical resistance and excellent processability.

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## 2. Experimental

### 2.1. Materials

Dibenzoylmethane (DBM), europium oxide ( $\text{Eu}_2\text{O}_3$ , 99.999%), 2-Thenyltrifluoroacetone (TTA), 1,10-phenanthroline monohydrate (Phen), and diphenyliodonium hexafluorophosphate (PI) were purchased from Aldrich (USA), Energy Chemical (Shanghai, China) and TCI (Tokyo, Japan). Methacrylic acid (HMA), glycidyl methacrylate (GMA) and other reagents were purchased from Aladdin. They were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN), freshly recrystallized, was used as free-radical initiator. Conventional methods were used to purify other reagents before use.

### 2.2. Measurements

The  $^1\text{H}$  NMR (400 MHz) spectra were measured on a Bruker ADVANCE NMR spectrometer (Swiss). The chemical shifts relative to TMS for  $^1\text{H}$  NMR as an internal reference are reported on the ppm scale. The Fourier transformed infrared (FTIR) patterns of the samples, as thin KBr pellets and KBr coating, were measured on a Perkin-Elmer Spectrum One-B FTIR infrared spectrophotometer (USA). Average molar masses and molar mass distributions were determined by gel permeation chromatography (GPC) on a Waters 410 GPC (USA) with polystyrene as the standard and THF as the solvent. Differential scanning calorimetry (DSC) was performed with a NETZSCH DSC 204 analyzer (Germany) at a scan rate of  $10^\circ\text{C}/\text{min}$  under nitrogen. Thermal stability, measured by a 5% weight loss of the polymer samples, was analyzed using a Perkin-Elmer TGA 7 analyzer (USA) at a heating rate of  $10^\circ\text{C}/\text{min}$  in air. Atomic force microscopy (AFM) observations of the film surfaces were carried out using a commercial instrument (Digital Instrument, Nanoscope IIIA, USA) under ambient conditions at room temperature. All tapping mode images were measured with microfabricated rectangular crystal silicon cantilevers (Nanosensor). Photoluminescence (PL) spectra were conducted on a Perkin-Elmer LS55 luminescent spectrometer (USA) with a xenon lamp as a light source, an ex-slit width of 7.0 nm and em-slit widths for the complexes and polymer as 5.0 nm and 4.0 nm, respectively. The UV-Vis absorption spectra were recorded on a Perkin-Elmer LAMBDA35 (USA). Scanning electron microscopy (SEM) was performed on a JEOL JSM 6700F electron microscope (Japan) with a primary electron energy of 3 kV. UV irradiation experiments for thin polymer films were carried out using a 400 W and 365 nm wavelength UV lamp. Fluorescence microscopic image was performed on an Olympus BX51 fluorescence microscopy (Japan). Luminescent lifetimes were recorded by a FL 920 fluorescence decay spectrometer (Edinburgh Instrument, UK), using a hydrogen lamp as the excitation source (with a pulse width of 1.2–1.8 ns).

### 2.3. Synthesis of europium chloride hexahydrate ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ )

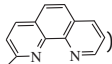
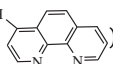
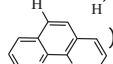
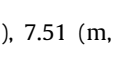
A total of 2 mmol of  $\text{Eu}_2\text{O}_3$  were dissolved in 15 mL of hydrochloric acid (HCl, 35 wt%) under stirring at  $100^\circ\text{C}$ . The product ( $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ ) was obtained after evaporating excess HCl, washing with deionized water, and drying under vacuum. Finally, the product was obtained as a solid white powder.

### 2.4. Synthesis of europium-containing organic complexes ( $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$ (EDPM))

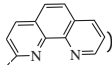
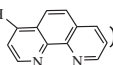
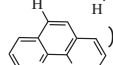
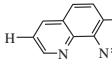



As shown in Scheme 1, DBM (0.896 g, 4 mmol) and Phen (0.396 g, 2 mmol) were dissolved in ethanol (30 mL, 95%) and then mixed with HMA liquid (0.181 g, 2.1 mmol). The pH value was

carefully controlled in the range of 7.0–8.0 by using a 1 M NaOH solution. The obtained solution was stirred and purged under  $\text{N}_2$  for 10 h at  $25^\circ\text{C}$ . Then, 30 mL of 66.67 mM  $\text{EuCl}_3$ /ethanol solution was added slowly. After the addition of the  $\text{EuCl}_3$ , the precipitate appeared. The precipitate was separated using centrifugation, washed with ethanol several times and then dried under vacuum at  $60^\circ\text{C}$ . Finally, the as-synthesized product was recrystallized using chloroform ( $\text{CHCl}_3$ ). The other three complexes  $\text{Eu}(\text{TTA})_2(\text{Phen})(\text{MA})$  (ETPM),  $\text{Eu}(\text{DBM})_3(\text{MA})$  (EDM) and  $\text{Eu}(\text{TTA})_3(\text{MA})$  (ETM) were synthesized by using a method similar to the one described above and are shown in Scheme 1.

