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Influences of matrices and concentrations on luminescent characteristics of $Eu(TTA)_3(H_2O)_2$/polymer composites

Hong-Guo Liu[a,b,*], Fei Xiao[a], Wan-Song Zhang[c], Younghua Chung[b], Hyo-Jin Seo[d], Kiwan Jang[b], Yong-Ill Lee[b]

[a]*Key Laboratory for Colloid & Interface Chemistry of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Shanda Nan Road, Jinan 250100, China*
[b]*College of Natural Science, Changwon National University, Changwon 641-773, Republic of Korea*
[c]*Department of Math & Physics, University of Petroleum, Beijing 102249, China*
[d]*Department of Physics, Pukyoung National University, Pusan 608-737, Republic of Korea*

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Abstract

$Eu(TTA)_3(H_2O)_2$ (TTA: thenoyltrifluoroacetone) was doped in polyvinylpyrrolidone (PVP), poly(ethylene oxide) (PEO) and poly(vinyl stearate) (PVS) with different molar ratios. The composites formed were investigated by using photoluminescent spectroscopy, luminescent decay experiments and X-ray diffractometry. It was found that the composites have distinct emission properties in different matrices, probably arising from various symmetrical sites of Eu(III) due to the interactions between the complex and the corresponding polymers. In addition, the emission properties of the composites of $Eu(TTA)_3(H_2O)_2$/PEO vary greatly with the molar ratios of the complex and polymer, showing the influence of the compositions, which can be attributed to different composite structures, such as a crystalline and an amorphous one, while the luminescence of the other two series of the composites changes slightly with the compositions. The luminescence can be tuned by changing the matrices and the compositions conveniently.

Keywords: Europium complex; PVP; PEO; PVS; Luminescence

1. Introduction

Europium complexes have aroused much attention due to their unique luminescent properties arising from the "antenna effect" of the ligands and f–f transition of Eu(III). This leads to

*Corresponding author. Key Laboratory for Colloid & Interface Chemistry of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Shanda Nan Road, Jinan 250100, China. Tel.:/fax: 86 531 8364750.
E-mail address: hgliu@sdu.edu.cn (H.-G. Liu).

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important applications in laser, phosphor and optic-electrical devices. In order to prevent luminescence concentration quenching, to meliorate the thermal and mechanical stabilities, and to improve the processing ability, in general, europium complexes have been incorporated into matrices, for example, silica [1,2], ORMOSIL [3,4], mesoporous [5] or microporous [6] materials and polymers [7,8], to form composites. Among these composites, europium complex/polymer systems are the most interesting ones in point of processing, for example, the polymer composites are easy to form fibers compared with glass ones [9].

Europium complexes with thenoyltrifluoroacetone (TTA) show excellent luminescent properties. As early as in 1963, Wolff and Pressley [10] studied the lasing and luminescent properties of mixed systems of $Eu(TTA)_3(H_2O)_2$/poly(methyl methacrylate) (PMMA). Recently, Parra et al. [11] showed the effect of the concentration of doped $Eu(TTA)_3(H_2O)_2$ in epoxy resin on the luminescent properties; we have studied the luminescent properties and structures of the $Eu(TTA)_3(H_2O)_2$/PMMA composites with different compositions and other composite systems of Eu(III)-β-diketonates with PMMA [12]. Moreover, we have studied the composite systems of europium complexes with polymers systematically in recent years, and found that the ligands, polymers and concentrations have great influence on the luminescent properties of Eu(III) due to the variation of the microenvironments around the cations [13–16]. For the composites where Eu^{3+} ions occupy similar microenvironments, homogeneous broadening spectra can be obtained, which show good homochromatism; while for the composites where Eu^{3+} ions have different microenvironments, inhomogeneous broadening spectra can be obtained, which have important applications in optical information storage materials based on hole-burning spectroscopy. It is interesting to develop optic materials with tunable luminescent properties for their applications. In this paper, $Eu(TTA)_3(H_2O)_2$ was doped in three kinds of polymers, and the distinct luminescent properties of the composites were researched.

2. Experimental

2.1. Reagents and samples

Eu_2O_3 (99.95%), TTA (99%), PVP ($M_w \approx 29,000$), PEO ($M_w \approx 100,000$) and PVS ($M_w \approx 90,000$) were purchased from Aldrich Chemical Company, Inc. $Eu(TTA)_3(H_2O)_2$ was synthesized according to the literature methods [11] and dried in a vacuum drying oven.

2.2. Sample preparation and characterization

Mixed systems of $Eu(TTA)_3(H_2O)_2$ with polymers were prepared by dissolving these components with certain molar ratios into chloroform. The samples for photoluminescent (PL) spectroscopy, emission lifetime measurements were prepared by casting the chloroform solutions onto clean glass slides. The solvent was allowed to evaporate in air and then the samples were placed into a vacuum dry oven at room temperature for several hours.

PL spectra were obtained by a PC 2000 spectroscope (Ocean Optics Inc.) with the excitation at 325 nm using a He–Cd laser (Omnichrome, LC-500). Decay curves were obtained by monitoring the 612 nm emission by using 300 MHz-digital oscilloscope (LeCroy 9310, Switzerland) and triple grating monochromator (Spectra Pro-750 ARC Actron, Research Corporation, MA) under the excitation at 355 nm dye laser (Spectron SL 4000B/G, Spectron laser systems, UK) at room temperature. X-ray powder diffraction experiments were carried out on a Philips X'Pert MPD/PW3040 X-ray diffractometer with CuKα irradiation at 293 K.

3. Results and discussion

3.1. Composites of $Eu(TTA)_3(H_2O)_2$/PEO

The profiles of the emission spectra of the composites in PEO matrix depend strongly on the molar ratios, as shown in Fig. 1. It can be seen that the hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition bands for the composites with the molar ratios of Eu/O of