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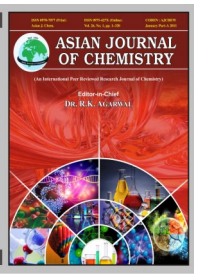

Luminescent Properties of Europium Complex Enhanced by Replacement of Water Molecules by 2,2'-Bipyridine

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The complex $[Eu(L)_3(bipy)]$ (where L = 2'-hydroxy-4'-methoxyacetophenone, bipy = 2,2'-bipyridine) was synthesized and characterized by elemental analysis, energy dispersive X-ray spectroscopy, ^{1}H NMR spectroscopy, infra red spectroscopy, TGA/DTA, scanning electron microscopy and the excitation as well as emission spectrum. The $[Eu(L)_3(bipy)]$ had regular shaped particles with size less than 1 μm without any phase separations and on excitation at 384 nm emits bright red luminescent with main peak at 612 nm. The complex emitting red luminescent might be used to make the electroluminescent (EL) devices.

Keywords: Eu^{3+}, Complex, Infrared, ^{1}H NMR, Elemental analysis, Luminescence.

INTRODUCTION

The structural tuning of lanthanide complexes as efficient light-conversion devices has become an important pursuit to researchers due to their excellent luminescence properties. The excellent luminescence of organic-metal complexes is due to energy transfer from organic ligand to central metal ion by "antenna effect", which can increase the luminescence efficiency. The β-diketones are excellent organic molecules to transfer energy to lanthanide ions[1-7]. The europium complexes mainly involve five narrow emission lines, corresponding to $^5D_0 \rightarrow {}^7F_j$ transitions, where j = 0, 1, 2, 3 and 4 emitting at ~580, ~590, ~610, ~650 and ~700 nm respectively, $^5D_0 \rightarrow {}^7F_2$ being the strongest with red emission of high color purity[8,9]. In recent years organic electroluminescent materials have been prepared representing a low cost fabrication route and low voltage operation for large area light display technology and large flat panel display. Organic light emitting diode (OLED) displays offer the thinnest profile of any color flat panel technology. The whole assembly can be very small as little as 2 mm in depth that can replace the heavy and bulky cathode-ray tube of the display systems. Now-a-days, organic luminescent materials are used commercially for example in laptop computers, mobile phones, car dashboards, advertisement panels, decorating lighting *etc*. Organic light-emitting diodes (OLEDs) have attracted great interest due to their potential application in the development of new optoelectronic components such as full-color and flat panel displays.

In present work the complex $[Eu(L)_3(bipy)]$ was synthesized and characterized by elemental analysis, energy dispersive X-ray spectroscopy, ^{1}H NMR spectroscopy, infra red spectroscopy, TGA/DTA, scanning electron microscopy and the excitation as well as emission spectrum. The complex emitting red luminescent might be used to make the electroluminescent devices.

EXPERIMENTAL

2'-Hydroxy-4'-methoxyacetophenone (99 %), 2,2'-bipyridine (99 %), $Eu(NO_3)_3.xH_2O$ (99.99 %), sodium hydroxide (99.998 %) were purchased from Aldrich. All chemicals are used without further purification. The complex [Eu(L)3(bipy)] was prepared by mixing alcoholic solutions of L and bipy with an aqueous solution of $Eu(NO_3)_3.xH_2O$ in 3:1:1 molar ratio with constant stirring on magnetic stirrer. The pH of mixture was adjusted to 7 with 0.05 M NaOH solution, this resulted into formation of white precipitates. These precipitates were stirred for 2 h at 40 °C and then allowed to stand for 1 h. The precipitates were filtered, washed with water and ethanol, dried in air and then vacuum desiccators. Elemental analytical data for the complex C % found = 55.12 (calc. = 55.29), N % found = 3.41 (calc. = 3.49) and H % found = 4.61 (calc. = 4.36) indicated that the stoichiometry of the complex to be 1: 3: 1 (europium: ligand: co-ligand). The chemical formula of the prepared complex was also confirmed by energy dispersive X-ray spectroscopy (EDS). The energy dispersive X-ray spectroscopy spectrum and percentage of various elements after

