

PREPARATION AND PHOTOLUMINESCENCE FEATURES OF EUROPIUM COMPLEX

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ABSTRACT: The lanthanide complex of europium ion with BAA (2-benzoylacetanilide) was successfully synthesized and their photoluminescence features were investigated. The BAA and its complex were characterized by various techniques such as IR, NMR, CHN elemental analysis, UV-visible and photoluminescence spectroscopy. The complex exhibited the luminescence of the europium(III) ion in visible region ascribed to the efficient energy transfer from ligand to the central metal. Upon excitation at 395 nm, the emission spectra of complex showed characteristic peaks of europium ion at 580 nm, 591 nm, 613 nm and 651 nm assigned to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_3$ electronic transitions, which originate due to transition between excited 5D_0 state and ground 7F_j ($j = 0, 1, 2$ and 3) state of europium ion. The color coordinates of the complex located in the red region of the chromaticity diagram. These results suggested that the complex can be potential applied for display devices.

Keywords: Europium ion, IR, UV-visible, photoluminescence features.

1. INTRODUCTION

The lanthanide complexes based on organic ligands have been widely explored due to their attractive photophysical features. These characteristic features make them promising candidate for light emitting devices [1] and also have many applications in the field of laser materials [2], electroluminescent materials [3], sensory materials [4], luminescence probe [5] and full color light emitting display devices [6]. Due to forbidden f-f transitions, the lanthanide metal ion exhibits low photoluminescence intensity upon UV excitation with low photochemical stability [7]. To improve the luminescence intensity and stability of the complexes, the central rare earth ion is coordinated with light harvesting organic ligand with high absorption coefficient. The organic ligand acts as photosensitizer which absorbs the energy over a wide UV-visible region and transfers it to the metal ion. The process of absorption of energy by the organic ligand and the transfer to central metal ion is known as sensitization which enhances the photoluminescence properties of the complexes [8]. As a sensitizer, the organic ligand must have strong coordination ability and high absorption coefficient. Among the organic ligands, benzoylacetanilide emerged as a good sensitizer for the rare earth complexes. It also possesses extended π -conjugation of two aromatic rings besides the above mentioned features.

In this report, the europium complex functionalized with BAA ligand was synthesized. The complex was characterized by using different techniques such as CHN elemental analysis, infrared (IR), 1H -NMR, UV-visible and photoluminescence (PL) spectroscopy. In order to investigate the photoluminescence features of europium(III) complex, the luminescence decay curves, excitation and emission spectra, CIE color coordinates were analyzed in detail.

2. Experimental

The chemicals such as aniline and ethyl benzoylacetate were of analytical grade and purchased from the commercial source. The lanthanide nitrates $[Eu(NO_3)_3 \cdot 5H_2O]$ was purchased from the Sigma Aldrich and used as such without purification. The 2-benzoylacetanilide was synthesized and purified by recrystallization process.

