Photoluminescence properties of Sm(III) complex with β-hydroxyketone ligand amplified by usage of biquinoline

Savita Khatri[1], Manoj[1], Poonam[1], S.P.Khatkar[2], Rajesh Kumar[1*]
[1]Department of Chemistry, UIET, [2]Department of Chemistry, Maharshi Dayanand University

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Abstract: Here, Newer ternary Sm(III) ion complex, Sm(HDMPE)$_3$.biq is synthesized through usage of solution precipitation method which is further characterized by numerous techniques such as elemental analysis, ^{1}H-NMR, FT-IR and photoluminescence spectroscopy. Here, we have also probed luminescence decay time as well as color coordinates of the evolved complex. When the excitation of the evolved complex is monitored at 373 nm in solid state at room temperature, it showcased pure sharp emission bands from f-f transitions of samarium ion, $^4G_{5/2}\rightarrow{}^6H_{5/2}$, $^4G_{5/2}\rightarrow{}^6H_{7/2}$ and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ at 564 nm, 600 nm and 646 nm respectively. The Sm(III) ion can be efficiently sensitized alone by 1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone (HDMPE) but the introduction of ancillary ligand biquinoline (biq) have outcomed in amplified photoluminescence. The photoluminescence emission spectra showcased that ternary complex might be a promising candidate for usage in advanced displays and lighting systems.

Keywords: - Samarium complex, elemental analysis, ^{1}H-NMR, FT-IR and amplified photoluminescence properties.

1. INTRODUCTION

Today, Ln^{3+} ion in combination with organic ligands have generated complexes which have garnered significant thoughtfulness of research fraternity. These complexes have exhibited extraordinary solicitations in numerous arenas such as biomedical sensors as well as bio-medical imaging. Here, when doped in polymers, these complexes can be used for sensing minute quantities of biomolecules which then can have various solicitations such as assessing physical state of any patient [1], [2] for usage in organic light emitting diodes [3]-[8] or for amplification of optical properties [9], [10]. These Ln^{3+} ion complexes have showcased distinctive photo-luminescent characteristics like high color purity, narrow emission bandwidths in the visible as well as near-infrared regions of the spectra, large Stokes shifts and lifetimes up to several milliseconds [11]. Nevertheless, direct excitation of Ln^{3+} ion is not efficacious as these ions exhibits feeble fluorescent properties primarily owing to its low quantum yield as well as small absorption cross-section [12]. Henceforth, any strong absorbing organic chromophore like β-diketone, β-hydroxyketone or β-aminoketone were employed as light gatherer for sensitizing Ln^{3+} ion through antenna effect [13]-[15] which will ultimately enhance Ln^{3+} ion emission. Finally, 1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone (HDMPE) is picked as prime ligand primarily owing to its dual role of bridging varied building blocks as well as chelating central metal ion which outcomes in amplified photoluminescence as well as quantum yield.

Ancillary ligands like 1, 10-phenanthroline or bathophenanthroline or bipyridine are recurrently picked up by most researchers for carrying out synthesis of ternary lanthanide metal complexes as these bidentate chelating ligands replaces water molecules from coordination sphere of central metal ions [16]-[18], thereby satisfies coordination number of lanthanide ions which will ultimately lead to amplified luminescence, antimicrobial properties as well as antioxidant properties. Consequently, for seeking newer photoluminescent materials having outstanding luminescence properties, biquinoline (biq) is picked here as ancillary ligand for synthesizing one newer ternary Sm(III) ion complex “Sm(HDMPE)$_3$.biq” through usage of 1-(2-hydroxy-4,6-dimethoxyphenyl)ethanone (HDMPE) as prime ligand. The complex formed is characterized by elemental analysis and numerous spectroscopic techniques. The photoluminescence emission spectrum of this complex shows the introduction of ancillary ligand biquinoline (biq) have outcomed in amplified photoluminescence. Hence this ternary complex might be a promising candidate for usage in advanced displays and lighting systems.

