

# Luminescence and Electronic Spectral Studies of Some Synthesized Lanthanide Complexes Using Benzoic Acid Derivative and *o*-Phenanthroline

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**Abstract** Lanthanide complexes of *p*-nitrobenzoic acid (*p*-NBA) and *o*-phenanthroline (*o*-phen) namely  $[\text{Ln}_2(\text{Phen})_2(\text{p-NBA})_3(\text{NO}_3)_2] \cdot 2\text{H}_2\text{O}$  where, Ln = Sm(III), Tb(III), Dy(III) and  $[\text{Eu}_2(\text{Phen})_2(\text{p-NBA})_3] \cdot 4\text{H}_2\text{O}$  were synthesized and further characterized by Elemental analysis, UV spectroscopy, IR spectroscopy, <sup>1</sup>HNMR spectroscopy. Luminescence measurements were performed on all compounds in ethanolic solution. These complexes have showed narrow emission indicating that the organic ligands are better energy absorber and capable of transferring energy to the Ln (III) ion. Furthermore, we reported electronic spectral studies on  $[\text{Eu}_2(\text{Phen})_2(\text{p-NBA})_3] \cdot 4\text{H}_2\text{O}$  in order to calculate following parameters, viz: Oscillator strength (*f*), Judd–Ofelt parameters  $\Omega_\lambda$  ( $\lambda=2,4,6$ ) and Radiative parameters.  $[\text{Eu}_2(\text{Phen})_2(\text{p-NBA})_3] \cdot 4\text{H}_2\text{O}$  showed the strongest emission at 613 nm corresponds to  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  hypersensitive transition, this emission is very sensitive to the environment. However, the larger value of  $\Omega_2$  supports the presence of the hypersensitive transition  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  which strictly depends on the nature of ligand. All electronic spectral parameters were calculated systemically.

**Keywords** Lanthanides · *p*-nitrobenzoic acid (*p*-NBA) · *o*-phenanthroline (*o*-phen) · Luminescence · Hypersensitive transition · Radiative parameters

## Introduction

Lanthanides exhibit characteristic luminescence emissions due to their unfilled  $-4f$  orbital, where electrons are well shielded by the outer electrons and are hardly involved in bonding. Highly luminescent lanthanide complexes can be basically attained by an efficient ligand. First, light is to be absorbed by the attached organic ligands (chromophores). This absorbed energy is then transferred onto one or several excited states of the metal ion, and, finally, the metal ion radiates the absorbed energy. The efficacy of energy transfer can be attained by adjusting the energy gap between the lowest triplet state of the ligand and the emitting level Ln (III) [1, 2]. Hence, it is necessary to use a suitable organic ligand which can alter the luminescence property [3]. All these highly luminescent lanthanide complexes are found in visible region [4]. The unique electronic properties of Ln(III) includes (larger shift values, longer relaxation time, sharp emission peaks) which makes them capable for various applications. Therefore, Lanthanides are extensively used in designing of chemical and biological sensors, and optical devices [5].

It was observed that incorporation of a neutral ligands like (2, 2'-bipyridine, *o*-phenanthroline, etc.) in lanthanide complexes, raises the quantum yield [6, 7]. However, aromatic carboxylates are also used as sensitizing ligands for enhancing lanthanide luminescence property, as they can chelate effectively and can enhance luminescence *via* anionic carboxylate groups [8]. Many ternary lanthanide complexes were prepared with -N containing compounds such as, *o*-phenanthroline or 2, 2'-bipyridyl and benzoic acid derivatives. The ternary complexes of Gd (III), Eu(III), and Tb(III) with aromatic carboxylic acids and *o*-phenanthroline as a second ligand have been synthesized by Yan et al. [9–12].  $[\text{Dy}(\text{p-NBA})_3\text{Phen}]_2 \cdot 3\text{H}_2\text{O}$  and  $[\text{Dy}(\text{m-NBA})_3\text{Phen}]_2 \cdot 4\text{H}_2\text{O}$  complexes were prepared and their thermal studies have been reported [13]. Hilder

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et al. synthesized several complexes of Eu (III) and Tb (III) with *o*-, *m*- and *p*-nitrobenzoic acids and studied their photophysical properties [14]. Lanthanides such as Eu (III) and Tb (III) have been intensively studied for their intense, long-lived emission in the visible region, which enable them to be used in various applications ranging from biological assays to display devices and many more [15]. Some workers have calculated the radiative lifetime of Nd (DTPA)<sup>2-</sup>, Yb (DTPA)<sup>2-</sup> [16]. The sizeable energy gap displayed by Eu (III) and Tb (III) explains why luminescent probes containing these ions have been so popular during the last decades. In the present work luminescence properties of the synthesized complexes have been studied. Electronic spectral studies on Eu (III) complex is possible because of availability of reduce matrix values in literature.

