

FLUORESCENCE PROPERTIES OF MICROCOMPOSITES EUROPIUM TRIETHYLENE GLYCOL PICRATE COMPLEX DOPED IN POLYMER

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ABSTRACT

The aim of this study was to synthesize high luminescence materials containing the optimal combination of ternary europiumpicrate complex and matrices. The ternary europium-picrate-triethylene glycol (Eu-EO3-Pic) complex was doped in poly(methyl methacrylate), PMMA. The composites were impregnated in several matrices to form thin films via spin coating technique. The microparticles of Eu-EO3-Pic complex were prepared by reprecipitation-evaporation, then they were compared to analogous complex or microcomposite prepared by in-situ method. The Eu-EO3-Pic/PMMA microcomposites were characterized by fluorescence spectroscopy in acetone solution. The particle sizes distribution of microcomposites synthesized by reprecipitation-evaporation method (110.3 to 426.8 nm) were smaller compared to the microcomposites by in-situ method (641.7 nm). The PMMA was able to significantly enhance the fluorescence intensity of Eu-EO3-Pic microparticles. The fluorescence intensity of microcomposite by in situ-preparation was lower than that found in the microcomposites by reprecipitation-evaporation method. We also investigated the effect of different matrices on the photophysical properties. The effective intermolecular energy transfer from PMMA to the Eu-EO3-Pic complex would produce high sensitization efficiency. These microcomposites are very potential used as the emission material for organic light emitting devices.

Keywords: Europium; Fluorescence; Microcomposite; PMMA; Precipitation-evaporation

1. INTRODUCTION

The direct trivalent lanthanide ion photo excitation is unefficient due to the low absorption coefficient of the 4f-4f electronic transitions which are forbidden and the non-radiative deactivation of their excited states by O-H and C-H vibrations (Xu et al., 2012). To enhance the luminescence intensity of the lanthanide complexes and to reduce the lanthanide concentration, they could be incorporated into several matrices, such as mesoporous materials, silica gel, glass films, polymer, zeolite and titania (Jayakannan et al., 2012; Feng & Zhang, 2012; Tiseanu et al., 2007). These methods are also possible to prevent luminescent quenching and to enhance the thermal stability as well as to improve the processing ability (Liu et al., 2004). The polymer thin-film's technique/method in integrated optic technology provides an interesting incorporation of lanthanide complexes with polymer. Polymethyl methacrylate (PMMA) is an important non-toxic synthetic polymer that have been used in many applications such as in biomedical, medicinal dispenser, food handling equipment, aircraft glazing, lighting, and

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transportation (Chai et al., 2009). PMMA is able to be incorporated into organic and inorganic matrices in a film's productions, where it can increase the electrical conductivity, photoconductivity, photo-induced charge transfer, photo luminescent, mechanical and magnetic properties (Chai et al., 2009). Therefore, PMMA is an ideal matrix that will provide mechanical strength, flexibility, ease of processing and controllable cost (Feng & Zhang, 2013) of lanthanide complex.

In particular, these interesting properties have been attracted much attentions recently. The nanoparticle technologies are believed as a big jump in material technologies (Scholes & Rumbles, 2006). There are several reports on the fabrication methods of the organic and inorganic nanoparticles and microcrystals, including the reprecipitation based on high solubility and low-solubility of organic compounds in different solvents and a single reaction based on the pyrolysis of organometallic reagents by injection into a hot coordinating solvent (Oikawa et al., 2010; Murray et al., 1993). However, the fabrication methods of the heavy metal complexes micro-nanoparticles of are less studied, due to the extra efforts required in synthesizing the lanthanide complexes.

In this paper, the fabrication technique of the micro and nano-particles of ternary europium-picric acid-triethylene glycol (Eu-EO3-Pic) complex, namely the combination of reprecipitation and evaporation method were developed. In principal, the complex would be decomposed into the appropriate solvent and both solvents that do not dissolve to each other in solvent, followed by the evaporation of the dispersion onto substrates. On the other hand, the preparation of micro and nano-particles by single system (in-situ method) and the mixed system were also studied. The micro and nano-particles of Eu-EO3-Pic resulted were doped into PMMA. Three types of matrices/substrate such as scrapped aluminium (Al), unscrapped Al and glass were used as thin films matrices via spin coating method.