2.1 Synthesis of 2-benzoylacetanilide (BAA) ligand

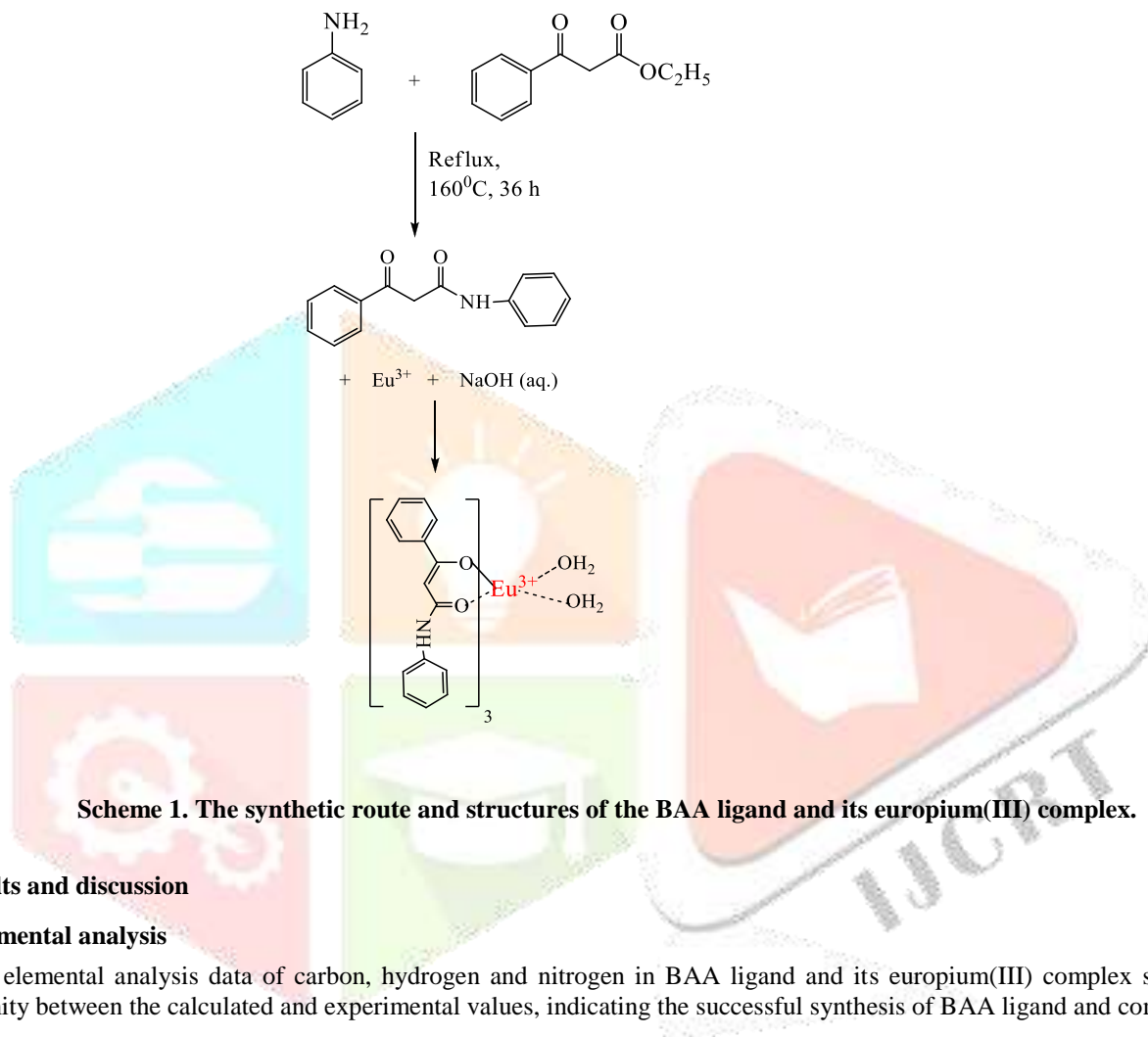
The synthetic route of ligand BAA has been illustrated in scheme 3.1.1. In a round bottom flask, 9.1 mL (0.1 mol) of aniline was added to the 17.3 mL (0.1 mol) of ethyl benzoylacetate. Then, the resulting reaction mixture was refluxed on the heating mantle at about 160°C for 35 h. The progress of the reaction was monitored by TLC (thin layer chromatography). After the refluxing, 300 mL hot water was added to the reaction mixture and heated to boiling. Reaction mixture was filtered and cooled. Then, mixture was kept in the ice bath till the white solid was separated. Finally, the obtained solid was dried in hot air oven with 75% yield and 107°C melting point [9-10]. IR (KBr): cm^{-1} 3301 (s), 3199 (m), 3139 (m), 3088 (m), 1660 (s), 1562 (s), 1500 (s), 1447 (s), 1407 (s), 1341 (s), 1248 (m), 1208 (m), 1168 (m), 1079 (m), 999 (m), 964 (m), 893 (m), 871 (m), 750 (s), 680 (s), 596 (w); 1H -NMR (400 MHz): δ 14.10 (s, 1H, enolic OH), 9.3 (s, 1H, NH), 7.10-8.02 (m, 10H, Ar-H), 5.68 (s, 1H, enol CH), 4.01 (s, 2H, keto $-CH_2$) ppm. Elemental analysis calculated for $C_{15}H_{13}NO_2$: C, 75.31; H, 5.43; N, 5.85; Found C, 75.28; H, 5.32; N, 5.78.

2.2 Synthesis of europium(III) complex

The europium complex was synthesized with the help of ethanolic solution of BAA (0.76 g, 3.2 mmol) and an aqueous solution of europium metal nitrate (0.42 g, 1.0 mmol). The solution was constantly stirred by keeping it on the magnetic stirrer. The pH of resulting mixture was adjusted to 6.0-6.5 with 0.05 M aqueous NaOH solution and the solution was kept at 50-55°C temperature for 3

h. The white precipitates appeared during stirring which were collected by vacuum filtration, washed with distilled water. Then, washed with ethanol to remove the residue of free ligand and finally dried the precipitates in hot air oven to obtain the off white powder [11-12].

Eu(BAA)₃(H₂O)₂ (C1): off white powder, 78% yield; IR (KBr): cm⁻¹ 3300, 3056, 1620, 1554, 1501, 1474, 1425, 1310, 1235, 1195, 1101, 1071, 1008, 897, 760, 690, 472; ¹H-NMR (400 MHz): δ 9.8 (s, 3H, NH), 7.40-8.20 (m, 30H, Ar-H), 3.28 (s, 3H, enol CH) ppm. Elemental analysis calculated for EuC₄₅H₄₀N₃O₈: C, 59.82; H, 4.43; N, 4.65; Eu, 16.85; Found C, 59.82; H, 4.42; N, 4.62; Eu, 16.80.