## Experiment

The following chemicals of analytical grade were procured commercially and used without further purification. Sm(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Dy(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, Tb(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, EuCl<sub>3</sub>·5H<sub>2</sub>O were obtained from CDH (India).

## Synthesis

### [Sm<sub>2</sub>(Phen)<sub>2</sub>(*p*-NBA)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O Complex 1

0.2 mmol of 1,10-phenanthroline and 0.6 mmol of *p*-nitrobenzoic acid were dissolved in appropriate amount of ethanol, the pH was adjusted to 6–7 by using 1.0 mol/L NaOH solution to obtain the ligand solution. Again, 0.2 mmol of Sm (NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O was dissolved in C<sub>2</sub>H<sub>5</sub>OH. After that the ligand solution was added slowly into the Ln (III) solution and then the resulting solution was stirred for 1 hr. Finally, the mother liquor was kept for slow evaporation; pinkish colored crystalline solid was obtained after 3 weeks. Yield 0.935 g (71 %) and melting point obtained as 70–72 °C.

The synthesis procedures for Complexes 2–4 are similar to that of Complex 1, using the appropriate metal salts.

[Eu<sub>2</sub>(Phen)<sub>2</sub>(*p*-NBA)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O **Complex 2** Yield 0.418 g (31 %) and melting point obtained as 84–86 °C.

[Tb<sub>2</sub>(Phen)<sub>2</sub>(*p*-NBA)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O **Complex 3** Yield 0.855 g (65 %) and melting point obtained as 80–82 °C.

[Dy<sub>2</sub>(Phen)<sub>2</sub>(*p*-NBA)<sub>3</sub>(NO<sub>3</sub>)<sub>2</sub>].2H<sub>2</sub>O **Complex 4** Yield 0.835 g (63 %) and melting point obtained as 78–80 °C.

## Characterization

Elemental analysis was performed by Thermo Scientific (FLASH 2000) CHN Elemental Analyser, IR spectral data

was obtained by Shimadzu FT-IR spectrometer using KBr (4000–400 cm<sup>-1</sup>) pallets. <sup>1</sup>H-NMR spectra were recorded in Bruker Avance II 400 MHz. The absorbance of the compound were measured in ethanolic solution on Systronics 2201 double beam UV-Vis spectrophotometer and Fluorescence spectra were recorded on Shimadzu RF 5301 spectrofluorometer equipped with a Xe lamp as the excitation source.

## Results and discussion

### Elemental analysis

The results obtained for elemental analyses are listed in Table 1. The result in the table indicates that the experimental values are in well agreement with theoretical values, indicating that the complex may have a composition of [Ln<sub>2</sub>(*p*-NBA)<sub>3</sub>(*o*-phen)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O] (Ln = Sm(III), Tb(III), Dy(III)) and [Ln<sub>2</sub>(*p*-NBA)<sub>3</sub>(*o*-phen)<sub>2</sub>·4H<sub>2</sub>O] Ln = Eu(III).

### UV-Visible Spectra

The absorption spectra for both ligands and their corresponding complexes as **Complexes 1–4** respectively were recorded in 1.0 × 10<sup>-5</sup> mol/L ethanolic solution. λ<sub>max</sub> value obtained for *o*-phenanthroline and *p*-NBA are 264 nm and 254 nm respectively. The absorption band of all the **Complexes 1–4** obtained in range 260–300 nm exhibits π-π\* transition. A slight shift in wavelength (red shift) confirms that the complexation takes place. The absorption spectra are shown in Fig. 1 and Table 2.