The aim of this study is to produce the thin films through in-situ and precipitate-evaporation methods that have high luminescence materials containing ternary europium picric acid complex. The fluorescent intensity between the complexes and their composites were compared in order to evaluate the effects of PMMA and different matrices on the fluorescent behaviour. The photophysical characteristics of microcomposites from different preparation methods and different matrices were investigated in detail.

2. METHODOLOGY

2.1. Materials

Triethylene glycol [$C_6H_{14}O_4$, 99%] and polymethylmethacrylate (PMMA) with MW = 120000 was purchased from Acros (New Jersey, USA). Picric acid (Pic) [$(NO_2)_3C_6H_2OH$], >98% was purchased from BDH (Poole, England). Europium nitrate hexahydrate, $Eu(NO_3)_3 \cdot 6H_2O$ (99.9% purity) was purchased from Johnson Matthey Electronics (New Jersey, USA). Other chemicals were of analar grade and were used without further purification. The substrates were glass substrate, scrapped Al substrate and unscrapped Al substrate.

2.2. Synthesis of Microparticle Complex by Precipitation-evaporation Method

The Eu-EO3-Pic complex has been synthesized previously (Saleh et al., 2011). The microparticles of Eu-EO3-Pic complex were prepared by mixing crystalline solids of Eu-EO3-Pic complex (0.02 g) in 1 mL aquabidest at 40°C in a reaction tube. A clear yellow solution was obtained and kept at a room temperature. The solution of EO3-Eu-Pic complex was dispersed on a glass slide with a ratio of Eu-EO3-Pic:chloroform of 1:2 (v/v), where chloroform was added on glass slide by drop-wise. After that, the glass slide was dried in a desiccator and microparticles were obtained after several hours.

2.3. Preparation of Microcomposite Ternary Europium Complex Doped in PMMA

Mixed system of the microparticle Eu-EO3-Pic complex with PMMA was synthesized by dissolving these components with certain molar ratio in acetone. The composite was prepared with mixing the microparticle Eu-EO3-Pic (0.0025 g) and PMMA (0.98g) in 10 mL acetone. After completely dissolved, the solution was coated into scrapped Al, unscrapped Al and glass substrates, respectively, by spin coating technique with a speed of 100 rpm.

2.4. Physical Measurements

Fluorescent properties of microparticles Eu-EO3-Pic and its composites were determined using a Hitachi Spectrophotometer Model F2000 at room temperature with a xenon light source, and the excitation and emission slits used were both 10 nm. The microparticles Eu-EO3-Pic and its composites (0.01 g) were dissolved in 5 mL acetonitrile. The emission spectrum of the solution was scanned from 220 to 800 nm at 240 nm/min. Particle size of microparticles Eu-EO3-Pic and its composites were measured by using Particle Size Analyzer Zetasizer Nano series, Malvern ZEN 1600. Spin coating was achieved by pouring the solution on a clean substrate to fully cover it. The solution was spin-coated onto $100 \times 50 \times 2$ mm³ substrate with a rotation range from 100 to 150 rpm for 1 min.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Fluorescence Studies

The combination of reprecipitation and evaporation method is a promising technique to obtain the micro-nanoparticles of Eu-EO3-Pic by simple method. In principal, the complex would be decomposed into the appropriate solvent and both solvents that do not dissolve to each other in solvent (immiscible). In this study, aquabidest serves to dissociate the EO3 and Pic ligands and the Eu metal ions in complex, while chloroform acts to disperse the complex onto aquabidest that produced the micro- and nano-particles. The smaller particle size of Eu-EO3-Pic compound produced physical and chemical properties that are more attractive for sensor, display, and optical fibers. The ternary Eu-EO3-Pic complex has been successfully prepared into the hybrid materials in situ. Some great advantages such as good thermal stability, good mechanical resistance and excellent fluorescence color purity could be obtained (Feng & Zhang, 2013).

