Journal of Non-Crystalline Solids 448 (2016) 89–95

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

# Differentiation of photon generation in single- and bi- ligand europium complexes doped poly methyl methacrylate

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ARTICLE INFO

*Article history:*
Received 22 April 2016
Received in revised form 13 June 2016
Accepted 25 June 2016
Available online 20 July 2016

*Keywords:*
Single- and bi- ligand europium complexes
Differentiation photon generation
Poly methyl methacrylate

ABSTRACT

Eu(DBM)$_3$ and Eu(DBM)$_3$Phen were introduced into poly methyl methacrylate (PMMA) in comparative, and the differential luminescence behaviors were revealed under ultraviolet (UV) radiation. The comparison of excitation behavior between Eu(DBM)$_3$ and Eu(DBM)$_3$Phen doped PMMAs indicates that the introduction of Phen ligand largely enhances the excitation intensity of europium in the entire UV region. The total quantum yield of Eu(DBM)$_3$Phen doped PMMA was derived to be (9.34 ± 0.14)%, and it is about 8 times higher than that of the Eu(DBM)$_3$ doped PMMA under 373 nm UVA light emitting diode (UVA-LED) excitation, which confirms the effective utilization of UVA radiation by introducing Phen ligand. Similar results on absolute spectral parameters of the bi-ligand under the excitation of 308 nm UVB light emitting diode (UVB-LED) further support the availability for photon conversion. The brilliant red fluorescence of Eu(DBM)$_3$Phen doped PMMA under direct sunlight demonstrates the contribution of Phen to modify the solar spectrum and enhance the UV radiation conversion efficiency, which make the Eu(DBM)$_3$Phen doped PMMA an attractive UV radiation conversion layer for solar cell.

## 1. Introduction

Despite the fact that relevant photovoltaic technologies have been developed for more than half a century, the products of solar energy still remain costly, largely due to their lower conversion efficiency [1–3]. The major limitation to the efficiency of solar cell is that only a small part of solar radiation can be utilized by the battery device, and most of the ultraviolet (UV) radiation is wasted on the mismatch with the absorption of solar cell [4,5]. Furthermore, UV radiation produces light oxidation dye effect in the dye-sensitized solar cells, which weakens the performance and further affects the efficiency of solar cells [6–8].

A large number of reports have been done on lanthanide complexes for their usage of UV radiation for solar cell [9–21], and europium complexes with 4f orbital characteristic emission have been regarded as attractive photoelectrical materials particularly [22–27]. Europium β-diketonate complexes exhibit intriguing luminescence properties [28–30], however, the fluorescence intensity and stability of single-ligand europium β-diketonate complexes still remain to be improved under UV irradiation [31–35]. It has been reported that the fluorescence intensity can be enhanced by introducing cooperative ligand, and the UV stability can be increased by doping them into the matrices, such as silica based materials and polymers [36–39].

1,10-Phenanthroline (Phen) is one of the UV light-harvesting organic ligands, and it is well known for the strong coordination ability with rare earth (RE) ions because its two nitrogen atoms can coordinate with RE ions to form stable five-member ring structure [40–43]. In this paper, Phen is introduced into the europium dibenzoylmethane (DBM) complexes as the cooperative bi-ligand to enhance characteristic luminescence intensity and poly methyl methacrylate (PMMA) is adopted as the matrix material for its high visible transparency, excellent weather resistance and high mechanical strength [22,44–50]. The responses to UV radiation in Eu(DBM)$_3$ and Eu(DBM)$_3$Phen doped PMMAs were compared, and the brighter red luminescence recorded in Eu(DBM)$_3$Phen doped PMMA indicates that Phen plays an effective role in the enhancement of characteristic luminescence intensity. The absolute spectral parameters further confirm that the Eu(DBM)$_3$Phen doped PMMA is promising in the application to improve the photoelectric conversion efficiency of solar cell.

## 2. Experiments

Single-ligand Eu(DBM)$_3$ and bi-ligand Eu(DBM)$_3$Phen were synthesized according to the procedure reported by L.R. Melby [51]. In the fabrication process of complexes doped PMMA, a certain amount of PMMA powder was dissolved in tetrahydrofuran (THF) solution followed by the addition of the Eu(DBM)$_3$ and Eu(DBM)$_3$Phen, respectively. The well-mixed solutions were heated at 50 °C for 1 h using a thermostat water bath and the samples were obtained by evaporating the solvent slowly.

