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Synthesis and photoluminescent properties of orange light emitting Sm(III) complex with 2-hydroxy-4-methoxy-2-(4-chlorophenyl)acetophenone and 2,2'-bipyridine

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ABSTRACT

New β-hydroxyketone ligand 2-hydroxy-4-methoxy-2-(4-chlorophenyl)acetophenone (CHME) and its ternary Sm(III) complex Sm(CHME)3.bipy were synthesized. The ligand as well as complex were characterized by elemental analysis, FT-IR, ^{1}H-NMR and photoluminescent spectroscopic techniques. Elemental analysis were in high agreement with the calculated data of the synthesized ligand and Sm(III) complex. The result of ^{1}H-NMR and infrared spectra showed that the free ligand CHME was coordinated with Sm(III) ion through the phenolic hydroxyl group, carbonyl group and nitrogen atoms of the ancillary ligand 2,2′-bipyridine. The ancillary ligand acting as a light harvesting center was involved as a result complex showed good luminescent properties. The emission spectrum of complex was recorded in solid state at room temperature on monitoring excitation at λex = 385 nm. The CIE color coordinates (x, y) of the complex is located at 0.4356, 0.4966 which lie in orange spectral region.

Keywords: Sm(III) complex, β-hydroxyketone, elemental analysis, 2,2′-bipyridine, photoluminescent property

I. INTRODUCTION

Recently the luminescent trivalent rare earth ion complexes have attracted a special attention due to their superior photoluminescent properties such as narrow emission bands for high color purity, large stokes shifts, long lifetimes, high quantum efficiency and good thermal stability [1-3]. Nowadays, attempt have been made to synthesize and study the coordinated complexes of trivalent rare earth ions (Eu^{3+}, $Tb^{3+}$and Sm^{3+}) with organic ligands especially β-hydroxyketones, β-diketones, aromatic carboxylic acids, pyridine derivatives, nucleic acids, quinoline, cryptands and several other macrocyclic ligands [4-10]. Among these organic ligands a lot of focus is on the synthesis of rare earth complexes with β-hydroxyketones ligand due to their unique physiochemical properties and various applications. Lehn in the beginning of 1990s gave idea about the use of rare earth complexes as light converting molecular devices (LCMDs) [11] which are potentially useful in practical applications as in clinical analysis where trivalent rare earth ions have been used as very sensitive luminescent probes. The rare earth complexes with organic ligand are also explored for applications in full-color flat panel displays [12], laser materials [13, 14], fabrication of organic light emitting devices [15-17], amplifiers, sensors and magnetic molecular materials [18-21] due to sharp intensely luminescent f-f electronic transition. Although, f-f electronic transitions of rare earth ions have low intensity due to Laporte selection rule so the direct excitation of Sm(III) ion is quite inefficient The luminescence intensity of the rare earth complexes may be enhanced considerably by the excitation of the rare earth ion via the energy transfer from the strongly absorbing suitable organic chromophore, which is commonly used to sensitize rare earth ions via a process called “antenna effect” [22-24]. The β-hydroxyketones have been shown as excellent organic chromophore to transfer energy for the central rare earth ions and the emission wavelength of the rare earth complexes can be tuned by the choice of the rare earth ion [25, 26] i.e Sm(III) complexes emit bright orange emission at 601 nm. The energy transfer process depend upon the efficiency of the absorption by the ligand, the energy transfer between ligand to metal ion and the rare earth luminescence [27]. To improve the process of energy transfer and make it permanent, the triplet state of the ligand must be slightly above the emitting metastable level of the rare earth ion [28].

Moreover, the aromatic heterocyclic N-donors ancillary ligands such as 1, 10-phenanthroline, 2, 2′-bipyridyl and its derivative can also absorb energy and transfer to the rare earth ion [29, 30]. The ancillary ligand removes O-H groups from the inner coordination sphere of rare earth ion which enhance its luminescence intensity. The removal of solvent water molecules by aromatic heterocyclic N-donors ancillary ligand results in saturation of coordination sphere of rare earth ion and achieves coordination number higher than six which improves the photoluminescence intensity and thermal stability of the complexes [31].