2. EXPERIMENTAL

2.1 Materials and methods

Biquinoline, $Sm(NO_3)_3 6.H_2O$ (99.9), benzene-1, 3-5-triol, dimethyl sulphate, potassium carbonate and sodium hydroxide were purchased from Sigma-Aldrich and used as received without additional purification. The synthesized ligand HDMPE was recrystalized three times with methanol before synthesis of complexes. The elemental analysis was performed using thermoscientific flash 2000 elemental analyzer. The percentage of Sm(III) was estimated by complexometric titration with EDTA. The ^{1}H-NMR spectra were measured on Bruker Avance II 400 spectrometer using tetramethylsilane (TMS) as an internal reference (chemical shift in δ ppm). Infrared spectra were recorded (Perkin Elmer spectrum 400) from 4000–400 cm^{-1} in KBr pellets. The excitation and emission spectra was measured using Hitachi F-7000 fluorescence spectrophotometer with excitation and emission slits of 2.5 nm and with PMT at 400 V at room temperature in solid state. The lifetime value of the complex was calculated by the software of the spectrophotometer (FL solution for F-7000) by monitoring $^4G_{5/2} \rightarrow {}^6H_{7/2}$ emission line of Sm^{3+} at room temperature in solid state.

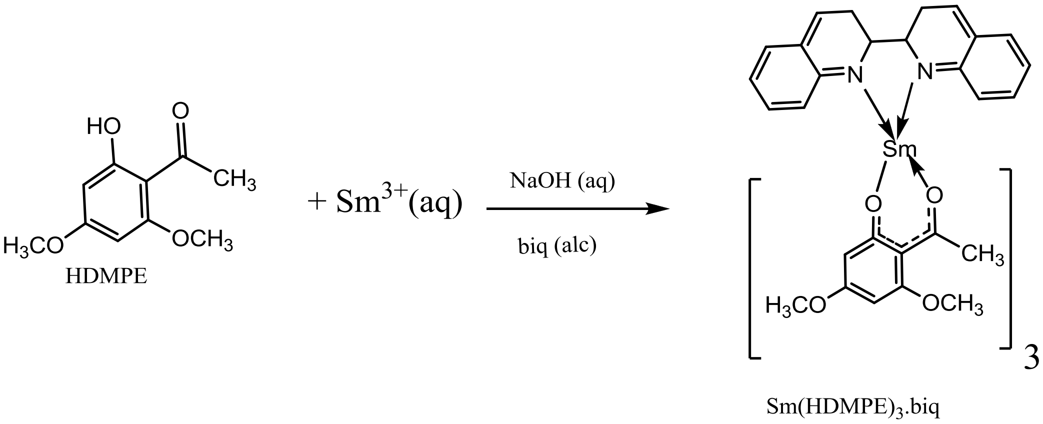
2.2 Synthesis

2.2.1 Synthesis of ligand 1-(2-hydroxy-4, 6-dimethoxyphenyl)ethan-1-one (HDMPE)

The ligand HDMPE was synthesized by adopting conventional method as per literature [18], [19].

2.2.2 Synthesis of complex Sm(HDMPE)$_3$.biq

Scheme 1 The complex was synthesized by mixing ethanolic solution of 3 mmol HDMPE ligand, and 1 mmol biq with ethanolic solution of 1 mmol $Sm(NO_3)_3.6H_2O$. Afterwards the pH of mixture was adjusted to 6.5 - 7, using NaOH (0.05 M) solution with constant stirring. This resulted into formation of white precipitates. These precipitates were stirred for 3 h at about 40°C and then allowed to digest for 1 h. Finally, a suction filter was used to filter precipitates, washed with doubly distilled water and then with ethanol, dried in vacuum oven at 50 °C. The obtained complex was white powder with 81 % yield. The powdered the complex was stored in sample tube in vacuum desiccator.



Scheme 1. The synthetic route and structure of Sm(HDMPE)$_3$.biq.

3. RESULTS AND DISCUSSION

3.1 Solubility

The complex Sm(HDMPE)$_3$.biq was stable under atmospheric condition. The complex Sm(HDMPE)$_3$.biq was found to be soluble in dimethylsulfoxide, dimethylformamide, chloroform and acetone, sparingly soluble in methanol and ethanol but insoluble in benzene and hexane.