Scheme 1. The synthetic route and structures of the BAA ligand and its europium(III) complex.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis data of carbon, hydrogen and nitrogen in BAA ligand and its europium(III) complex showed the high conformity between the calculated and experimental values, indicating the successful synthesis of BAA ligand and complex.

3.2 FT- IR and NMR spectral analysis

The IR spectrum of complex showed a number of notable changes with respect to the IR spectrum of free BAA ligand. These changes in the IR spectrum were observed due to coordination of BAA ligand with the europium metal ion. The -OH stretching vibrations of water molecules were overlapped with the -NH stretching vibrations of the BAA ligand in 3300 cm⁻¹ region. In the IR spectrum of BAA ligand, the strong band at 1660 cm⁻¹ assigned to the >CO stretching vibration. This band is shifted to 1620 cm⁻¹ value in the spectrum of complex which indicated that the >CO group was involved in the coordination [13]. The absorption band of >C=C stretching vibration was located at 1562 cm⁻¹ in the spectrum of BAA ligand, which was shifted to 1554 cm⁻¹ value in the spectrum of complex, suggesting the extended π-conjugated system of the complex and ligand coordinated to the metal ion in the enol form. No change was observed in the bending (1500 cm⁻¹) as well as stretching vibration (3300 cm⁻¹) of N-H in the spectra of ligand and complex. This revealed that the NH group of BAA ligand did not participate in the coordination process. All above absorption bands and their results concluded that the europium(III) ion was bound to the ligand through oxygen atom of >CO group of BAA ligand.

As the BAA ligand coordinated with the europium ion, the ¹H-NMR spectra of complex was different from the spectrum of ligand due to the paramagnetic behavior of europium metal ion. The singlets at 14.10 ppm, 9.3 ppm, 5.68 and 4.01 appeared in the spectrum of BAA ligand which were assigned to the enolic -OH proton, NH proton, enolic =CH proton and keto -CH₂ protons, respectively. Out of these singlets, the peaks of keto -CH₂ and enolic -OH protons disappeared in the spectrum of complex, indicating

the binding of ligand in enolic form. In the spectra of complex, the signal of enolic =CH protons shifted to upfield at about 3.2 ppm with respect to the signal of free ligand due to the paramagnetic nature of the europium and close proximity of these protons with the binding site [14].

3.3 UV-visible absorption spectra

Figure 1 shows the UV-visible absorption spectra of BAA ligand and europium(III) complex with 10^{-5} mol/L concentration in DMSO solvent. The strong absorption bands were observed in 280-450 nm range in which maxima of BAA ligand was located at 318 nm, attributing to the $\pi-\pi^*$ transition of the mainly aromatic ring in ligand [15]. The absorption bands of complex exhibited red shift in comparison to the BAA ligand which can be easily explained on the basis of extended π -conjugation in the complex. The absorption in the complex is also ascribed to the $\pi-\pi^*$ transition of organic ligand because metal ion has low absorption coefficient, indicating the sensitization of central metal ion by the organic ligand in an effective manner.

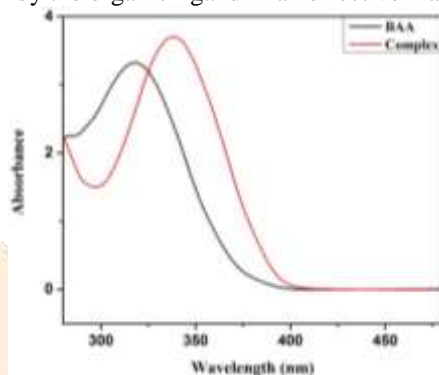


Fig. 1. The UV-visible absorption spectra of BAA ligand and europium complex in DMSO solvent.

3.4 Photoluminescence behavior

Figure 2 shows the excitation spectrum of europium complex monitoring at emission maxima of 613 nm in solid state. The excitation spectrum of the complex was recorded in 200-550 nm range at room temperature in which the maximum intensity observed at 395 nm [16]. This maxima is ascribed to ${}^7F_0 \rightarrow {}^5L_6$ transition of europium ion and corresponds to the $\pi-\pi^*$ transition of organic ligand in europium(III) complex.