Over the last decade, significant efforts have been devoted to the synthesis and pursuit of novel β-hydroxyketone ligands due to their potential application in the fabrication of OLEDs. In this section the synthesis and characterization of novel β-hydroxyketone ligand 2-hydroxy-4-methoxy-2-(4-chlorophenyl) acetophenone (CHME) has been reported. Utilizing this β-hydroxyketone ligand as the main ligand and 2, 2′-bipyridine (bipy) as ancillary ligand, novel Sm(III) complex was synthesized, characterized and their photoluminescent properties were studied in detail with the purpose of developing novel photoluminescent materials.

II. EXPERIMENTAL

A. Instrumental methods and materials

Samarium nitrate hexahydrate [$Sm(NO_3)_3.6H_2O$] and ancillary ligand were purchased from Sigma-Aldrich. The basic reactant for the synthesis of β-hydroxyketone ligand 2-hydroxy-4-methoxy-2-(4-chlorophenyl)acetophenone (CHME) were purchased from Hi-Media Pvt Ltd. The reagent employed were of analytical grade and used without any further purification. The structure was confirmed by elemental analysis, FT-IR and ^{1}H-NMR spectra.

Analysis of C, H, N and O were performed on thermo scientific flash 2000 elemental analyzer, while the samarium ion in the complex was estimated by complexometric titration with EDTA. The nuclear magnetic resonance spectra were recorded on Bruker Avance II 400 spectrometer (400 MHZ) in dimethylsulfoxide solution. FT-IR spectra were measured using KBr pellets with Perkin Elmer spectrum 400 FT-IR spectrophotometer in the spectral range 4000–400 cm^{-1}. The photoluminescence spectra such as excitation as well as emission spectra were recorded with Hitachi F-7000 fluorescence spectrophotometer with excitation and emission slits at 2.5 nm and with PMT at 400 V in solid state at room temperature. The Xenon lamp was the excitation source of fluorescence spectrophotometer. The spectra were recorded in digital form in the regions of 200-500 nm (excitation spectra) and 500-700 nm (emission spectra) for Sm(III) complex.

B. Synthesis 1 Synthesis of ligand 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME)

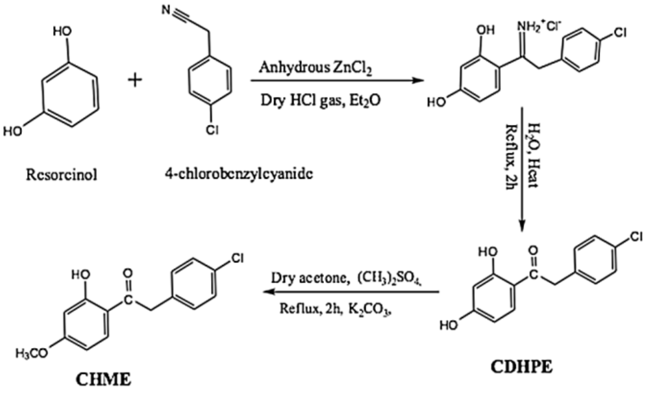
The ligand was synthesized in two steps by using Houben-Hoesch reaction mechanism between resorcinol and 4-chlorobenzylcyanide [32]. The first step involves the preparation of 2-(4-chlorophenyl)-1-(2, 4-dihydroxyphenyl) ethan-1-one (CDHPE) and the second step involves the preparation of 2-(4-chloro phenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME) which are described as follows:

a) Synthesis of 2-(4-chlorophenyl)-1-(2,4-dihydroxyphenyl)ethan-1-one (CDHPE):

A mixture of resorcinol (20 g), 4-chlorobenzylcyanide (15 g) and powdered anhydrous $ZnCl_2$ (4 g) were added in dry ether (100 mL). The mixture was cooled at 0 ^{O}C and rapid HCl gas was passed for 5 h. After leaving overnight in ice chest, the orange yellow precipitate of ketimine hydrochloride was separated by decanting ether and washed twice with dry ether (20 mL). The solid was refluxed with water (200 mL) for 1 h. On cooling 2-(4-chlorophenyl)-1-(2, 4-dihydroxyphenyl)ethan-1-one (CDHPE) was separated as pale yellow needles, which were filtered and dried at 120 ^{O}C.

b) Synthesis of 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME):