3.2 Elemental analysis, ^{1}H-NMR and IR Spectra

The elemental analysis data for Sm(HDMPE)$_3$.biq ($C_{48}H_{45}O_{12}N_2Sm$) was found (calculated) % C, 57.86 (58.01); H, 4.48 (4.57); N, 2.77 (2.82); O, 19.21 (19.35); Sm, 14.81 (15.15). IR (KBr):cm^{-1} 3130 (m), 2462 (m), 2321 (w), 1618 (m), 1589 (s), 1536 (s), 1484 (s), 1376 (s), 1332 (m), 1243 (s), 1214 (m), 1145 (m), 1129 (s), 1058 (m), 903 (m), 870 (s), 843 (m), 828 (s), 783 (m), 766(s), 688 (s), 623 (m), 588 (m), 436 (m). ^{1}HNMR (400 MHz, DMSO): d 2.63 (bs, 9H, CH3), 3.48 (bs, 18H, OCH3), 6.23 (bs, 6H, Ar-H), 7.56 (d, 2H, biq), 7.78 (d, 2H, biq), 8.12 (d, 2H, biq), 8.27 (d, 2H, biq), 8.54 (d, 2H, biq), 8.89 (d, 2H, biq).

The above elemental analytical data indicate the stoichiometry of the ternary complex Sm(HDMPE)$_3$.biq to be 3:1:1 (HDMPE: Sm: biq). The ^{1}H-NMR spectrum of the ligand HDMPE showed singlet at δ 13.84 due to phenolic proton which disappeared in the complex Sm(HDMPE)$_3$.biq was indicating that ligand is coordinated with Sm(III) ion through the oxygen atom of phenolic OH group of the ligand HDMPE. The FT-IR spectra of ligand HDMPE exhibits abroad absorption band at 3430 cm^{-1} assigned to ν(O-H) stretching vibration [20]-[22] which disappeared in the IR spectra of complex the Sm(HDMPE)$_3$.biq. The ligand also displays the intense C=O stretching vibration band at 1640 cm^{-1}, which was red shifted 22 cm^{-1} in complex the Sm(HDMPE)$_3$.biq, indicating that phenolic and carbonyl group of HDMPE participated in coordination with Sm(III) ion [23]. The strong absorption band at 1589 cm^{-1} in complex the Sm(HDMPE)$_3$.biq assigned to C=N stretching vibration, provided good evidence that the nitrogen atoms of biq were coordinating with the Sm(III) ion [18], [24]. The peak for Ph-O vibration of the ligand HDMPE present at 1270 cm^{-1} showed a red shift of 27 cm^{-1} in the complex Sm(HDMPE)$_3$.biq, indicating that the phenolic group is involved in coordination with the Sm(III) ion. The appearance of absorption bands at 588 cm^{-1}and at 436 cm^{-1} in the complex Sm(HDMPE)$_3$.biq was assigned to ν(Sm-N) and ν(Sm-O) [18], [25] respectively, which affirms that the nitrogen atoms of the biq and oxygen atoms of the ligand HDMPE participated in coordination with the Sm(III) ion. Finally, it can be concluded from the FT-IR and ^{1}H-NMR spectra of the ligand HDMPE and complex Sm(HDMPE)$_3$.biq, that the coordination of Sm(III) was through the oxygen atoms of phenolic and carbonyl group of ligand HDMPE and nitrogen atoms of the biq.

3.3 Photoluminescent properties

Figure 1 depicts the excitation profile of the Sm(III) complex Sm(HDMPE)$_3$.biq, recorded by monitoring $^4G_{5/2}\rightarrow{}^6H_{7/2}$ transition, inset shows the excitation spectrum of ligand HDMPE. The excitation spectrum of ligand HDMPE shows a broad band extending from 260 to 435 nm centred at 350 nm. While the excitation spectra for the solid complex Sm(HDMPE)$_3$.biq, narrates the broad excitation band corresponding to characteristic f-f transitions of Sm(III) in the region 250-450 nm. While two excitation peaks centred at 373 nm and 401 nm appeared in the complex Sm(HDMPE)$_3$.biq, which are assigned to the electronic transition $^6H_{5/2}\rightarrow{}^4D_{1/2}+{}^6P_{7/2}$ and $^6H_{5/2}\rightarrow{}^4F_{7/2}$ respectively. The excitation range from 345- 420 is fairly appropriate to meet the demands of UV LED. From the excitation spectra of complex Sm(HDMPE)$_3$.biq, it was found that the intensity of f-f transition at 373 nm was high as compared with the other transition and has been chosen for the measurement of emission spectra. The most intense peak at 373 nm apparently show that the complex Sm(HDMPE)$_3$.biq effectively excited by near ultra violet light.

