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Synthesis and Efficient Photoluminescence Properties of europium (III) Complexes by Adding Second Ancillary Ligands.

Satish Kumar¹, Manju Bala¹, Dayawati², VB Taxak¹, and SP Khatkar^{1*}.

¹Department of Chemistry, Maharshi Dayanand University, Rohtak 124001, Haryana, India.

²Govt. PG College, Jhajjar 124103, Haryana, India.

ABSTRACT

The synthesis and photoluminescence characteristics of europium (III) metal complexes with organic ligand HMBP (where HMBP = 2-hydroxy-4-methoxy benzophenone) and second ancillary ligand such as 2,2'-bipyridyl (bipy) and 2,2'-biquinoline (biq) are reported. The ligand HMBP was synthesized by eco-friendly microwave method in solvent free condition. The synthesized europium complexes as well as ligand HMBP were characterized by elemental analysis, ¹H-NMR, FT-IR, photoluminescence (PL) spectroscopy. The luminescence properties of the complexes showed that the Eu(III) ion could be sensitized more efficiently by the ligand and second ancillary ligands containing nitrogen atom further enhanced the luminescent intensity of the europium (III) ternary complexes relative to Eu(HMBP)₃.H₂O binary complex. In addition to excitation and emission spectra, CIE chromaticity coordinate diagram, decay curve and relative quantum yield were calculated and analyzed to support the photophysical properties of the europium (III) complexes.

Keywords: Photoluminescence, europium (III) ternary complexes, infrared (IR), 2,2'-biquinoline, relative quantum yield

**Corresponding author*

INTRODUCTION

Recently europium (III) β -diketonate complexes have received great attention due to their excellent luminescence properties with high color purity and extremely sharp emission bands in the visible range [1-3]. These complexes exhibit a wide range of promising applications in chemical sensing [4-5], bioassays [6], telecommunication [7], optoelectronic devices [8] having potential comparable to the next generation low cost flat panel displays and as a sensor/ labels in biomedical diagnosis. Among the numerous organic ligands, hydroxy derivative of ketone possess negative charged binding sites that lead to formation of neutral metal-ligand complexes [9]. These have high absorption coefficient within a large wavelength range which is consequence of extended π -conjugated system and targeted to effective sensitization of europium metal ion to emit in red region which shifts its excitation band of complexes to visible region [10-14]. During this sensitization, europium metal ion gets excited through the excitation energy provided by the ligand via its triplet energy levels [15-16]. Europium (III) complexes exhibited efficient energy transfer from excited ligand to chelated europium ion leading to intense emission and high luminescence relative to ligand to metal energy transfer and radiative and non-radiative processes of the complexes [17-21]. The photophysical properties can be facilitated by introducing aromatic heterocyclic compounds containing nitrogen atoms as a second ligand such as 2,2'-bipyridyl and 2,2'-biquinoline. These second ligands further enhance the luminescence by satisfying the high co-ordination number of central europium ion and through easy charge transfer via flattening of structure. In the present report, the ligand HMBP is used as the first ligand and nitrogen heterocyclic ligands are used as second ligand in order to synthesize new europium complexes. These new europium complexes were characterized by elemental analysis, FT-IR, $^1\text{H-NMR}$ and PL spectroscopy. In addition to photoluminescence, decay curve and relative quantum yield were calculated and analyzed.