#### 2.4.1. EDPM

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 10.83 (m, 2H, , 10.43 (m, 2H, , 9.97 (m, 2H, , 8.86 (m, 2H, , 7.99 (m, 1H,  $=\text{CH}_a(\text{H}_b)$ ), 7.51 (m, 1H,  $=\text{CH}_b(\text{H}_a)$ ), 6.90 (s, 2H,  $=\text{CH}-$ ), 6.79 (m, 12H,  $-\text{Ph}$ ), 6.01 (m, 8H,  $-\text{Ph}$ ), 3.05 (s, 3H,  $\text{CH}_3$ ); IR (KBr,  $\text{cm}^{-1}$ ): 1620 (w,  $\text{C}=\text{C}$ ), 1595 (vs,  $\text{C}=\text{O}$ ).




#### 2.4.2. ETPM

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 10.23 (m, 2H, , 10.13 (m, 2H, , 9.48 (m, 2H, , 8.47 (m, 2H, , 7.85 (m, 1H,  $=\text{CH}_a(\text{H}_b)$ ), 7.58 (m, 1H,  $=\text{CH}_b(\text{H}_a)$ ), 6.98 (s, 2H,  $=\text{CH}-$ ), 6.95 (m, 2H, , 6.51 (m, 2H, , 6.21 (m, 2H, , 3.20 (s, 3H,  $\text{CH}_3$ ); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1628$  (w,  $\text{C}=\text{C}$ ), 1100–1300 (m, C–F), 1598 (vs,  $\text{C}=\text{O}$ ).

#### 2.4.3. EDM

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.99–7.97 (m, 12H,  $-\text{Ph}$ ), 7.69 (s, 3H,  $=\text{CH}-$ ), 7.68 (m, 6H,  $-\text{Ph}$ ), 7.50–7.48 (m, 12H,  $-\text{Ph}$ ), 6.46 (m, 1H,  $=\text{CH}_a(\text{H}_b)$ ), 5.56 (m, 1H,  $=\text{CH}_b(\text{H}_a)$ ), 1.89 (s, 3H,  $\text{CH}_3$ ); IR (KBr,  $\text{cm}^{-1}$ ): 1664 (w,  $\text{C}=\text{C}$ ), 1595 (vs,  $\text{C}=\text{O}$ ).

#### 2.4.4. ETM

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.69 (m, 3H, , 7.63 (m, 3H, , 7.12 (m, 3H, , 6.82 (s, 3H,  $=\text{CH}-$ ), 6.15 (m, 1H,  $=\text{CH}_a(\text{H}_b)$ ), 5.82 (m, 1H,  $=\text{CH}_b(\text{H}_a)$ ), 2.00 (s, 3H,  $\text{CH}_3$ ); IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1620$  (w,  $\text{C}=\text{C}$ ), 1100–1300 (m, C–F), 1598 (vs,  $\text{C}=\text{O}$ ).

### 2.5. Free radical copolymerization of Poly (GMA-co- $\text{Eu}(\text{DBM})_2(\text{Phen})(\text{MA})$ ) (PGE 5) with optimum proportions

As shown in Scheme 2, EDPM (1.0 g, 1.2 mmol), GMA (3.5 g, 25 mmol) and AIBN (0.025 g, 0.15 mmol) were dissolved in N,N-dimethylformamide (DMF, 20 mL) with stirring under a nitrogen atmosphere. The resulting solution was then heated at  $75^\circ\text{C}$  for 6 h. The above mixture was transferred to a 500 mL beaker containing 200 mL of methanol under stirring. The flocculent precipitate was separated using centrifugation and then dried in vacuum. Finally, the product was purified by precipitation in methanol three times. The supernatant methanol solution was separated and then determined by PL spectrometer to exhibit no fluorescence. The yield of PGE 5 was above 92%. The molecular

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