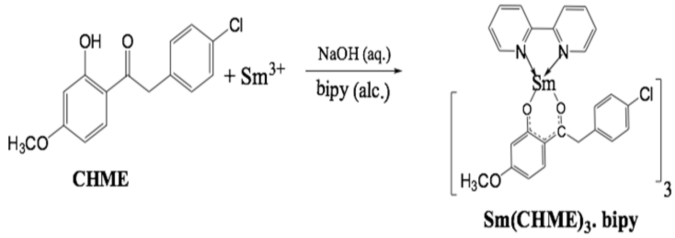
A solution of CDHPE (5 g) in dry acetone (50 mL) was refluxed with dimethyl sulphate (7.3 mL) and freshly ignited potassium carbonate (25 g) for 2 h. The inorganic salt was filtered and washed with hot acetone. Acetone was distilled off from filtrate and ice cold water was added to oily residue when colorless solid separated out. Solid was filtered, washed with water and recrystalized three times with methanol to give CHME. The progress of the reaction was monitored by thin layer chromatography. CHME was obtained as white crystals with 78 % yield, m.pt 219-220 ^{O}C. The synthetic route of ligand 2-(4-chlorophenyl)-1-(2-hydroxy-4-methoxyphenyl)ethan-1-one (CHME) is given in Scheme 1. The elemental analysis data for CHME ($C_{15}H_{13}O_3Cl$) was found (calc.) % C, 65.18 (65.10); H, 4.76 (4.73); O, 17.29 (17.34). IR (KBr) cm^{-1}: 3429 (b), 3055 (m), 3022 (w), 2940 (w), 2842 (w), 1650 (s), 1633 (s), 1596 (s), 1567 (s), 1494 (s), 1439 (s), 1351 (s), 1310 (m), 1291 (s), 1229 (s), 1207 (s), 1197 (s), 1084 (s), 1028 (s), 994 (s), 822 (s), 810 (s), 777 (s), 600 (s), 581 (s). ^{1}H-NMR (400MHz, DMSO): δ 3.83 (s, 3H, OCH$_3$), 4.18 (s, 2H, CH$_2$), 6.42 (s, 1H, Ar-H), 6.43 (s, 1H, Ar-H), 7.24 (d, 2H, Ar-H), 7.30 (d, 2H, Ar-H), 7.57 (s, 1H, Ar-H), 12.61 (s, 1H, OH).



Scheme 1. The synthetic route of ligand CHME.

c) Synthesis of complex Sm(CHME)$_3$.bipy :

Sm(CHME)$_3$.bipy complex was synthesized by adding 3 mmol CHME and 1 mmol of 2, 2′-bipyridine dissolved in ethanol to an aqueous solution of 1 mmol $Sm(NO_3)_3.6H_2O$ with constant stirring on magnetic stirrer. The pH value of the mixture was adjusted to 7-8 by adding 0.05 M NaOH aqueous solution. The mixture was stirred for 3 h at 35 ^{O}C and then allowed to stand for 1 h. White precipitates appeared in the reaction mixture which were purified by washing with deionized water and then with ethanol to remove the free ligand. Sm(CHME)$_3$.bipy complex was white powder with 80 % yield (Scheme 2). The elemental analysis data for Sm(CHME)$_3$.bipy ($C_{55}H_{44}O_9Cl_3N_2Sm$) was found (calc.) % C, 58.32 (58.27); H, 3.94 (3.91); O, 12.76 (12.70); N, 2.52 (2.47); Sm, 13.34 (13.26). IR (KBr) cm^{-1}: 3072 (w), 2938 (m), 1890 (w), 1626 (s), 1573 (s), 1521 (s), 1420 (s), 1360 (s), 1242 (s), 1221 (s), 1133 (s), 1092 (s), 1012 (m), 977 (m), 843 (m), 812 (m), 802 (m), 586 (m), 484 (m). ^{1}H-NMR (400MHz, DMSO): δ 3.78 (s,9H,OCH$_3$), 4.22 (s,6H,CH$_2$), 6.50 (bd, 6H, Ar-H), 7.32 (b, 14H, 12Ar-H, 2bipy), 8.21 (s, 3H, Ar-H), 8.48 (d, 2H, bipy), 8.82 (d, 2H, bipy), 9.34 (d, 2H, bipy).



Scheme 2. The synthetic route and structure of Sm(CHME)$_3$.bipy complex with CHME.