The emission spectra of bulk Eu-EO3-Pic complex, microparticles of Eu-EO3-Pic and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salt is shown in Figure 1. The hypersensitive peak of microparticles of Eu-EO3-Pic at 616 nm that is assigned to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition was observed. The broad peak at 490 and 495 nm exhibited the energy transfer from the ligand to the europium central metal ion is ineffective and not complete. In the Eu-EO3-Pic complex, the hypersensitive peak at 614 nm is very low. This can be explained by participation of nitro groups from the picrate anions in the quenching process and formed a channel of degradation of the excitation energy through $\pi^* \rightarrow n$ transition of nitro group (Saleh et al., 2011). The hypersensitive peak of the bulk crystal Eu-EO3-Pic complex and its solution in the emission spectra was significantly different. This may be due to the coordinating effects of the solvent in the formation of complex, i.e. solvent effect where vibrational quenching of the complex excited state may occur through a high energy oscillator on the solvent molecule (Kusrini & Saleh, 2009).

The excitation and fluorescence spectra of PMMA in acetone solution exhibited broad band at 375 and 450 nm, respectively. The fluorescence intensity of the Eu^{3+} ion in microcomposite Eu-EO3-Pic /PMMA is higher than those found in the only Eu-EO3-Pic complex in aquabidest solution. It can be seen that the Eu-EO3-Pic complex in aquabidest solution with fluorescence intensity of 0.031 a.u., while microparticles of EO3-Eu-Pic had fluorescence intensity of 0.5 a.u. The Eu-EO3-Pic/PMMA microcomposite showed the fluorescence intensity is much higher at 125.4 a.u. (Figure 2). From these studies, incorporation of ternary Eu-EO3-

Pic complex into polymer has improved the fluorescence property of complex and also avoids self-quenching due to the concentration effect. We noted the polymer (PMMA) is significantly enhancing the fluorescence intensity of microcomposites. One of the advantages of lanthanide complexes doped polymers is that they possess the complexes properties, so they can be processed from solution and are mechanically flexible. In addition, incorporation with polymer could prevent luminescent quenching from picrate anion, thus improving and increasing the fluorescence intensity (Liu et al., 2004; Xu et al., 2012). When microparticles Eu-EO3-Pic is incorporated into polymer, the quenching effect can be effectively reduced. This data was similar to the results that have been reported by Yan (2003). He reported the synthesis of terbium complex incorporated into microporous silica gel and the polymerization with methyl methacrylate and ethyl methacrylate. In this study, PMMA is ideal matrix for the Eu-EO3-Pic complex because it has a high molecular weight that wraps the Eu^{3+} ion and keeps the donor and acceptor close. This produced the effective intermolecular energy transfer and increases the high sensitization efficiency.