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http://dx.doi.org/10.1016/j.jnoncrysol.2016.06.035
0022-3093/

The excitation and emission spectra were recorded by a Hitachi F-7000 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were characterized by American TA company SDT 600. The samples were heated from 25 to 800 °C by heating rate 10 °C/min under $N_2$ atmosphere. Transmittance spectrum was measured by Perkin Elmer UV-VIS-NIR Lambda 19 double beam spectrophotometer. Using the Metricon 2010 prism coupler, the refractive indices ($\pm 0.0001$) of the 1.0 wt% $Eu(DBM)_3$ and 1.0 wt% $Eu(DBM)_3$Phen doped PMMAs were measured to be 1.4880 and 1.4890 at 632.8 nm, and 1.4782 and 1.4781 at 1536 nm, respectively. The refractive indices at other wavelengths can be calculated by Cauchy's equation $n = A + B/\lambda^2$ with $A = 1.4760$ and $B = 5159$ $nm^2$ for $Eu(DBM)_3$ doped PMMA, and $A = 1.4795$ and $B = 5305$ $nm^2$ for $Eu(DBM)_3$Phen doped PMMA.

The absolute spectral parameters of $Eu(DBM)_3$ and $Eu(DBM)_3$Phen doped PMMAs were measured in an integrating sphere of 3.3-inch inner diameter (Labsphere), which was connected to a CCD detector (Ocean Optics, USB4000) with a 600 μm-core optical fiber. The currents of the exciting 308 nm UVB light emitting diode (UVB-LED) and 373 nm UVA light emitting diode (UVA-LED) were fixed at 20 and 270 mA, respectively. A standard halogen lamp (EVERFINE, D062) was used to calibrate this measurement system. The luminescence pictures of the samples were taken using a Sony α200 digital camera.

## 3. Results

Fig. 1(a) and (b) are the transmittance spectra of 0.2 wt% $Eu(DBM)_3$ and 0.2 wt% $Eu(DBM)_3$Phen doped PMMAs, respectively. Both of them show up to 80% transparency, which indicates the PMMA is a suitable matrix for rare earth complexes doped photoelectric materials. The $Eu(DBM)_3$ and $Eu(DBM)_3$Phen doped PMMAs exhibit excellent nature light transparency as shown in the inserted photos in Fig. 1(a) and (b).

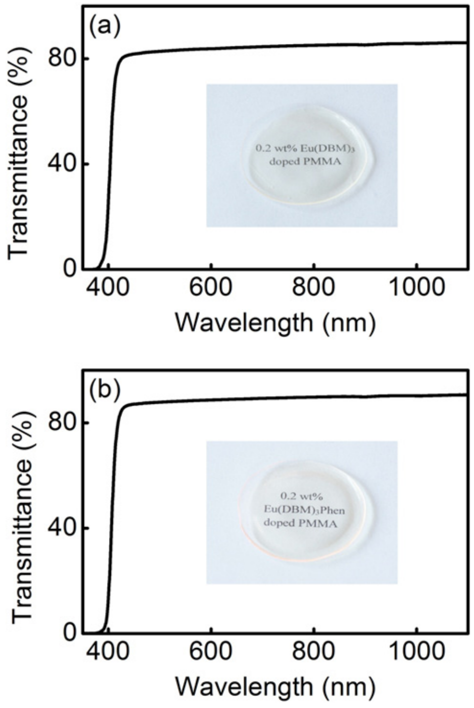

**Fig. 1.** Transmittance spectra of (a) 0.2 wt% $Eu(DBM)_3$ doped PMMA (Thickness: $d = 0.36 \pm 0.02$ mm), (b) 0.2 wt% $Eu(DBM)_3$Phen doped PMMA (Thickness: $d = 0.30 \pm 0.02$ mm). Inserted photographs: 0.2 wt% $Eu(DBM)_3$ and 0.2 wt% $Eu(DBM)_3$Phen doped PMMAs under nature light, respectively.