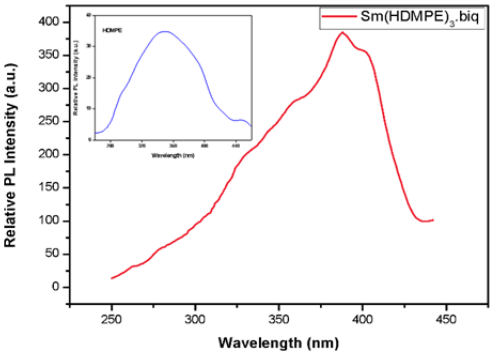


Figure 1 **Photoluminescence excitation spectra of Sm(HDMPE)$_3$.biq, monitored at λ_{em} = 600 nm in solid state at room temperature and inset shows the excitation spectrum of ligand HDMPE.**

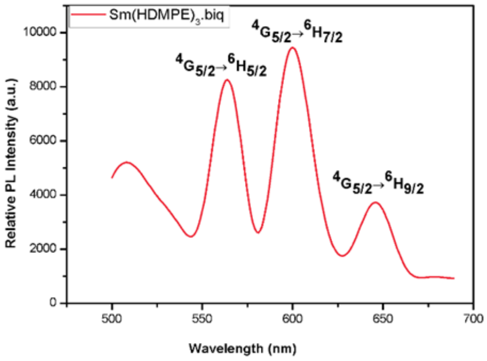


Figure 2 **Photoluminescence emission spectra of Sm(HDMPE)$_3$.biq in solid state at room temperature, monitored at λ_{ex} = 373 nm.**

The emission profile of Sm(HDMPE)$_3$.biq (Figure 2) shows three identified emission peaks corresponding to characteristic emission transition $^4G_{5/2}\rightarrow{}^6H_{5/2}$(magnetic dipole transition), $^4G_{5/2}\rightarrow{}^6H_{7/2}$ (mixed magnetic-electric dipole transition) and $^4G_{5/2}\rightarrow{}^6H_{9/2}$ (electric dipole transition) at 564 nm, 600 nm and 646 nm respectively [26]-[28] on monitoring the excitation at 373 nm in solid state at room temperature as shown in Table 1. Different from the ternary Sm(HDMPE)$_3$.biq complex, the magnetic dipole transition $^4G_{5/2}\rightarrow{}^6H_{5/2}$ is the strongest emission in case of binary complex [22], [29]. The magnetic-electric dipole transition $^4G_{5/2}\rightarrow{}^6H_{7/2}$ was strongest in case of ternary complex Sm(HDMPE)$_3$.biq while the electric dipole $^4G_{5/2}\rightarrow{}^6H_{9/2}$ transition was subsidiary in most of Sm(III) complexes [30], [31] .

Table 1 **Photoluminescence data of Sm(HDMPE)$_3$.biq in solid state.**

Complex	λ_{ex} (nm)	λ_{em} (nm)	Assignment	τ (ms)	*x* and *y* coordinates
Sm(HDMPE)$_3$.biq	373	564 600 646	$^4G_{5/2}\rightarrow{}^6H_{5/2}$ $^4G_{5/2}\rightarrow{}^6H_{7/2}$ $^4G_{5/2}\rightarrow{}^6H_{9/2}$	0.904	0.4934, 0.4736

The photoluminescence intensity of ternary complex was amplified as compared to the binary complex, because in the ternary complex OH groups was removed from the inner coordination sphere of Sm(III) ion. The replacement of water molecules by aromatic N-donors ancillary ligand 'biq' results in amplified photoluminescence intensity and stability of complexes [23], [32].