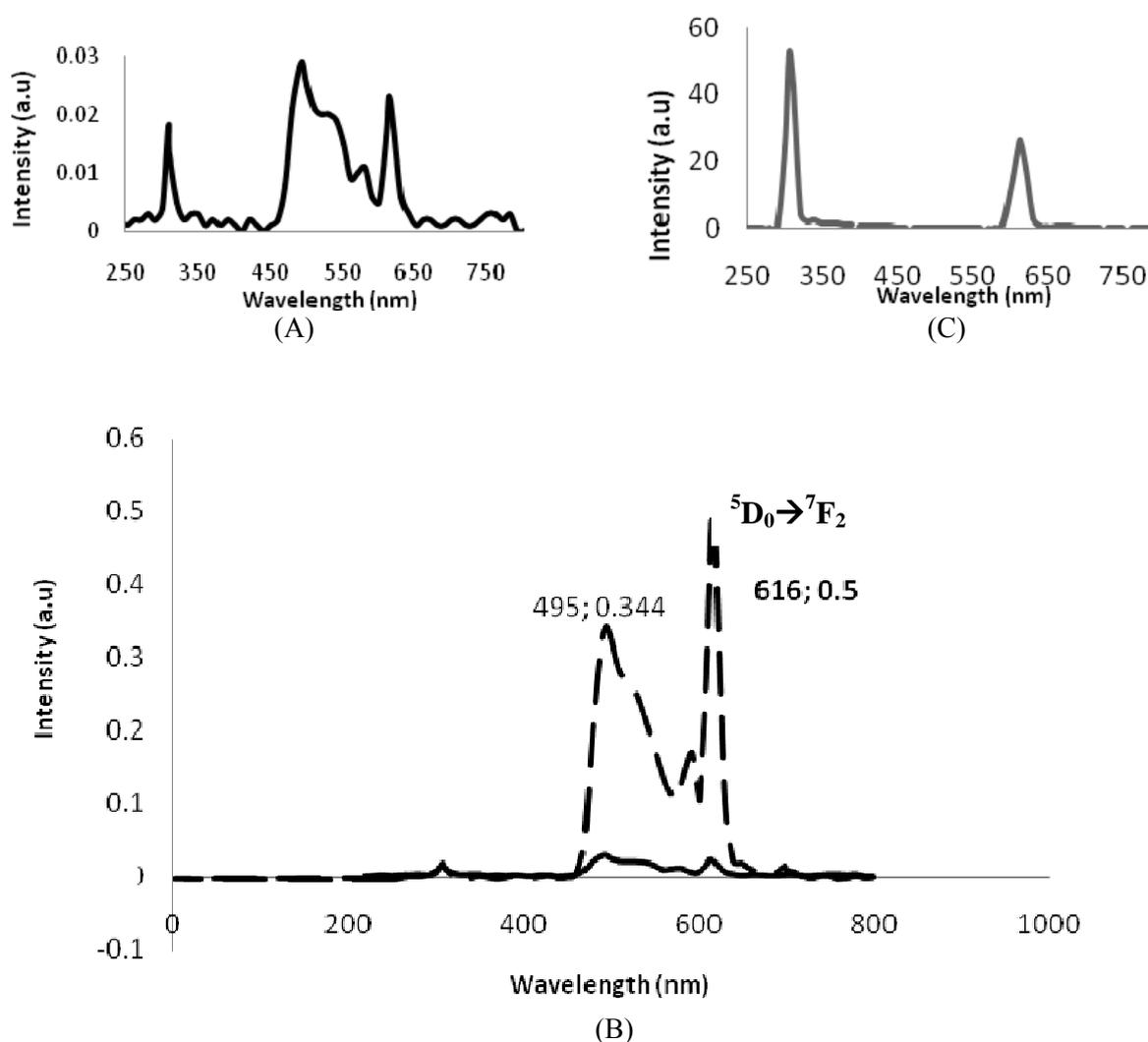


Figure 1 The emission spectra of bulk Eu-EO3-Pic complex in aquabidest solution (A), microparticles of Eu-EO3-Pic (B) and $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ salt (C)