EXPERIMENTAL

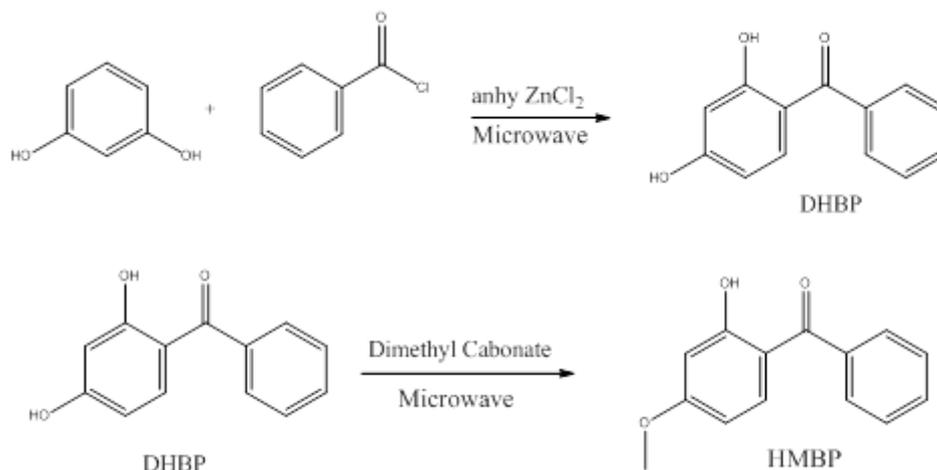
Materials and Instrumentation

All the solvents employed in this study were reagent grade and used without further purification. High purity europium nitrate $[\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ was purchased from sigma Aldrich and the ligand HMBP was synthesized and recrystallized three times in ethanol. The elemental analysis (C, H, and N) was performed using a Perkin Elmer 2400 CHN Elemental Analyzer. By exploiting complexometric titration using hexadentate ethylenediaminetetracetate (EDTA) the percentage of Eu(III) was determined. The $^1\text{H-NMR}$ spectra were measured with a Bruker Avance II 400 NMR spectrometer in dimethyl sulphoxide (DMSO) as a solvent with tetramethyl silane (TMS) as internal standard. The FT-IR spectra were recorded in the $4000\text{-}400\text{ cm}^{-1}$ region on a Perkin Elmer Spectrum 400 spectrometer with KBr pellets. Excitation spectra, emission spectra and luminescence lifetime were performed on a HITACHI F-7000 fluorescence spectrophotometer (xenon lamp). Luminescence quantum yields for Eu (III) complexes were measured by using 1, 8-ANS (1-anilino-8-naphthalene sulphonic acid) as a reference compound. All the measurements were recorded at room temperature in solid state.

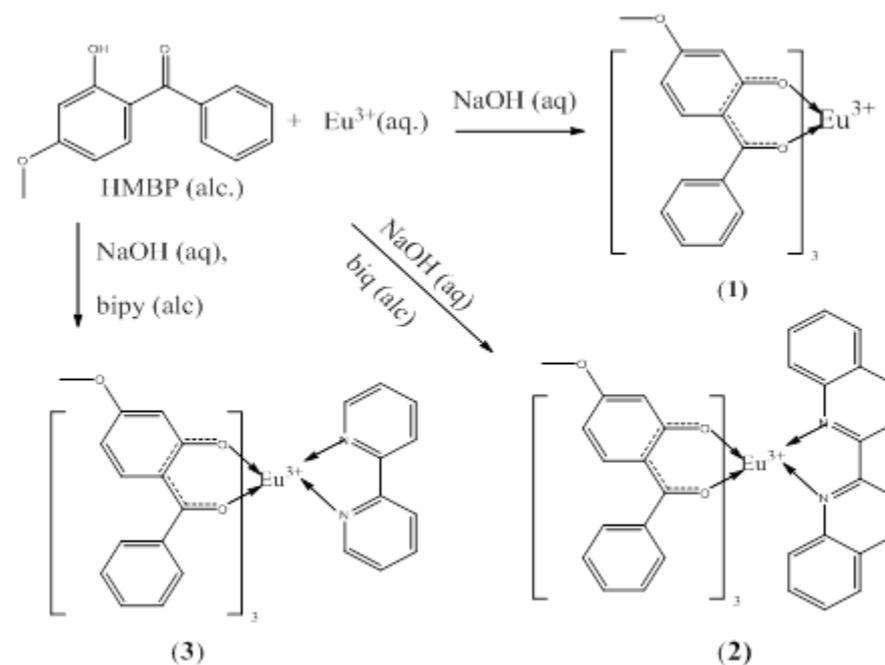
Synthesis of ligand

2,4-dihydroxy benzophenone (DHBP): To the mixture of resorcinol and benzoyl chloride add anhydrous zinc chloride in the 1:1 ratio for the 55 seconds at the temperature $50\text{-}55^\circ\text{C}$ in solvent free condition under microwave irradiation. Zinc chloride catalyzed the Friedel-Craft acylation reaction. Pale yellow powder obtained was recrystallized three times with ethanol. The yield and melting point of the resulting product was found to be 70% and 145°C (lit $144\text{-}146^\circ\text{C}$) respectively [22].