calculations was, C % found = 54.97 (calc. = 55.29), O % found =17.34 (calc. = 17.93) and Eu % found = 18.76 (calc. = 18.93). The elemental analysis of the complex was performed on the Perkin Elmer 2400 elemental analyzer. ^{1}H NMR spectrum was recorded on Bruker Avance 300 spectrometer (300 MHz) using chloroform ($CDCl_3$) as solvent, infrared spectrum (4000-400 cm^{-1}) was recorded with Perkin Elmer spectrum RX-I FT infrared spectrophotometer, thermal analysis was carried out by using simultaneous thermal analyzer (STA; Scinco, STA S-1500) with heating rate of 5 °C/min, scanning electron microscopy of the complex was performed by JEOL JSM-6510 scanning electron microscope operating at 10 Kv. The excitation and emission spectra were recorded by using HITACHI F-7000 fluorescence spectrophotometer.

RESULTS AND DISCUSSION

The complex was found to be soluble in dimethyl sulfoxide, dimethyl formamide, chloroform, dichloromethane and acetone, sparingly soluble in methanol, ethanol and ethyl acetate but insoluble in benzene, hexane and toluene. Values for various ^{1}H NMR chemical shifts for $[Eu(L)_3(bipy)]$ are: 2.70 (s, 9H, 3-OCH_3), 3.9 (s, 9H, 3-CH_3), 7.05 (m, 6H, Aromatic), 7.79-7.86 (m, 6H, Aromatic), 7.90 (bs, 3H, Aromatic), 10.35 (d, 2H, Aromatic). All chemical shifts are given in ppm with respect to tetramethylsilane (TMS). The infra-red studies showed the characteristic stretching peak at 1638 cm^{-1} due to C=O group of the free L shifted to 1612 cm^{-1} in the complex, indicated that the C=O group of the L participated in coordination with Eu^{3+} ions. The peak for Ph-O vibration (Ph = phenyl) at 1255 cm^{-1} in free L shifted to 1241 cm^{-1} in the complex which indicate that the Ph-O group coordinated with Eu^{3+} ions. C-N vibration mode of bipy appeared at 1498 and 1410 cm^{-1} shifted to 1474 and 1388 cm^{-1} in complex as well as the benzene ring C-H bending vibration peaks of bipy in high frequency region appearing at 864 and 739 cm^{-1} are shifted to 841 and 724 cm^{-1}, indicating that the chemical bonds are formed between Eu^{3+} ions and nitrogen atoms of bipy. The bands 1417 cm^{-1} and 1452 cm^{-1}, 1517 cm^{-1} were assigned to C-C skeletal vibrational stretching of aromatic ring. Finally, the absorption peak at about 431 cm^{-1} in complex can be assigned to the Eu-O vibration absorption band[10]. Overall, the results indicated that bipy coordinated with the Eu^{3+} ions through nitrogen while L coordinated with the Eu^{3+} ions through oxygen atoms of C=O group and phenolic group as shown in Fig. 1. The TGA/DTA curves of the complex (Fig. 2) show weight loss at about 320 °C is due to elimination of bipy and the weight loss at about 510 °C is due to elimination or decomposition of L. However, above 510 °C the complex $[Eu(L)_3(bipy)]$ completely get decomposed to form Eu_2O_3 as residue. The DTA curve above base line indicates that the decomposition is exothermic in both steps. The surface morphological features (shape and particle size) of the powder complex were studied by scanning electron microscopy. The scanning electron micrographs for the complex showed (Fig. 3) that the material obtained had regular shaped particles with size less than 1 μm without any phase separations. The complex may facilitate the future applications with good optical properties. The emission spectrum of complex is shown in Fig. 4