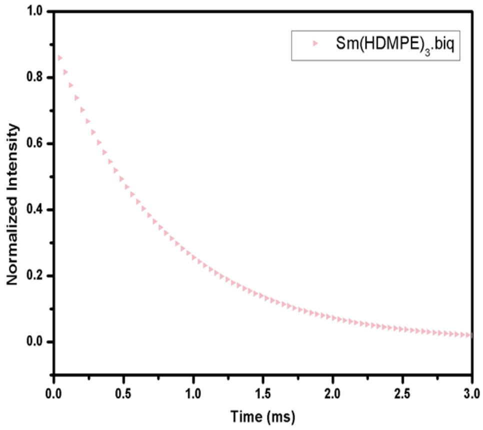


Figure 3 Luminescence decay curves for Sm(HDMPE)$_3$.biq in solid state at room temperature, monitored at λ_{ex} = 373 nm and λ_{em} = 600 nm.

Further, it was noticed that the ancillary ligands in the ternary complex amplified photoluminescence intensity greatly due to the coordination effect between the ligand and ancillary ligands which is beneficial for efficient intermolecular energy transfer from ligand to Sm^{3+} ion. In the lanthanide complexes the intensity ratio of the electric dipole transition to the magnetic dipole transition act spectroscopic probe to determine the local environment around luminescent center. The Sm(HDMPE)$_3$.biq possess low intensity ratio indicating that the Sm(III) ion occupies site symmetry with an inversion centre.
Figure 3 shows the photoluminescence decay curves for complex Sm(HDMPE)$_3$.biq at λ_{em}= 600 nm and λ_{ex}= 373 nm in solid state at room temperature. The decay curve of this luminescent ternary complex obey single exponential curve, which can be represented by the equation $I=I_o \exp(-t/\tau)$, where τ is the radiative decay time, I and I_o are the luminescence intensities at time t and 0, respectively. The life time value calculated for complex was found to be 0.904 ms as presented in Table 1.

With the help of Commission Internationale De Eclairage (CIE) chromaticity coordinate diagram, the emission color of the luminescent complex have been analyzed and tabulated in Table 1. The CIE color coordinates (*x*, *y*) of the complex are located at 0.4934, 0.4736 which lie in deep orange spectral region as shown in Figure 4, suggesting promising application of this complex in advanced display and lighting systems.

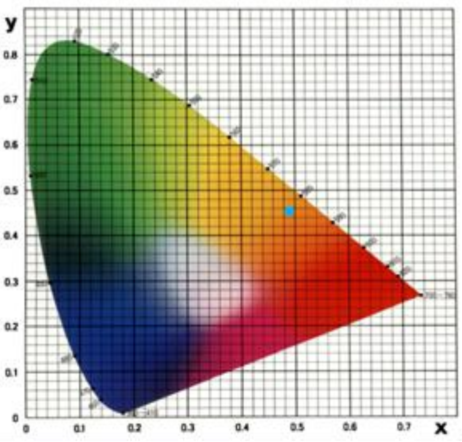


Figure 4 **CIE coordinate diagram of Sm(HDMPE)$_3$.biq**

CONCLUSION

In this work, one newer ternary Sm(III) complex, Sm(HDMPE)$_3$.biq have been synthesized which is further characterized through various techniques like elemental analysis, FT-IR, ^{1}H-NMR and photoluminescence spectroscopy. Variation in FT-IR and NMR spectra of free ligand (HDMPE) and evolved complex have indicated that oxygen atoms of both phenolic as well as carbonyl group of prime ligand and nitrogen atoms of ancillary ligand (biq) were effectively coordinated to Sm(III) ion. Furthermore, the preferred coordination environment is well-matched for sensitizing luminescence of Sm(III) ion with prime ligand HDMPE and ancillary ligand, leads to highly efficient and saturated orange photoluminescence. In conclusion, this evolved complex Sm(HDMPE)$_3$.biq has showcased excellent luminescent properties, consequently can have potential solicitations for usage as light emitting materials in lighting systems.

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