

P-57 : Synthesis, Characterization and Luminescent Properties of Eu-Containing Polyoxometalate

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Abstract

Sodium salt of photoluminescent Eu-containing polyoxometalate (Eu-POM) was newly synthesized and its chemical structure and physical properties characterized. The Eu-POM was unstable outside the pH range 5.5-8.5, and a pH just over 7 gave the best yield. We have investigated the photoluminescent properties of Eu-POM with changing the reactants ratio of heteropolytungstate and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. The Eu-POM was characterized by UV/Vis, FT-IR, $^1\text{H-NMR}$, PL and XPS. Eu-POM emits orange light of 590nm when excited with the light of 280nm. Furthermore, we made dodecyltrimethylammonium (DDTA) salt of Eu-POM (Eu-POM/DDTA) by exchange of the counter cation. The Eu-POM/DDTA is soluble in common organic solvents, while Eu-POM is only soluble in water. And it emits reddish orange light of 625nm when excited with light of 250nm.

1. Introduction

Luminescent rare earth complexes have been of great interest due to their characteristic high fluorescence efficiencies, good fluorescence monochromatocity, and very narrow line fluorescence bands [1,2]. They have many practical applications, such as fluorescent probes in biochemistry, laser, and electroluminescent optical devices [3,4]. Light-emitting devices activated by lanthanide ions such as Eu^{3+} , Tb^{3+} and Dy^{3+} provide emissions with good efficiency by intramolecular 4f electron transitions. Academic interest and potential practical applications have prompted further investigations of lanthanide complexes in nonlinear optics, light-emitting devices [5,6]. Recently, polyoxometalates have attracted much attention because of their characteristic catalytic, electronic, magnetic and optical properties [7,8].

Polyoxometalates constitute a distinctive class of inorganic compounds, which have been received increasing interest in recent years. The structures of polyoxometalates can be described as molecular fragments of close-packed metal oxides with the general formula $\text{X}_a\text{M}_b\text{O}_c^{n-}$ (M=Mo, W, V... and X=P, Si, B...) [9]. The best-known type of polyoxometalates is the Keggin structure, composed of a central heteroatom surrounded by four M_3O_{13} groups (M=Mo, W). The polyoxometalates have potential applications in various fields such as bifunctional catalysis, magnetic nanoparticles, energy transfer, luminescence, and antiviral chemotherapy [10,11]. Recently, Mingotaud *et al.* have demonstrated that organic-inorganic ultrathin films containing organized layers of such Keggin polyanions can be readily built by using the Langmuir-Blodgett (LB) technique [12]. We also have reported that a polyoxometalate with carboxyl groups can be fabricated into organic-inorganic hybrid LB films through the electrostatic interaction between oppositely-charged carboxylate-ammonium salt [13]. When the central heteroatom of the Keggin ion has unpaired electronic

spins, the built-up films present some magnetic properties [14]. Meanwhile, T. Yamase has prepared EL device by using the polyoxometaloeuropate [15] and Zhang *et al.* have shown effective energy transfer and luminescence of LB films based on europium-substituted heteropolytungstate [16]. Therefore, the polyoxometalates are supposed to be functional nanoparticles by substituting various atoms as component elements. Accommodating functional rare earth ions in organic-modified metal oxide cages, they can be used in the construction of hybrid organic-inorganic functional materials.

In this study, we report on photoluminescent properties of novel Eu-POMs, which were prepared by changing the reactants ratio of heteropolytungstate and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$. We have also synthesized an organic-inorganic hybrid Eu-POM (Eu-POM/DDTA) by exchange of the counter cation from sodium to dodecyltrimethylammonium (DDTA). The Eu-POM/DDTA is soluble in common organic solvents, while Eu-POM is only soluble in water. The photoluminescent property of Eu-POM/DDTA was also investigated.

2. Experimental

2.1 Materials

Sodium tungstate dihydrate, europium chloride hexahydrate, acetic acid glacial, and dodecyltrimethylammonium bromide were purchased from Aldrich Chemicals and used without further purification.