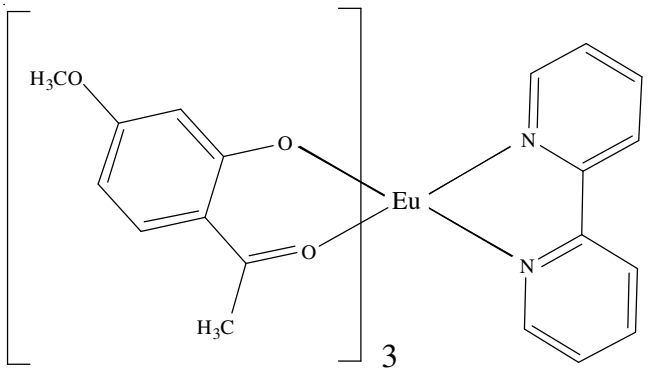

Fig. 1. Proposed structure of $[Eu(L)_3(bipy)]$

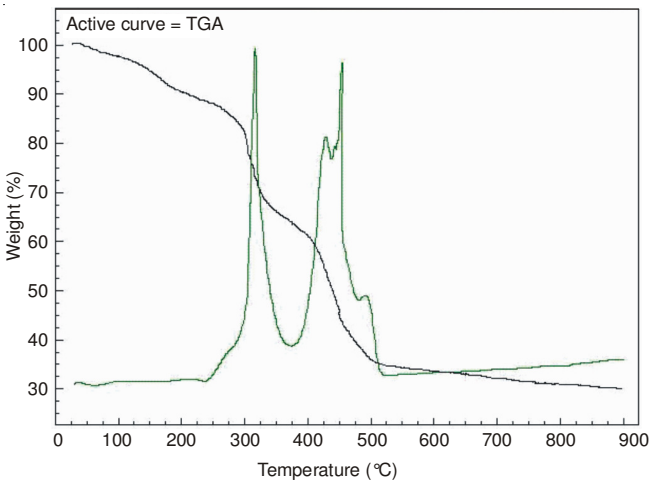

Fig. 2. TGA/DTA curves of $[Eu(L)_3(bipy)]$

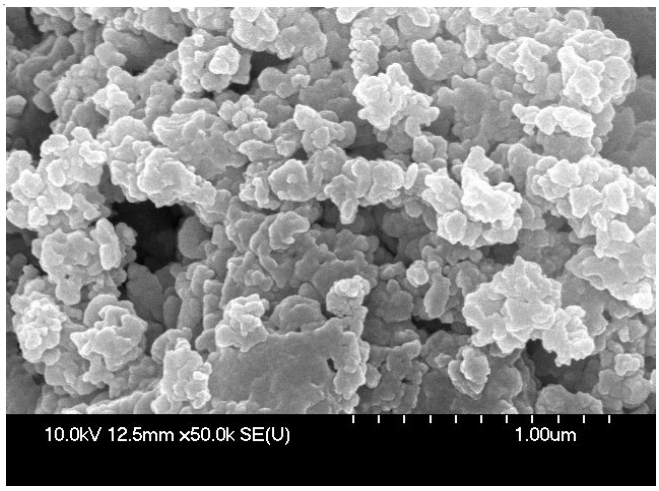

Fig. 3. SEM image of $[Eu(L)_3(bipy)]$

was recorded at room temperature taking λex = 384 nm. The emission spectrum of $[Eu(L)_3(bipy)]$ consists of five peaks at 582 nm ($^5D_0 \rightarrow {}^7F_0$), 590 nm ($^5D_0 \rightarrow {}^7F_1$), 612 nm ($^5D_0 \rightarrow {}^7F_2$), 650 nm ($^5D_0 \rightarrow {}^7F_3$) and 704 nm ($^5D_0 \rightarrow {}^7F_4$). Among these, the emission at 612 nm from the ($^5D_0 \rightarrow {}^7F_2$) electronic transition is the strongest and in agreement with the low symmetry around the Eu^{3+} ion[11]. This peak was sharp and had high color purity, while the transition ($^5D_0 \rightarrow {}^7F_0$) weakest in $[Eu(L)_3(bipy)]$. The emission color was analyzed and confirmed with help of the *Commission Internationale de Eclairage* (CIE) chromaticity coordinate diagram[3,4]. The color coordinates for the complex