2-hydroxy-4-methoxy benzophenone (HMBP): HMBP was synthesized from 2,4-dihydroxy benzophenone and dimethyl carbonate (DMC) using microwave irradiation procedure as described above. The solid residue was recrystallized from ethanol. HMBP obtained as a light yellow solid with yield 52% and melting point to be noted 65°C ; IR (KBr): cm^{-1} 3431 (b), 3174 (w), 3068 (w), 2945 (w), 2841 (w), 2727 (w), 1636 (s), 1589 (m), 1506 (s), 1434 (s), 1386 (s), 1262 (m), 1101 (m), 1024 (m), 911 (m), 816 (m), 709 (m), 602 (m); $^1\text{H-NMR}$ (400 MHz, DMSO): δ 12.34 (s, 1H, OH), 7.62 (d, 1H, Ar-H), 7.61 (m, 2H, Ar-H), 7.57 (m, 2H, Ar-H), 7.46 (m, 1H, Ar-H), 6.60 (d, 1H, Ar-H), 6.55 (s, 1H, Ar-H), 3.82 (s, 3H, OCH₃).



Scheme 1: The synthetic route of the ligand HMBP



Scheme 2: The synthetic route and structure of the europium (III) complexes

Synthesis of europium complexes

Eu(HMBP)₃·H₂O (**1**): A solution of HMBP (6.2 mmol) in ethanol was added dropwise to a solution of europium nitrate (2.0 mmol) in water under constant stirring at 50-60°C for 2-3 hours. The pH was adjusted between 6.5-7.0 by adding 0.05 M aqueous solution of sodium hydroxide, pale yellow precipitate obtained, were separated by filtration, washed with distilled water and then with ethanol, dried at 50°C and finally in a vacuum desiccator.

Eu(HMBP)₃·H₂O (**1**): yellow powder, yield 84%; IR (KBr):cm⁻¹ 3063 (w), 2944 (w), 2837 (w), 1605 (s), 1595 (s), 1519 (s), 1446 (m), 1410 (m), 1244 (s), 1161 (m), 1030 (m), 970 (m), 840 (m), 697 (m), 554 (w), 471 (w); ¹H-NMR (400 MHz, DMSO): δ 8.21 (d, 3H, Ar-H), 8.03 (m, 6H, Ar-H), 7.48 (m, 6H, Ar-H), 7.35 (d, 3H, Ar-H), 7.04 (s, 3H, Ar-H), 6.58 (m, 3H, Ar-H), 3.81 (s, 9H, OCH₃); Anal. Cal. for EuC₄₂H₃₇O₁₁: C, 57.99; H, 4.25; Eu, 17.49; Found C, 57.74; H, 4.27; Eu, 17.28.

Eu(HMBP)₃·biq (**2**): A mixture of 2, 2'-biquinoline (2.0 mmol) and HMBP (6.2 mmol) was dissolved in ethanol and added to the aqueous solution of europium nitrate (2.0 mmol). The resulting mixture was stirred

and then follows the above complex formation procedure. The complex **2** was obtained as a yellow powder. In similar way, as adopted in the synthesis of complex **2** other europium complexes (**3**) were synthesized with the mixture of 2, 2'-bipyridyl (2.0 mmol) and HMBP (6.2 mmol) in ethanol and aqueous solution of europium nitrate (2.0 mmol).

Eu(HMBP)₃.biq (**2**): yellow powder, yield 82%; IR (KBr):cm⁻¹ 3052 (w), 2944 (w), 2837 (w), 1601 (s), 1565 (m), 1517 (s), 1446 (m), 1363 (m), 1256 (m), 1113 (s), 1030 (m), 970 (m), 840 (m), 756 (m), 697 (m), 602 (m), 554 (w), 459 (w), 412 (w); ¹H-NMR (400 MHz, DMSO): δ 8.41 (m, 4H, Ar-H), 8.21 (m, 4H, Ar-H), 8.03 (m, 4H, Ar-H), 7.47 (d, 3H, Ar-H), 7.43 (m, 6H, Ar-H), 7.32 (m, 6H, Ar-H), 7.23 (d, 3H, Ar-H), 6.52 (s, 3H, Ar-H), 6.49 (m, 3H, Ar-H), 3.83 (s, 9H, OCH₃); Anal. Cal. for EuC₆₀H₄₅N₂O₉: C, 66.97; H, 4.18; N, 1.30; Eu, 14.13; Found C, 66.18; H, 4.12; N, 1.02; Eu, 14.01.