Thermal property is of great significance to complexes doped PMMA for practical applications as optical materials, thus the DSC-TGA analyses of $Eu(DBM)_3$ and $Eu(DBM)_3$Phen doped PMMAs were carried out as illustrated in Fig. 2. The TGA curves of $Eu(DBM)_3$ and $Eu(DBM)_3$Phen doped PMMAs are similar and no weight loss is observed until 99 °C and 103 °C, respectively. Both of them show about 15% weight losses at 310 °C, which is attributed to the solvent removal from the samples, indicating that the $Eu(DBM)_3$ and $Eu(DBM)_3$Phen doped PMMAs have good thermal stability.

Fig. 3 shows the emission spectra of different concentration of $Eu(DBM)_3$ and $Eu(DBM)_3$Phen doped PMMAs under 365 nm UV radiation and the differential red luminescence are shown in the inserted photos from Fig. 3(a) to (d). Taking an example of 1.0 wt% $Eu(DBM)_3$Phen doped PMMA, bright red fluorescence is achieved, which is ascribed to the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ and 4) transitions of europium ion ($Eu^{3+}$), respectively. In the meantime, the emission intensity of 1.0 wt% $Eu(DBM)_3$Phen doped PMMA is obviously higher than that of the 1.0 wt% $Eu(DBM)_3$ doped PMMA. The ligand structure of $Eu(DBM)_3$ and $Eu(DBM)_3$Phen are illustrated in Fig. 4.

Fig. 5 shows the excitation spectra of 0.2 wt% Eu $(DBM)_3$ and 0.2 wt% $Eu(DBM)_3$Phen doped PMMAs by monitoring the emission at 614 nm. The excitation spectra are dominated by an intense broad band in the 220–420 nm, which can be assigned to the absorption of lanthanide organic complex. The intensity of 0.2 wt% $Eu(DBM)_3$Phen doped PMMA is much higher than that of 0.2 wt% Eu $(DBM)_3$ doped PMMA, indicating an enhancement of UV to visible photon conversion efficiency.

Integrating sphere coupled with CCD detector measurement was applied for absolute spectral parameter characterization, which provides external quantum yield to assess luminescence materials. Spectral power distributions of 1.0 wt% $Eu(DBM)_3$ and 1.0 wt% $Eu(DBM)_3$Phen doped PMMAs were measured. $P_{sam}$ and $P_{LED}$ were recorded under the excitation of 373 nm UVA-LED when the samples were located on and off the LED pump source in the integrating sphere. By subtracting the $P_{LED}$ component from the $P_{sam}$ component, the net spectral power distributions were obtained as depicted in Fig. 6. Bright red fluorescence is observed in $Eu(DBM)_3$ and $Eu(DBM)_3$Phen doped PMMAs under the excitation of 373 nm UVA-LED in an integrating sphere, as shown in the inserted photos of Fig. 6.

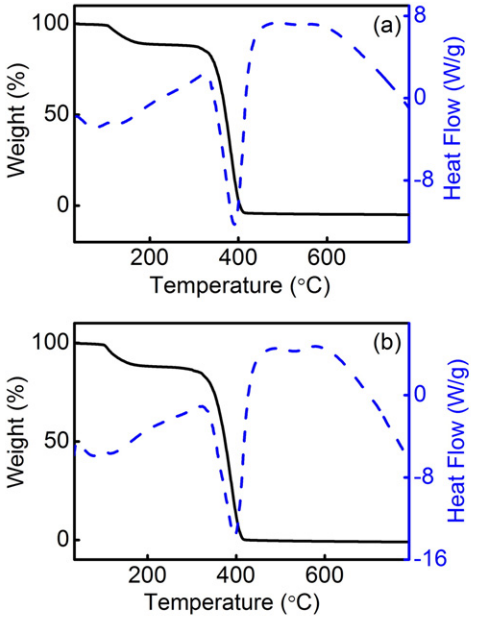

**Fig. 2.** DSC-TAG curves of (a) 1.0 wt% $Eu(DBM)_3$ and (b) 1.0 wt% $Eu(DBM)_3$Phen doped PMMAs.