2.2 Synthesis of Eu-POM and Eu-POM/DDTA

The preparative procedure of Eu-containing polyoxometalate (Eu-POM) was referred to previously described literature [17,18]. The molecular formula of Eu-POM was determined to $\text{EuW}_{10}\text{O}_{36}^{9-}$ (Figure 1). We made dodecyltrimethylammonium (DDTA) salt of Eu-POM (Eu-POM/DDTA) by exchange of the counter cation. Eu-POM/DDTA was prepared as follows: Dodecyltrimethylammonium bromide (0.2824g , $8.05 \times 10^{-4}\text{mol}$) was poured in Eu-POM aq. solution (50ml , $3.22 \times 10^{-3}\text{M}$) and the reaction mixture was refluxed under a nitrogen atmosphere at 80°C for 24 hours. After reaction the product was filtrated and dried for 5days in vacuum. After washing with ethanol, the product was filtrated once more. The filtrate was dried for 5 days in vacuum (yield: 10%). The Eu-POM/DDTA is soluble in common organic solvents such as ethanol and chloroform, while Eu-POM is only soluble in water. After consideration of XPS data, we calculated the binding ratio of Eu-POM and DDTA as 1:4. The $^1\text{H-NMR}$ spectrum of Eu-POM/DDTA showed the protons of dodecyltrimethylammonium ion at 3.3 (9H, s), 2.7 (2H, t), 1.2 (25H, s), and 0.9 (3H, t) ppm.

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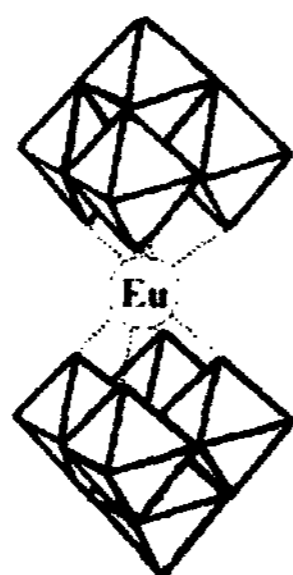


Figure 1. Schematic representation of Eu-POM

2.3 Instruments and measurement

UV-Vis absorption spectra were measured by a UV-VIS Spectrometer (Shimadzu UV-3100S). Fluorescence Spectrometer (HITACHI F-4500) was used for photoluminescence spectroscopy. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min with a DuPont 951 thermogravimetric analyzer. Differential scanning calorimetry (DSC) thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a scanning rate of 10 °C/min. FT-IR spectra were obtained with a Shimadzu 8201PC FT-IR Spectrometer using a KBr pellet. ¹H-NMR spectra were recorded on a Varian 300 MHz FT-NMR Spectrometer in methanol-d₄. X-Ray photoelectron spectroscopy (XPS) spectra were obtained on ESCALAB 250 XPS spectrometer (V.G Scientific).

3. Result and discussion

3.1 Structure characterization of Eu-POM and Eu-POM/DDTA

For the synthesis of polyoxometalates pH control is crucial during the reaction. In the case of Eu-POM, the product was stable within the pH range 5.5-8.5 and a pH just over 7 gave the best yield. The Eu-POM structure was characterized by FT-IR, UV/Vis, and XPS.

Figure 2 shows the FT-IR spectra of Eu-POM and Eu-POM/DDTA. The C-H stretching peaks of 2800-3000cm⁻¹ represent the introduction of alkyl amines into Eu-POM/DDTA. Except the peaks originated from organic part, the peak pattern of infrared spectra of both compounds is very similar. The low-wavenumber part of FT-IR spectra shows the characteristic peak pattern of polyoxometalate framework, therefore, we could confirm the general polyoxometalates' functional groups.

In Figure 3, the absorption spectrum of a diluted solution of Eu-POM shows the tail of an absorption band in the UV region with a shoulder at 250 nm. The absorption spectrum of Eu-POM is similar to the literature [18]. The peak at around 250nm may be assigned to O→W charge transition, which are the characteristic bands for some heteropolytungstate complexes [19].

After the exchange of counter ion with alkyl amine, the shoulder peak of 250nm was overlapped with the intensive absorption peak of Eu-POM/DDTA about 210nm, which was originated from ethanol. Any absorption was not detected in visible region. XPS spectrum of Eu-POM/DDTA shows in Figure 4. After the counter ion exchange, the intensive carbon peak emerged. From the quantitative analysis of the component elements we could estimate 4 counter cations were exchanged from sodium to DDTA.