Eu(HMBP)₃.bipy (**3**): yellow powder, yield 82%; IR (KBr):cm⁻¹; 3063 (w), 2944 (w), 2837 (w), 1601 (s), 1517 (s), 1519 (s), 1446 (m), 1363 (m), 1244 (s), 1113 (s), 1030 (m), 970 (m), 840 (m), 756 (m), 697 (m), 602 (m), 552 (w), 471 (w), 412 (w); ¹H-NMR (400 MHz, DMSO): δ 8.67 (m, 2H, Ar-H), 8.23 (m, 6H, Ar-H), 7.57 (m, 6H, Ar-H), 7.51 (m, 3H, Ar-H), 7.33 (m, 6H, Ar-H), 7.23 (d, 3H, Ar-H), 6.52 (d, 3H, Ar-H), 6.49 (s, 3H, Ar-H), 3.84 (s, 9H, OCH₃); Anal. Cal. for EuC₅₂H₄₁N₂O₉: C, 64.00; H, 4.23; N, 1.43; Eu, 15.58; Found C, 63.85; H, 4.01; N, 1.08; Eu, 15.35.

RESULT AND DISCUSSION

The composition and structure of Eu(III) complexes was analyzed by elemental analysis and spectroscopic studies. Elemental analysis was performed on Perkin-Elmer 2400 Elemental Analyzer and data of the analysis is tabulated in table 1.

It can be seen that stoichiometric ratio of the metal, ligand and second ligand is to be 1:3:1 in complexes. The results of the elemental analysis are in agreement with the calculated values assigned to the corresponding complexes.

Table 1: Elemental analytical data of complexes

Complexes	C(%) found (cal.)	H(%) found (cal.)	N(%) found (cal.)
1	57.74 (57.99)	4.27 (4.25)	-
2	66.18 (66.97)	4.12 (4.18)	1.02 (1.30)
3	63.85 (64.00)	4.01 (4.23)	1.08 (1.43)

Spectroscopic studies

FT-IR spectra of the complexes recorded on Perkin Elmer Spectrum 400 spectrometer and summarized in table 2. The IR spectra of ligand HMBP shows marked changes in comparison to their Eu(III) complexes which ascertained the formation of the complexes. The broad band of the -OH group in ligand at 3431 cm⁻¹ disappeared in complex indicating that -OH group is coordinated with the europium (III) metal ion. The >C=O stretching band of ligand at 1636 cm⁻¹ exhibited a lower shift in the complexes due to complexation of ligand with the metal ion through keto group. The Ph-O vibration of complexes appeared at lower value relative to ligand and indicated that -OH group included in the co-ordination with Eu³⁺. The new bands at 459-472 cm⁻¹ appeared in spectra of complexes only due to metal-oxygen vibrations and the bands in the range 549-554 cm⁻¹ assigned to the coordinated Eu-N vibrations in the spectra of complexes only.

Table 2: The characteristics IR bands (cm⁻¹) of the free ligand and the complexes

Compounds	v(O-H)	v(>C=O)	v(Ph-O)	v(Eu-N)	v(Eu-O)
HMBP	3431.32 (b)	1636.63 (s)	1262.20 (s)	-	-
1	-	1605.33 (s)	1253.41 (s)	-	463.98 (w)
2	-	1601.64 (s)	1256.72 (s)	554.87 (w)	459.82 (w)
3	-	1601.64 (s)	1244.72 (s)	552.42 (w)	471.89 (w)

b = broad, s = strong, m = medium, w = weak

The $^1\text{H-NMR}$ spectra of ligand and europium (III) complexes show the proton signal of O-H at 12.34 ppm in ligand disappeared in spectra of europium complexes which indicated that –OH group is involved in complexation with metal ion. The chemical shifts of aromatic protons moved to down field as a result of coordination of ligand HMBP to the central metal ion. These spectroscopic evidences indicated that the europium (III) ion is coordinated to main ligand via oxygen's of the carbonyl and hydroxyl group, while coordinated to the second ligand i.e. bipy or biq through nitrogen atoms.