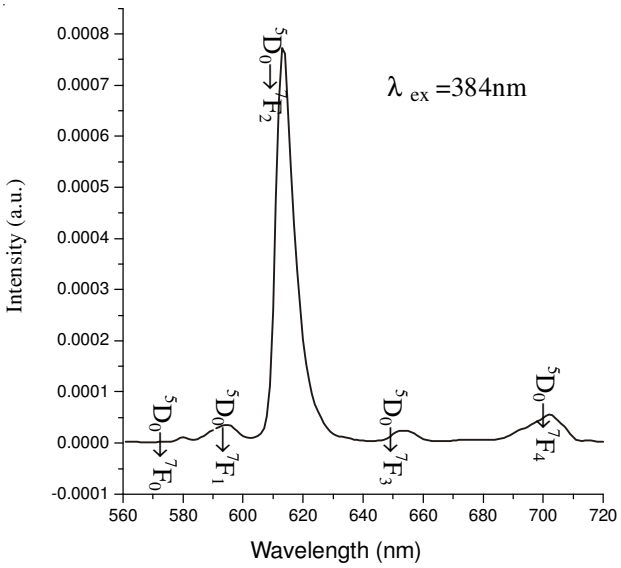

Fig. 4. Emission spectrum of $[Eu(L)_3(bipy)]$

are shown in Fig. 5. It is clear from the figure that color coordinates of the complex fall in red region (x = 0.6034 and y = 0.3098). The complex having bright red emission and good photoluminescence intensity (64.82 cd/m^2) might be promisingly applicable for various display applications. The present europium complex has high photoluminescent intensity (64.82 cd/m^2) than earlier reported complexes $Eu(L_1)_3{\cdot}2H_2O$ (61.17 cd/m^2), where L_1 = 2'-hydroxy-4'-methoxy-2-phenylacetophenone, $Eu(L_2)_3{\cdot}2H_2O$ (62.87 cd/m^2) where L_2 = 2'-hydroxy-4'-methoxy-2-(*p*-methoxyphenyl)acetophenone, $Eu(L_3)_3{\cdot}2H_2O$ (61.83 cd/m^2), where L_3 = 2'-hydroxy-4',6'-dimethoxy-2-phenylacetophenone, $Eu(L_4)_3.2H_2O$ (62.06 cd/m^2), where L_4 = 2'-hydroxy-4',6'-dimethoxy-2-(*p*-methoxyphenyl)acetophenone[3], $Eu(L)_3{\cdot}2H_2O$ (62.13 cd/m^2) where L = 2'-hydroxy-4'-methoxyacetophenone[4].

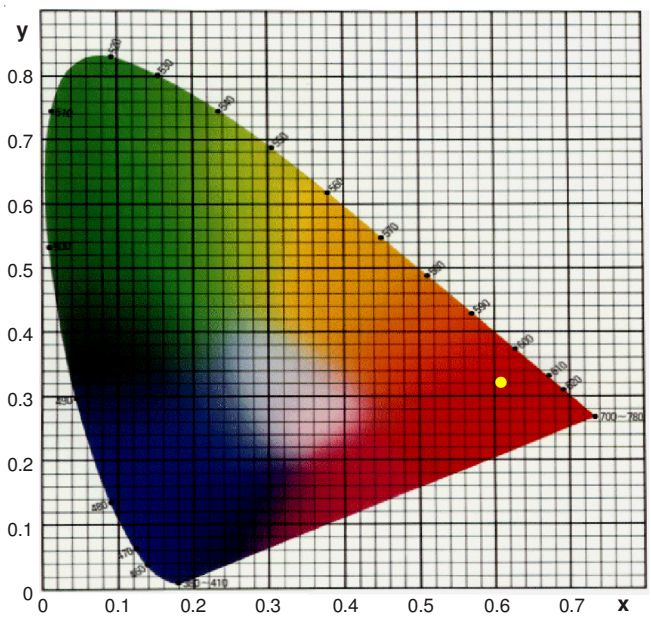

Fig. 5. CIE coordinates of $[Eu(L)_3(bipy)]$

Conclusion

The europium complex, $[Eu(L)_3(bipy)]$ have been synthesized. The synthesized complex is electroneutral molecule, in which the each central europium ion is wrapped with three L molecules and one bipy molecule. The L excites Eu^{3+} luminescence efficiently. The replacement of two water molecules by one bipy molecule increases the luminescence intensity and thermal stability of complex. The color coordinates of $[Eu(L)_3(bipy)]$ complex fall in red region (x = 0.6034 and y = 0.3098). The complex having bright red luminescence and good PL intensity (64.82 cd/m^2) might be promisingly applicable for various display applications.

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