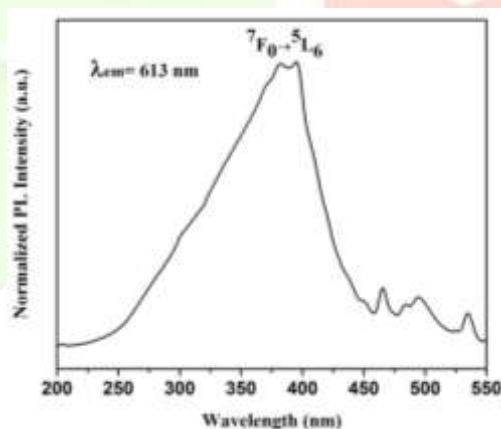


Fig. 2. The solid state excitation spectrum europium(III) complex monitored at room temperature.

Figure 3 displays the photoluminescence emission spectrum of europium(III) complex which was recorded at excitation maxima i.e 395 nm in the 420-750 nm region. The emission spectrum of complex manifest the characteristic peaks at 580 nm, 591 nm, 613 nm and 651 nm assigned to ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_3$ electronic transitions, which originate due to transition between excited 5D_0 state and ground 7F_j ($j = 0, 1, 2$ and 3) state of europium ion. The bands observed at 580 nm, 591 nm and 651 nm are of very low intensity. The most intense peak at 613 nm is an electric dipole transition (${}^5D_0 \rightarrow {}^7F_2$) which is highly sensitive to the chemical environment present around central europium ion. On the other hand, the peak at 590 nm (${}^5D_0 \rightarrow {}^7F_1$) is magnetic dipole transition which is insensitive to the local coordination environment of Eu^{3+} ion [17].

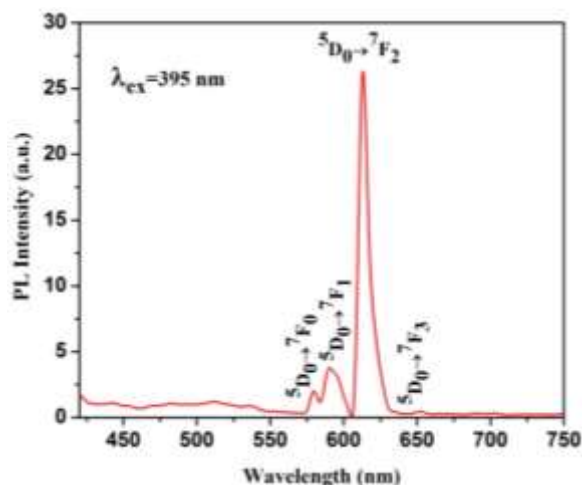


Fig. 3. The solid state luminescence emission spectrum of europium(III) complex excited at 395 nm.

The intensity of electric dipole transition is around 6-8 times higher than magnetic dipole transition, suggesting the presence of polarizable chemical environment and lack of an inversion center around the europium ion which results in the bright red emission color of the complex. Rest of peaks in emission spectra i.e. $^5D_1 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_3$ are forbidden in electric dipole as well as magnetic dipole therefore they have weak intensity.

The CIE (Commission Internationale de Eclairage) color coordinates of complex examined with the help of chromaticity coordinate diagram as shown in Fig. 4. The color coordinates are determined from the emission spectrum of complex. The chromaticity coordinates (0.5137, 0.3253) of the complex located in red region of color chromaticity diagram which indicated that europium complex find application as a red component in light emitting devices.

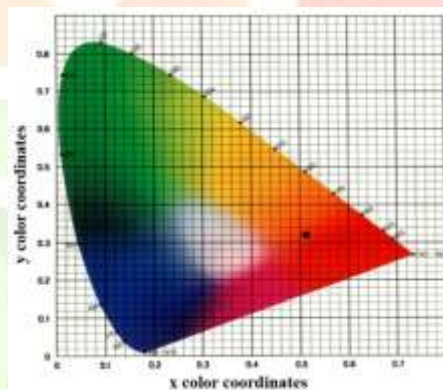


Fig. 4. The CIE color coordinates of europium(III) complex.

The photoluminescence decay time of europium complex is estimated from the photoluminescence decay curves of the complex. The curve was recorded by monitoring the highest intense emission peak ($^5D_0 \rightarrow ^7F_2$) at 613 nm in solid state as displayed in Fig. 5.

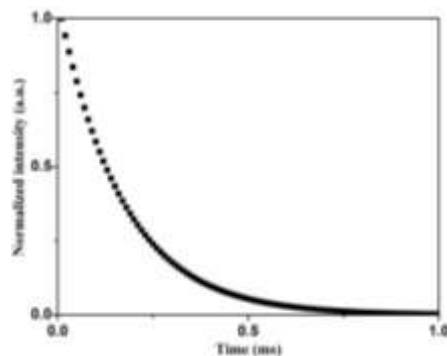


Fig. 5. The photoluminescence decay curve europium(III) complex.

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