Photophysical properties

The photoluminescence characteristics of synthesized europium (III) complexes **1-3** in solid state at room temperature are presented in Table 3. The excitation and emission spectra of europium complexes are depicted in Fig 1. The excitation spectra of **1-3** complexes were recorded by monitoring the strongest emission of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu(III) ion at 611 nm (**1**) and 613 nm (**2-3**) in the inset of Fig. 1 (a-c).

Table 3: Luminescence data and color coordinates of complexes

Complexes	$\lambda_{\text{ex.}}$ (nm) $^7\text{F}_0 \rightarrow ^5\text{L}_6$	$\lambda_{\text{em.}}$ (nm) $^5\text{D}_0 \rightarrow ^7\text{F}_2$	(x) and (y) coordinates	τ (ms)
1	396.7	611.10	0.5214, 0.3481	0.21
2	397.8	613.10	0.5134, 0.3316	0.27
3	396.6	613.10	0.5213, 0.3290	0.30

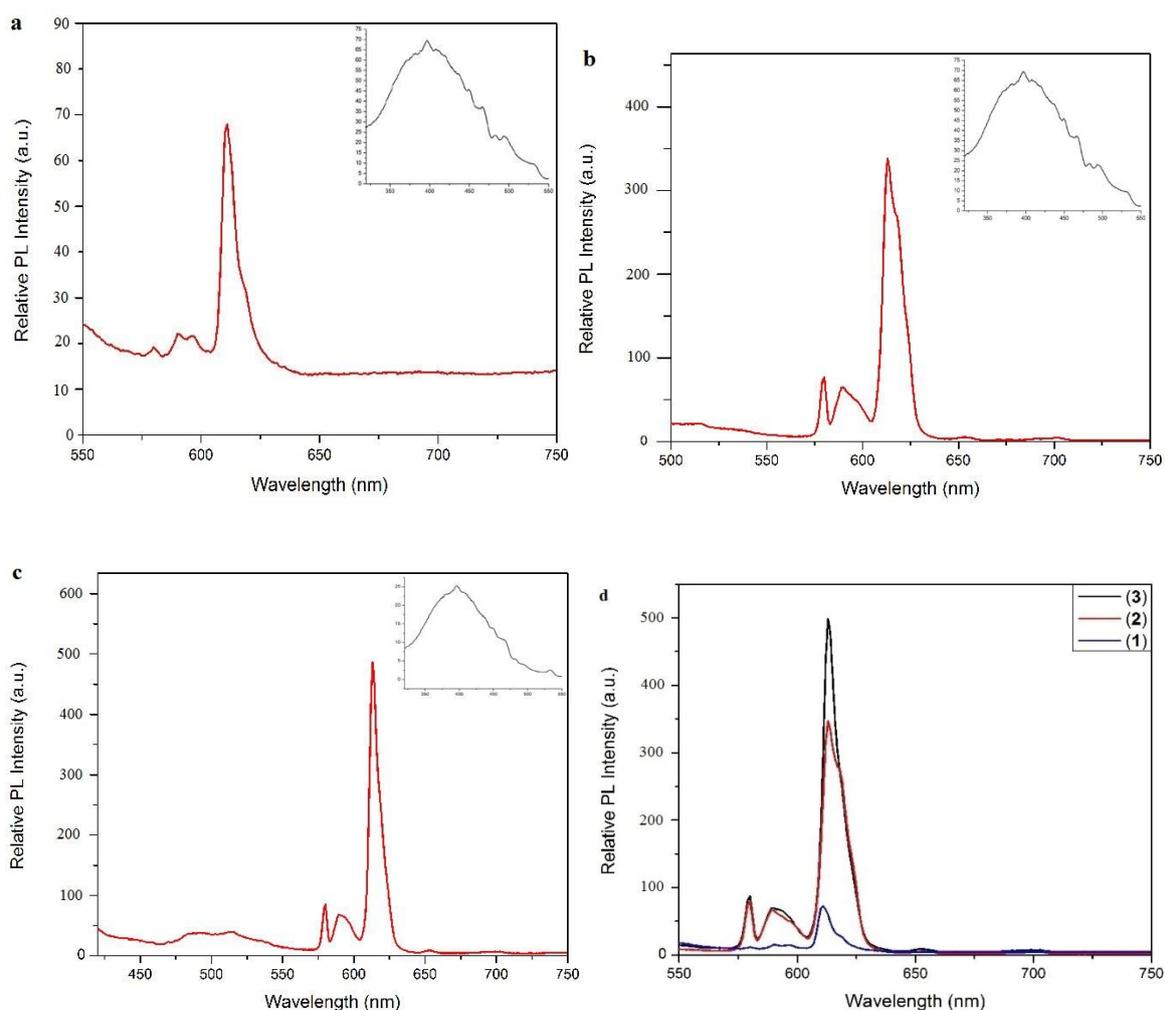


Figure 1: The luminescence excitation spectra (inset) and emission spectra of europium (III) complexes 1-3 (a-c, respectively) in solid state at room temperature. Comparison of emission intensities of complexes 1-3 (d) excited at 396 nm (1, 2) and 397 nm (3).

The spectra of these complexes show a broad band at 320-390 nm, which assigned to the $\pi\text{-}\pi^*$ electronic transition of ligand (HMBP). In addition, sharp band at 396 nm (**1**, **2**) or 397 nm (**3**), 416, 465 and 530 nm were attributed to ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_3$, ${}^7F_0 \rightarrow {}^5D_2$ and ${}^7F_0 \rightarrow {}^5D_1$ transition of europium (III) ion [23]. The emission spectra of Eu(III) complexes at room temperature upon excitation at 396 nm (**1**, **2**) and 397 nm (**3**) are shown in Fig.1. The emission spectra of complexes **1-3** show characteristics peaks of Eu(III) in range 550-750 nm which were assigned to the transition from the excited state 5D_0 to its low lying multiple level 7F_j ($j = 0, 1, 2, 3, 4$) of metal ion. The strongest peak at 611 nm (**1**) and 613 nm (**2-3**) associated with the intense ${}^5D_0 \rightarrow {}^7F_2$ transition of metal ion. The emission band ${}^5D_0 \rightarrow {}^7F_2$ at 611 or 613 nm is distinctly higher in intensity than the ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$ transition corresponding to the bands around 580 nm, 590 nm, 652 nm and 701 nm respectively. The strongest transition ${}^5D_0 \rightarrow {}^7F_2$ is an electric dipole transition and their intensity is hypersensitive to the coordination environment [24] and the transition ${}^5D_0 \rightarrow {}^7F_1$ is a parity-allowed magnetic dipole transition whose intensity is non-sensitive to the coordination environment [25]. The intensity ratio of ${}^5D_0 \rightarrow {}^7F_2$ and ${}^5D_0 \rightarrow {}^7F_1$ transitions showed that chemical environment around the europium (III) ion is highly polarizable and devoid of an inversion center. The spectra in Fig. 1-d clearly reveals that luminescence intensity of complexes **2-3** containing second ligand is greater than complex **1** which is consequence of extended π -conjugated system of second ligand. The color coordinates (x and y) of these europium (III) complexes observed from their emission spectra are listed in Table 3. The results are shown in Fig.2 which shows the bright red emission of complexes **1-3**.

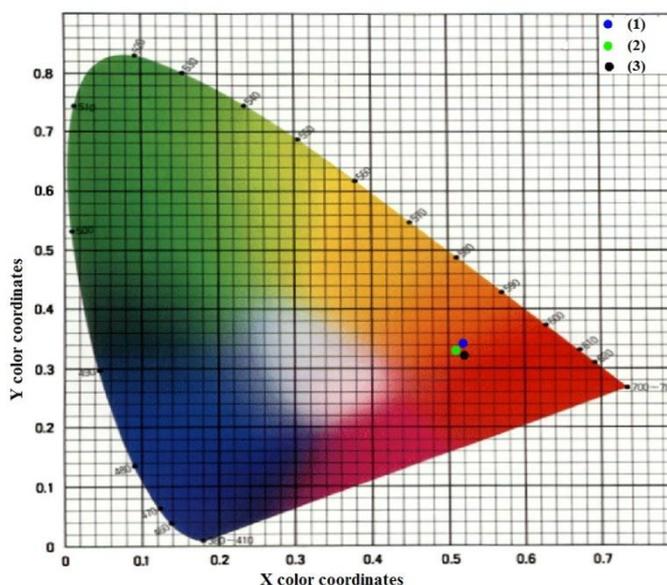


Figure 2: CIE coordinates of the europium (III) complexes **1-3** in solid state at room temperature.