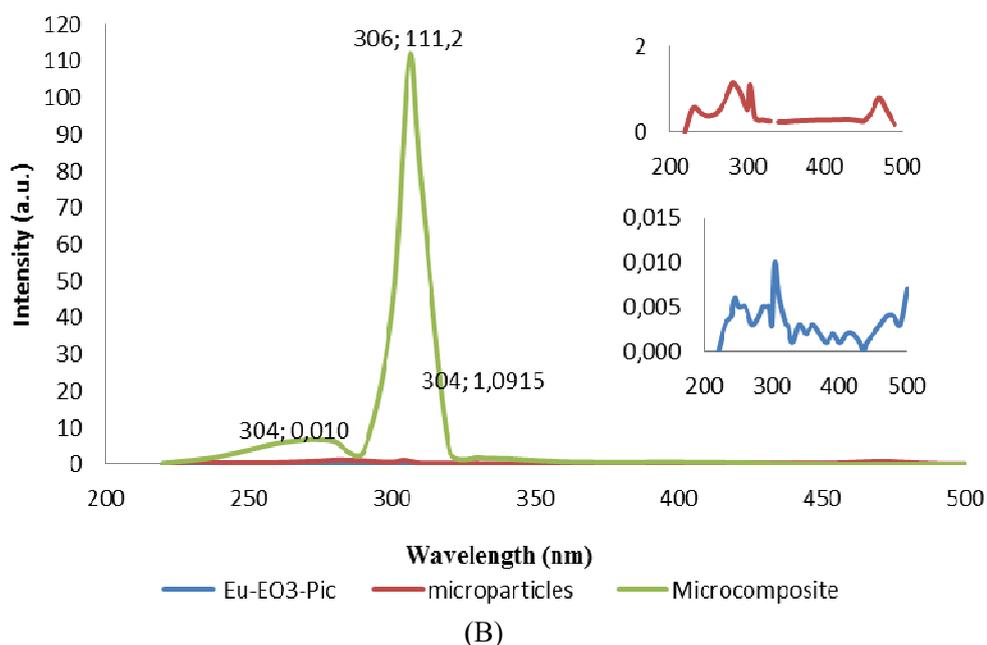
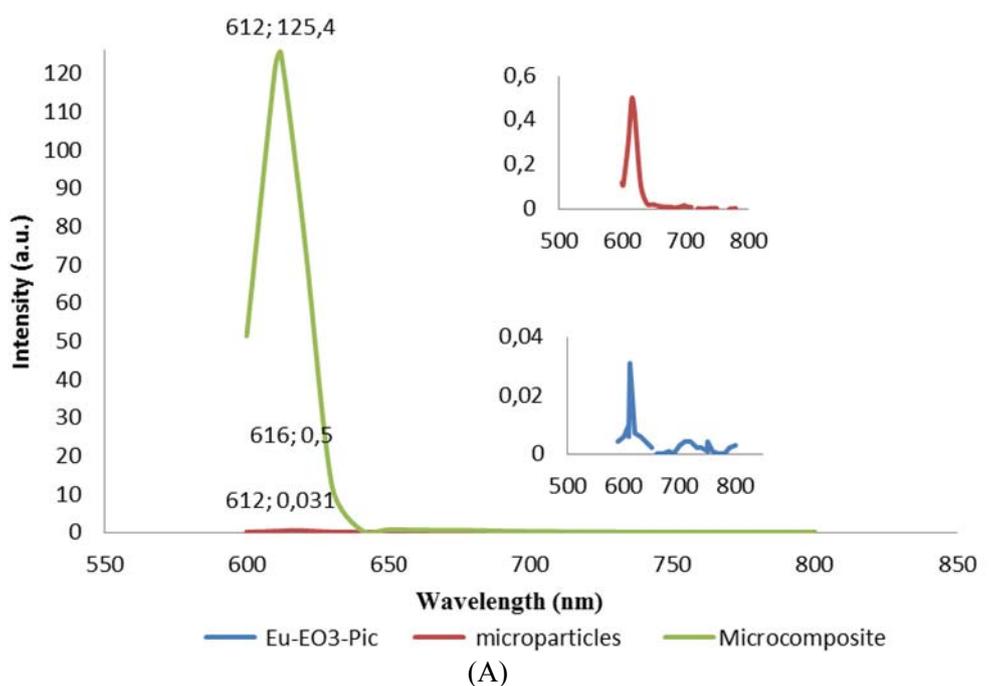


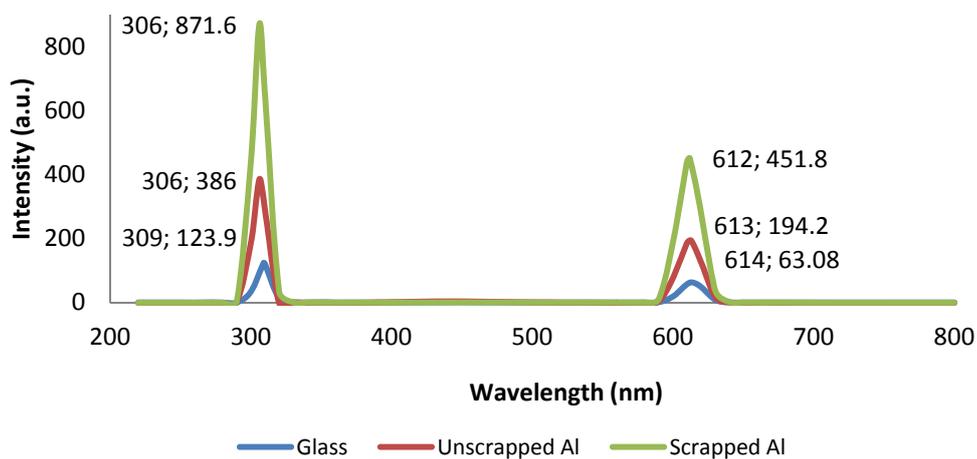
Figure 2 Comparison of excitation (A) and emission spectra (B) of pure Eu-EO3-Pic complex, microparticles Eu-EO3-Pic and microcomposite Eu-EO3-Pic/PMMA in glass substrate