A. Elemental analysis and solubility

The general formula of the synthesized ligand and its corresponding Sm(III)complex was confirmed by the elemental analysis. The data of the elemental analysis is shown in Table 1. The experimental results of elemental analysis were in high agreement with the calculated data of the synthesized Sm(III) complex, indicating that the composition of the complex is consistent with the formula of ternary complex Sm(CHME)$_3$.bipy

III. RESULTS AND DISCUSSION

Table 1. Elemental analysis data for ligand CHME and its corresponding Sm(III) complex.

Complexes	H (%) Found (calc.)	H (%) Found (calc.)	N (%) Found (calc.)	O (%) Found (calc.)	Sm (%) Found (calc.)
CHME	65.18 (65.10)	4.76 (4.73)	---	17.29 (17.34)	---
Sm(CHME)$_3$.bipy	58.32 (58.27)	3.94 (3.91)	2.52 (2.47)	12.76 (12.70)	13.34 (13.26)

The solubility of the complex was investigated in various solvents. As expected the Sm(III) complex were soluble in DMSO, DMF, chloroform, dichloromethane and acetone, sparingly soluble in methanol and ethanol but insoluble in hexane and benzene. The ligand and its complex were stable under atmospheric condition.

B. ^{1}H-NMR and IR spectra

The ^{1}H-NMR spectra of the ligand CHME and the Sm(III) complex were measured in DMSO. Compared with those of the respective Sm(III) complex, the ^{1}H-NMR spectra of the ligand CHME shows a singlet at δ 13.84 due to phenolic proton. This proton signal of OH band disappeared in the spectra of Sm(III) complex, indicating that oxygen atom of the phenolic OH coordinated with the Sm(III) ion. In order to collect more information regarding regarding complex and the free ligand CHME, the FT-IR spectra were also investigated, the related data are given in Table 2. The infrared spectra of the ligand CHME and its corresponding Sm(III) complex were measured in KBr pellets in the range 4000-400 cm^{-1}. The broad band appeared in the range 3500-3200 cm^{-1} centred at 3429 cm^{-1}, which was a typical peak of free OH stretching vibration in the spectrum of ligand, which was absent in the ternary complex, indicating that ligand was coordinated with Sm(III) ion through oxygen atom of phenolic group. The spectrum of CHME showed an intense band at 1633 cm^{-1}, which corresponds to the C=O stretching vibration band of carbonyl group. After coordination the C=O stretching frequency of the complex were red shifted to 7 cm^{-1} indicating that oxygen atoms in the carbonyl group were also coordinated with Sm(III) ion [33].

Table 2. The characteristic IR bands (cm-1) of the free ligand CHME and its corresponding Sm(III) complex.

Complexes	**ν(O-H)**	**ν(C=O)**	**ν(C=N)**	**ν(C=C)**	**ν(Ph-O)**	**ν(Sm-N)**	**ν(Sm-O)**
CHME	3429	1633	---	1567	1229	---	---
complex	---	1626	1573	1521	1221	586	484

A new absorption band appeared at 1573 cm^{-1} in the spectrum of complex, assigned to ν(C=N), indicating that nitrogen atom of the ancillary ligand participated in the coordination with the central metal ion. It was further confirmed by the presence of medium intensity band at 586 cm^{-1} attributed to the ν(Sm-N) band due to introduction of ancillary ligand [34, 35]. The appearance of ν(Sm-O) band at 484 cm^{-1} supports the chelation through the oxygen atom of the free ligand [36, 37]. Overall, the result of ^{1}H-NMR and infrared spectra indicated that the free ligand CHME was coordinated with Sm(III) ion through the phenolic hydroxyl group, carbonyl group and nitrogen atoms of the ancillary ligand 2, 2′-bipyridine.