3.2 Thermal stability of Eu-POM/DDTA

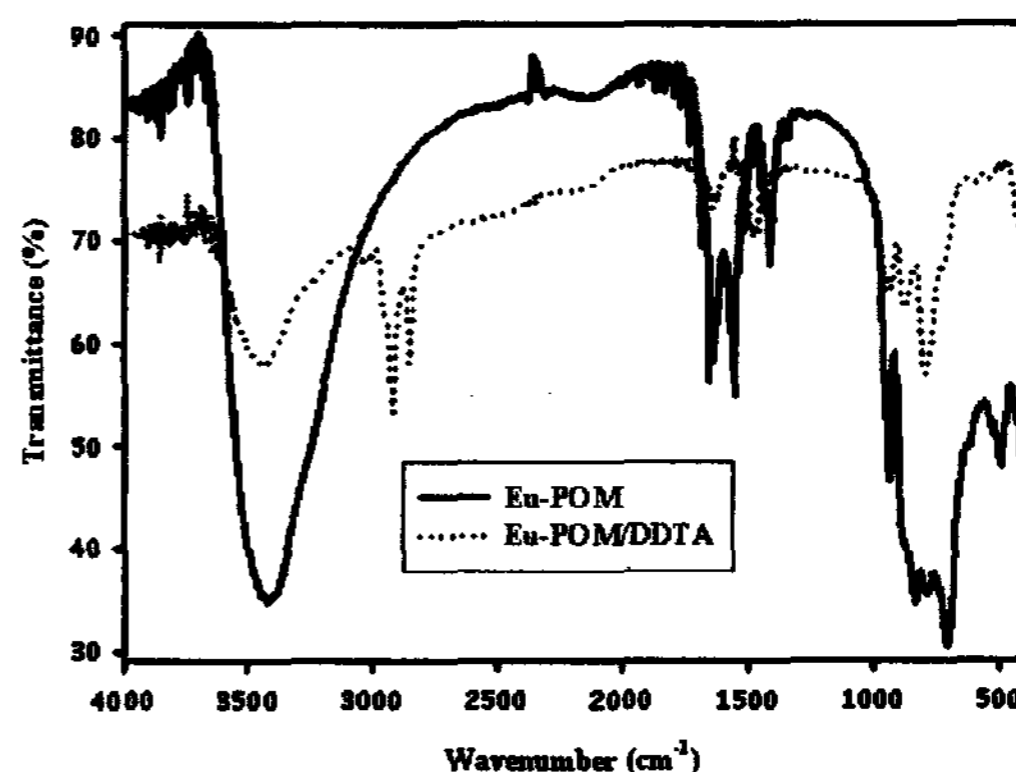


Figure 2. IR Spectra of Eu-POM and Eu-POM/DDTA

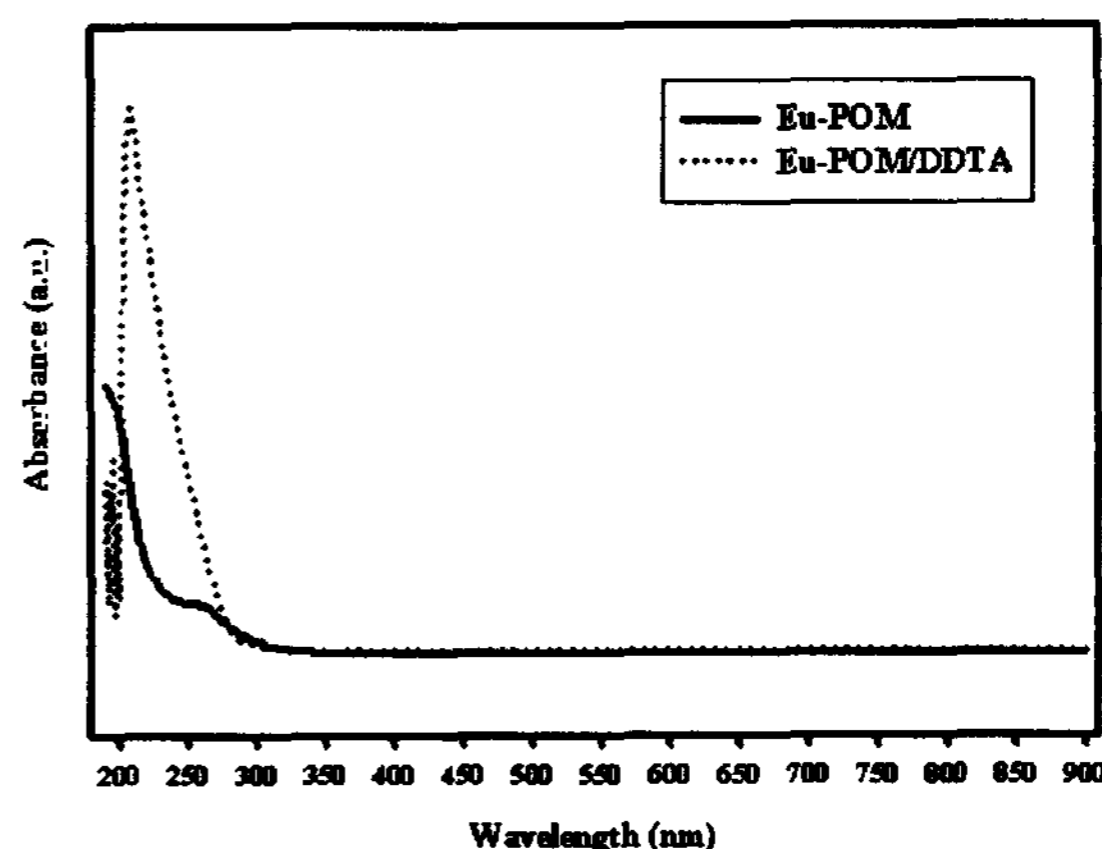


Figure 3. Absorption spectra of Eu-POM and Eu-POM/DDTA

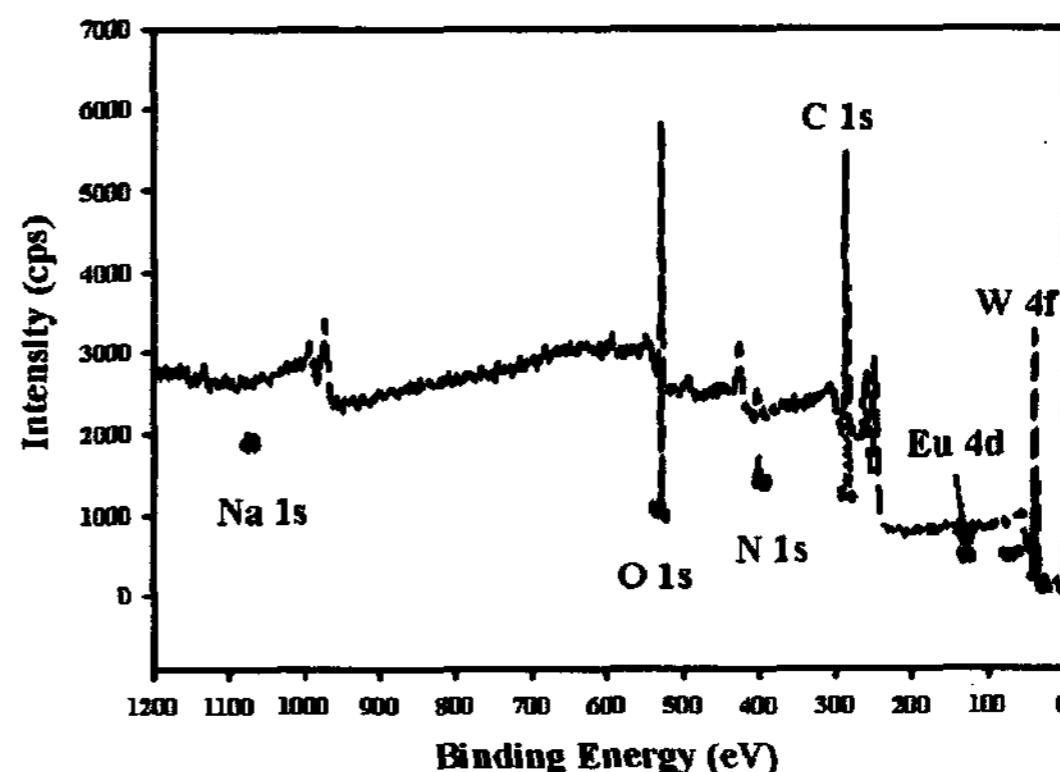


Figure 4. XPS Spectrum of Eu-POM/DDTA

Thermal stability of emitting materials is important for ELdevice application. The thermal properties of Eu-POM/DDTA were studied by DSC and TGA. Figure 5 shows a characteristic TGA profile of the Eu-POM/DDTA. Eu-POM/DDTA was stable up to 200 °C and became degradable. DSC measurement showed two exothermic peaks at 250 and 350 °C. TGA curve indicates the corresponding temperatures as inflection. After decomposition of organic moieties, weight percentage was sustained 60%.