3.2. Matrices Effect on the Fluorescence Intensities of Eu-EO3-Pic Complex

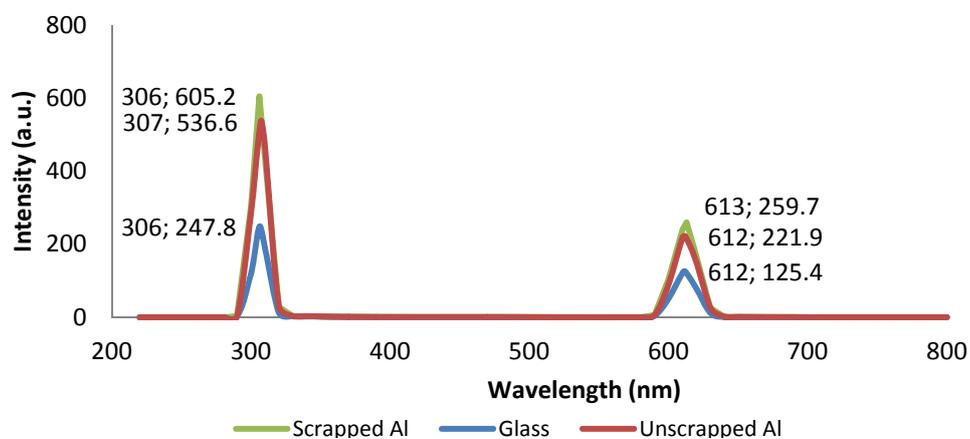
In order to observe the effect of matrices doped of the Eu-EO3-Pic complex on the fluorescence intensity, several different matrices are introduced into the microcomposites Eu-EO3-Pic/PMMA, result showed in Figures 3A and B. Comparison of the excitation and emission spectra of Eu-EO3-Pic/PMMA microcomposites onto different matrices (glass, unscrapped Al, scrapped Al) are shown in Figures 3A and B. Spin coating process of the three substrates onto

the microcomposites Eu-EO₃-Pic/PMMA were examined by one phase (in-situ) and three steps (reprecipitation and evaporation) method.

Comparing the emission intensity of the microcomposites Eu-EO₃-Pic/PMMA with that of the pure micro- and nanoparticles, there exist different phenomena. By in-situ method, the fluorescence hypersensitive peak intensities onto the glass substrate (614 nm; 63.08 a.u.), unscrapped Al (613 nm; 194.2 a.u.), scrapped Al (612 nm; 451.8 a.u.) (see Figure 3A). By three steps method, we obtained the fluorescence hypersensitive peak intensities onto the glass substrate (612 nm; 125.4 a.u.), unscrapped Al (612 nm; 221.9 a.u.), scrapped Al (613 nm; 259.7 a.u.) (see Figure 3B). The different matrices of microcomposite Eu-EO₃-Pic/PMMA influence the structure of host matrices and then affect the emission intensity of hybrid. The microcomposites coated with scrapped Al had the highest emission intensity compared to the unscrapped Al and glass, because the surface roughness could be able to give a pathway for coupling of incident light to surface plasmons and creation of far-field radiation from plasmons (Ray et al., 2007). Due to the electromagnetic properties of these interactions, it leads to increase the emission intensity of Al substrate. The thickness of the Al substrates affected the fluorescent intensity because of the micro- and nano-structures of the Eu-EO₃-Pic compound which were formed in the substrate surface.



(A)



(B)

Figure 3 Comparison excitation and emission spectra of microcomposites Eu-EO₃-Pic/PMMA onto difference matrices through in-situ (A) and three step (B)

3.3. Particle Size Distribution Studies

The particle size for microparticles of Eu-EO3-Pic prepared by reprecipitation-evaporation method was 439.3 nm (Figure 4). After it coated onto scrapped Al substrate, the particle size distribution of composite Eu-EO3-Pic/PMMA has changed to 110.3 nm (40.3%) and 426.8 nm (59.7%) (see Figure 5). We found the microcomposite of Eu-EO3-Pic/PMMA coated onto scrapped Al substrate that prepared by in-situ method had the particle size distribution of 641.7 nm (100%) (see Figure 6). The particle size distribution of composite Eu-EO3-Pic/PMMA synthesized by reprecipitation-evaporation method were smaller than those found in the composite Eu-EO3-Pic/PMMA by in-situ method. This may be due to the incorporation and interaction of PMMA with the Eu^{3+} ion, thus it takes place to some extent during the microparticles preparation.