C. Photoluminescent properties

The photoluminescent properties of free ligand CHME and its corresponding Sm(III) complex were investigated in the solid state at room temperature as depicted in Fig.1 and 2 respectively and collected data are tabulated in Table 3. The solid state excitation spectra of complex was investigated by monitoring emission at λ_{em} = 601 nm. The excitation spectrum of free CHME was also measured in order to understand the nature of excitation of complex. The excitation spectrum of free ligand shows two band in the region 300-440 nm, with peak maxima centred at 382 nm due to π-π* transition in the ligand, this excitation band red shifted by 3 nm with an enhanced intensity due to chelation between the Sm^{3+} ion and ligand. This suggest that the electronic transitions are mainly responsible for the excitation of the Sm(III) ion which are forbidden due to low molar extinction coefficient. Moreover, in the excitation spectrum of complex two more excitation bands are identified in the range 300-500 nm, which are assigned to electronic transitions of $^6H_{5/2} \rightarrow {}^4I_{13/2}$ (462 nm) and $^6H_{5/2} \rightarrow {}^4I_{11/2}$ (477 nm) of the Sm(III) ion [38]. Only the prominent excitation band at 385 nm has been selected for the measurement of emission spectrum of Sm(III) complex because other two excitation band did not give significant results in the emission spectra. The emission spectrum of complex was recorded in solid state at room temperature on monitoring excitation at λ_{ex} = 385 nm are shown in Fig.3. The emission spectrum was also recorded at λ_{ex} = 462 and 477 nm but no significant results were observed. The photoluminescence emission spectrum consists of three main emission

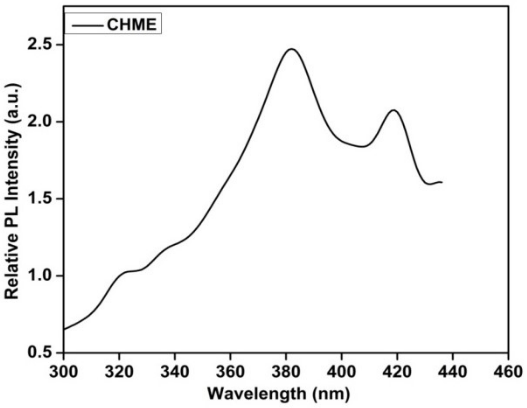


Figure 1. Photoluminescence excitation spectrum of ligand CHME in solid state at room temperature.

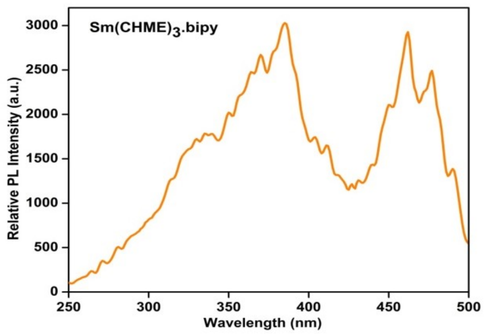


Figure 2. Photoluminescence excitation spectra of Sm(CHME)$_3$.bipy, monitored at λ_{em} = 601 nm in solid state at room temperature.

peaks with different intensity at 564 nm, 601 nm and 646 nm which belong to the transitions of ($^4G_{5/2}\rightarrow{}^6H_{5/2}$), ($^4G_{5/2}\rightarrow{}^6H_{7/2}$) and ($^4G_{5/2}\rightarrow{}^6H_{9/2}$) respectively of Sm^{3+} ion [39]. Among these three characteristic transitions, the magnetic–electric dipole transition of Sm^{3+} ion $^4G_{5/2}\rightarrow{}^6H_{7/2}$ at 601 nm exhibits an intense orange emission. It is important to mention that after the introduction of N-donors ancillary ligands in the ternary complex, the photoluminescence intensity of the Sm^{3+} ion was further enhanced. The ancillary ligands replaced the coordinated water molecules from the coordination sphere of the complex because thermal vibration of water molecules would consume part of the energy absorbed by the ligand, which decrease the photoluminescence intensity of rare earth complex.

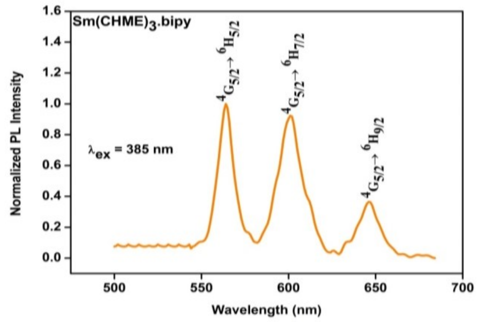


Figure 3. Photoluminescence emission spectra of Sm(CHME)$_3$.bipy in solid state at room temperature, monitored at λ_{ex} = 385 nm.