The emission color of all the three complexes were analyzed and confirmed with the help of CIE (commission de l'Eclairage) chromaticity coordinate diagram. Careful analysis revealed that the chromaticity coordinates for complex **3** ($x = 0.5213$, $y = 0.3290$) is more pure red than the complexes **1** ($x = 0.5214$, $y = 0.3481$), and **2** ($x = 0.5134$, $y = 0.3316$).

Luminescence decay time (τ) and relative quantum yield (η)

The photoluminescence properties of europium complexes **1-3** explained and understood in better way, the luminescence decay curves of the 5D_0 state of the Eu^{3+} complexes at room temperature in solid state were measured by monitoring the most intense ${}^5D_0 \rightarrow {}^7F_2$ transition at 611 or 613 nm and depicted in fig.3.

The decay curves of the complexes **1-3** exhibited mono-exponential behavior ($I = I_0 e^{-t/\tau}$ where I and I_0 are the luminescence intensities at time t and 0 respectively), indicating the presence of single chemical environment around the europium metal ion present in complexes. The decay time values (τ) of the complexes **1-3** are 0.21, 0.27, 0.30 ms respectively which were obtained from decay curves of the complexes and are tabulated in Table 2. The quenching of stretching vibrations of complex **1** may lead to its lower value as compared to complex **2** and **3**. The long lifetime values of complexes **2-3** relative to binary complex **1** can be attributed to the formation of the ternary system in complexes **2-3** [26]. The relative quantum efficiency by

using the 1,8-ANS as a reference compound were also investigated by monitoring the excitation and emission spectra of the complexes **1-3** and values found to be 1.0644, 0.817 and 0.0674 respectively. The luminescence quantum efficiency (η) and decay time (τ) of these complexes indicated that sensitization of europium metal ion by the ligand HMBP in presence of ancillary ligand like bipy or biq is more efficient and facilitate the energy transfer from ligand to central europium ion.

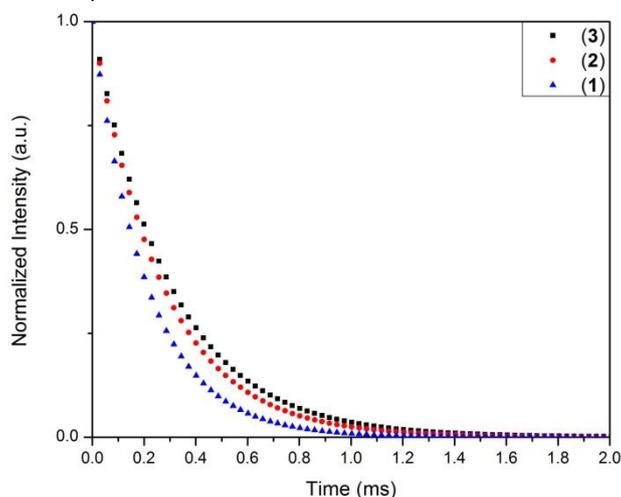


Figure 3: Luminescence decay curve for complexes **1-3** in solid state at room temperature monitored at 611 nm (**1**), and 613 nm (**2-3**).

CONCLUSION

In this work, the complex of 2-hydroxy-4-methoxybenzophenone with Eu^{3+} in ethanol solution have been synthesized and characterized. The emission spectra of all complexes display brilliant red luminescence characteristics of Eu^{3+} metal ion in visible region. The results of all the photophysical properties showed the presence of polarized chemical environment around the europium ion. The luminescence intensity, decay time (τ) and relative quantum yield (η) of complex **1** is further enhanced greatly by introduction of second ancillary ligands like bipy and biq. The photophysical properties show that Eu^{3+} metal ion is highly sensitized by ligand HMBP and secondary ligands which leads to longer decay time of the europium ternary complexes relative to complex **1**. The CIE chromaticity coordinate presented high red color purity. Brilliant photoluminescent behavior of these europium (III) complexes facilitated their promising applications as emitter in fabricating organic light emitting devices (OLEDs).

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