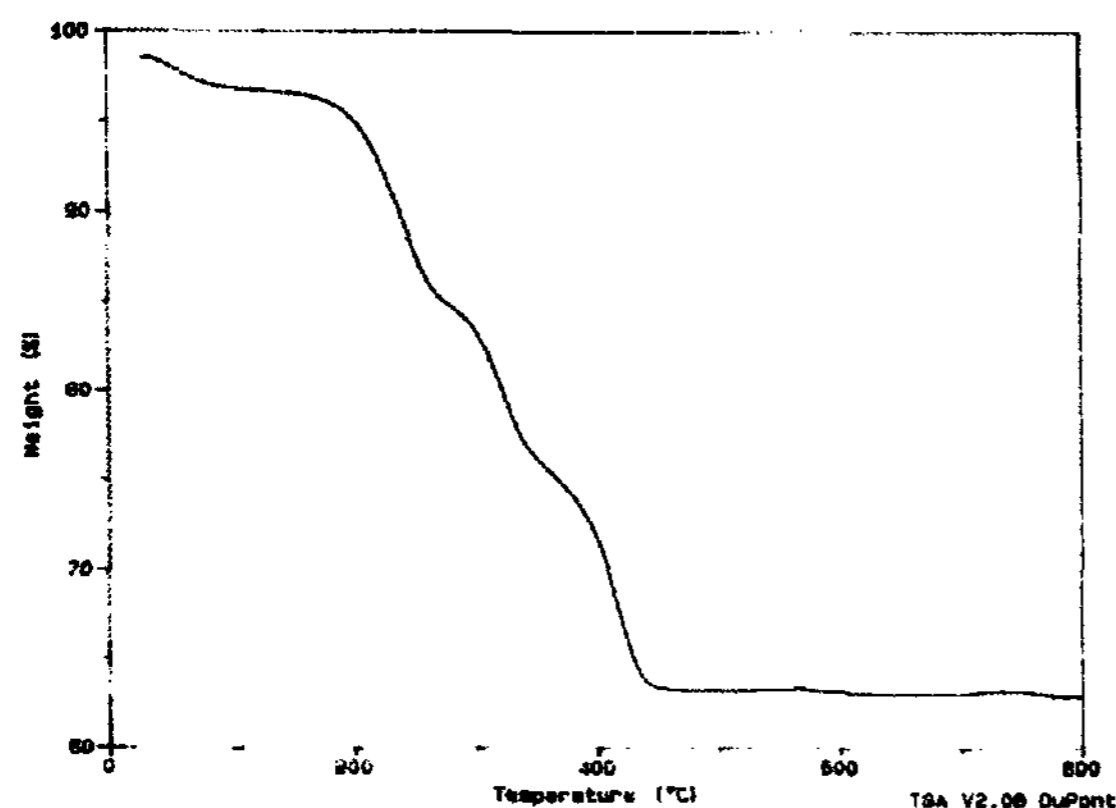


Figure 5. TGA thermogram of Eu-POM/DDTA

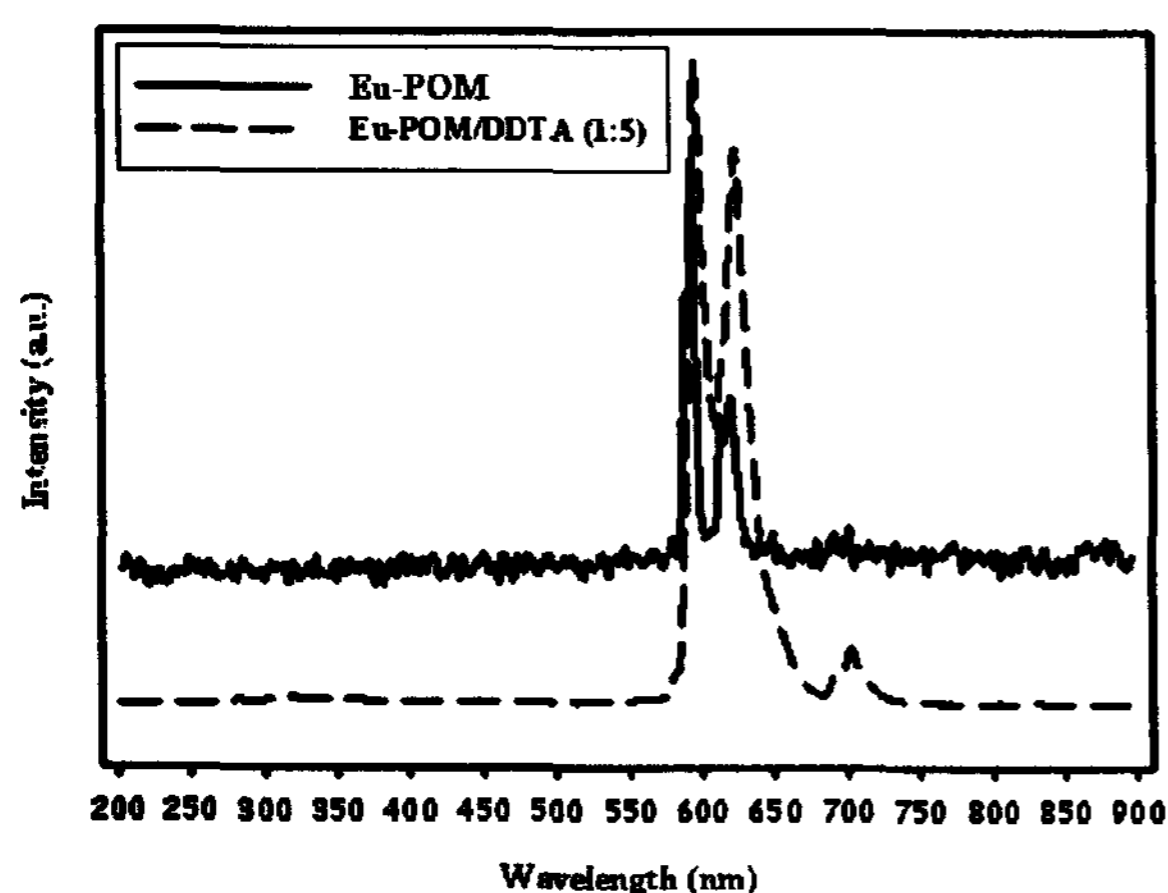


Figure 6. Photoluminescence spectra of Eu-POM and Eu-POM/DDTA

3.3 Photoluminescent Property of Eu-POM and Eu-POM/DDTA

The Eu-POM emits orange light of 590 and 610nm when excited with the light of 280nm, meanwhile Eu-POM/DDTA emits reddish orange light of 600 and 625nm with excitation at 250nm (Figure 6). The substitution of counter cations with organic groups have made the polyoxometalate slightly changed the emitting light together with the solubility. The emission spectra of Eu-POM shows the characteristic transition of Eu^{3+} ions, which are due to transitions within the $4f^6$ electron shell and transitions from $^5\text{D}_0$ metastable state to terminal levels, respectively. For the EuW_{10} , the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ peak splits into 590nm, and further the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ also splits into more levels from 620nm. Among the transitions, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ is the strongest, with $^5\text{D}_0 \rightarrow ^7\text{F}_2$ being next [20].

4. Conclusion

We have synthesized water-soluble Eu-containing polyoxometalate (Eu-POM) and its organic-soluble derivative

(Eu-POM/DDTA). The solubility change has an important meaning for device fabrication. That is, thin film preparation can be extended to various kinds of techniques such as chemical vapor deposition, casting, and spin coating. Eu-POM emits orange light and Eu-POM/DDTA reddish orange light.

Therefore, polyoxometalates (POM) are supposed to be a class for EL materials. The component elements of polyoxometalates can be substituted and the counter cations also exchanged. Therefore, polyoxometalates having photoelectronic functionalities are expected.

5. Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2003-002-D00114), Graduate Student Cultivation Program of Korea Industrial Technology Foundation and partly by BPRC of Inje University. We thank Dr. Mi-Sook Won in Korea Basic Science Institute (KBSI) Busan Branch for obtaining XPS analysis.

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