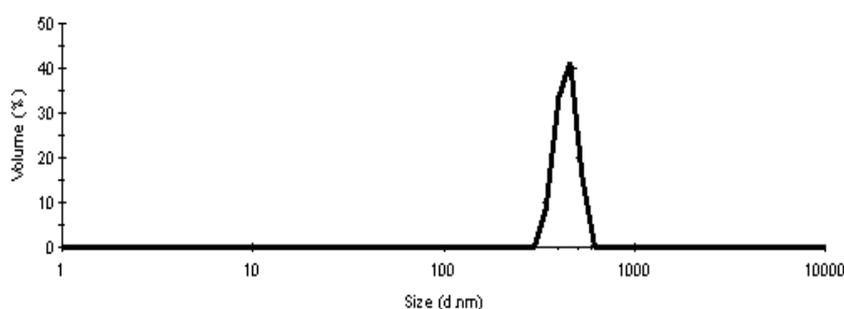


Figure 4 The particle size distribution of microparticle Eu-EO3-Pic by precipitation-evaporation method

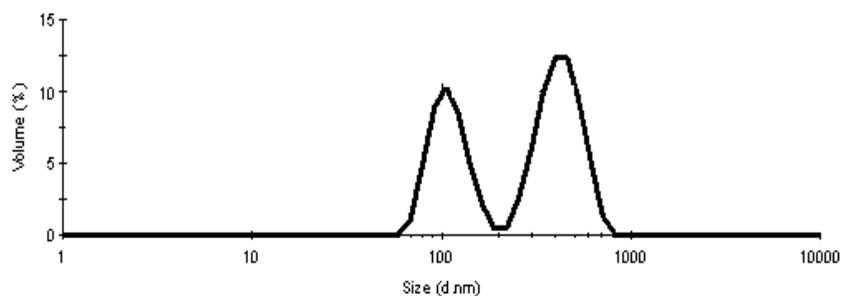


Figure 5 The particle size distribution of microcomposite Eu-EO3-Pic/PMMA by precipitation-evaporation method

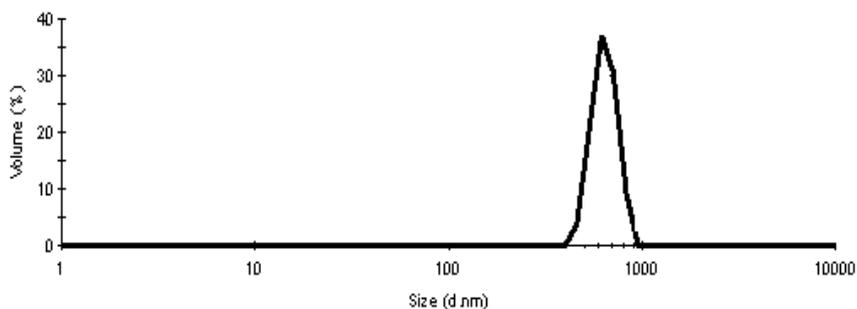


Figure 6 The particle size distribution of microcomposite Eu-EO3-Pic/PMMA coated by in-situ method

4. CONCLUSION

In this work, we reported the synthesis and characterization of the microparticles of ternary europium-picric-triethylene glycol complex by reprecipitation-evaporation and compared them to analogous complex or microcomposites that are prepared by in-situ methods. The fluorescence intensity of Eu-EO3-Pic/PMMA microcomposite by in situ-method was lower compared to the Eu-EO3-Pic/PMMA microcomposites by reprecipitation-evaporation method. We found the microcomposites of Eu-EO3-Pic/PMMA coated with scrapped Al substrate had the highest fluorescence intensity relative to the microcomposites Eu-EO3-Pic/PMMA coated onto unscrapped Al and glass substrates. The surface roughness of matrices could enhance the fluorescent intensity due to the electromagnetic interactions. The thickness of the Al substrates has influenced the fluorescent intensity because the micro- and nano-structures of the Eu-EO3-Pic complex that formed in the substrate surface. In further studies, the microcomposites Eu-EO3-Pic/PMMA were potential for fluorescence applications as polymer light-emitting diodes or as active polymer optical fibers in photosensor.

5. ACKNOWLEDGEMENT

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