The photoluminescence decay curves for rare earth Sm(III) complex was monitored at λ_{em} = 601 nm and λ_{ex} = 385 nm of the Sm^{3+} ion. Fig.4 depicts the decay curve of complex in solid state at room temperature. The lifetime value were calculated by applying 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 decay curve of the luminescent complex shows monoexponential behaviour, which suggests the presence of single Sm^{3+} ion luminescent species in the chemical environment of the complex and having only one site symmetry in the complex, which resemble with the emission spectra of the complex. The life time values calculated for complex was found to be 0.956 ms. It was found that the value of lifetime becomes longer with the increasing π-conjugation system with the introduction of ancillary ligand in the complex.

Generally, the replacement of water molecules (strong luminescence quenchers) with N-Donors ancillary ligand increases the polarizability of Sm^{3+} ion chemical environment.

Table 3. Photoluminescence data, decay time and color coordinates of Sm(CHME)3.bipy

Sm(CHME)$_3$.bipy	**λ_{ex} (nm)**	**λ_{em} (nm)**	**Assignment**	**τ (ms)**	***x* and *y* coordinates**
	385	546	$^4G_{5/2}\rightarrow{}^6H_{5/2}$	0.956	0.4356, 0.4966
		600	$^4G_{5/2}\rightarrow{}^6H_{7/2}$		
		646	$^4G_{5/2}\rightarrow{}^6H_{9/2}$		

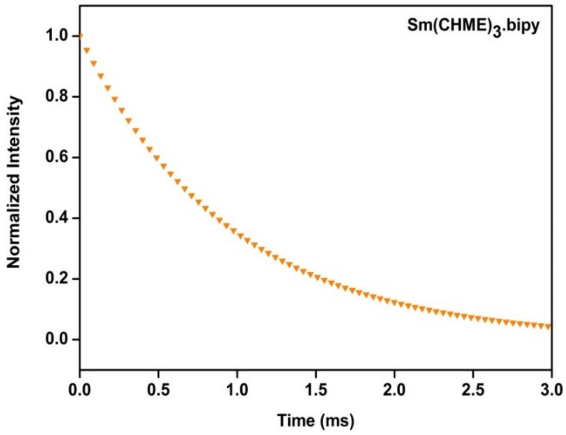


Figure 4. Luminescence decay curve for Sm(CHME)$_3$.bipy in solid state at room temperature, monitored at λ_{ex} = 385 nm and λ_{em} = 601 nm.

In order to confirm the emission color of rare earth Sm(III) complex, the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates was calculated from their corresponding photoluminescent spectra excited at λ_{ex} = 385 nm of the Sm^{3+} ion. The CIE color coordinates (*x*, *y*) of the complex is located at 0.4356, 0.4966 which lie in orange spectral region as shown in Fig.5, suggesting promising application of the complex in organic light emitting devices.

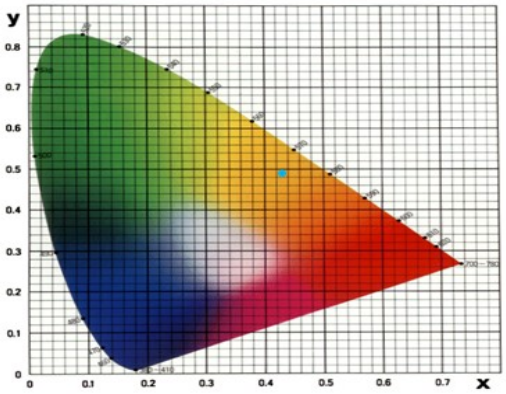


Figure 5. CIE colour coordinates of Sm(CHME)$_3$.bipy

IV. CONCLUSION

In conclusion, a new orange light emitting complex Sm(CHME)3.bipy was synthesized successfully and its structure was confirmed by elemental analysis , FT-IR, ^{1}HNMR and photoluminescence spectroscopy. The emission spectra for the complex displayed characteristic emission lines for samarium ion in solid state. The decay curve of the luminescent complex shows monoexponential behaviour, which suggests the presence of single Sm^{3+} ion luminescent species in the chemical environment of the complex and having only one site symmetry in the complex. The CIE color coordinates (*x*, *y*) of the complex is located in orange spectral region suggesting promising application of the complex in orange light emitting devices.

V. ACKNOWLEDGEMENTS

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