### IR Spectra

IR spectra of the complexes recorded in range of 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>. The infrared spectra of the complexes were compared with that of the organic ligands. The characteristic absorption of *p*-NBA δ<sub>OH</sub> (-COOH) completely disappears. The peaks assigned for stretching vibration of free ligand were found to be shifted in spectra of complexes. The peak arises from ν<sub>C=O</sub> asymmetric and symmetric vibrational stretching of COO<sup>-</sup> for different complexes are listed in Table 3. The relative value of (Δν = ν<sub>asym</sub> - ν<sub>sym</sub>) lies between 172 and 175 cm<sup>-1</sup> which confirms the coordination of COO<sup>-</sup> to Ln (III) ion [17]. The peak obtained at 1383 cm<sup>-1</sup> for **Complex 1**, 1383 cm<sup>-1</sup> for **Complex 3**, 1383 cm<sup>-1</sup> for **Complex 4** may be attributed to coordinate -NO<sub>3</sub> with Ln (III) ion [18]. The characteristic peaks obtained for Ln-O and Ln-N bonding is mentioned in Table 3.

### NMR Spectra

The <sup>1</sup>H-NMR spectra for Ln (III) complex were measured in the D<sub>2</sub>O solvent using TMS as an internal standard at room

**Table 1** Percentage of elements as Cal (Found)

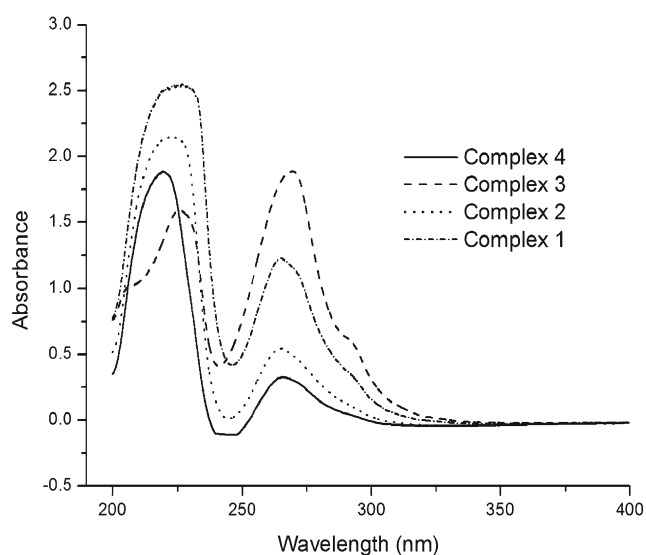
Complexes	C%	N%	O%	H%
[Sm <sub>2</sub> ( <i>o</i> -phen) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O]	40.74 (40.78)	9.50 (9.52)	24.12 (24.13)	2.96 (2.98)
[Eu <sub>2</sub> ( <i>o</i> -phen) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ·4H <sub>2</sub> O]	42.30 (42.31)	7.67 (7.69)	22.54 (22.55)	3.71 (3.72)
[Tb <sub>2</sub> ( <i>o</i> -phen) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O]	40.22 (40.24)	9.38 (9.40)	23.81 (23.83)	2.93 (2.95)
[Dy <sub>2</sub> ( <i>o</i> -Phen) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O]	40.55 (40.58)	9.46 (9.48)	22.81 (22.82)	2.80 (2.82)

temperature. The obtained spectra were compared with spectra of *o*-phenanthroline and *p*-nitrobenzoic acid. It was observed that chemical shift value of proton of –COOH disappear, suggesting the complexation between –COO and metal ion. The NMR data for **Complex 1** are as follows  $\delta$  8.70–8.67 doublet (2H),  $\delta$  7.87 singlet (6H),  $\delta$  8.21–8.19 doublet (2H),  $\delta$  8.081–8.062 doublet (2H). For **Complex 2**  $\delta$  8.55–8.63 doublet (2H),  $\delta$  7.53 singlet (6H), **Complex 3**  $\delta$  8.08–8.05 doublet (2H),  $\delta$  8.23–8.20 doublet, **Complex 4**  $\delta$  8.08–8.06 doublet (2H),  $\delta$  8.22–8.8.19 doublet (2H),  $\delta$  8.7–8.5 (6H) (Table 4).

On the basis of obtained spectral data the probable structure of Complexes can be drawn as in Figs. 6 and 7.

### Luminescence Studies and Quantum Yield Calculations

The emission spectra for all complexes were recorded at room temperature in accordance with their excitation wavelength. The emission spectrum obtained for **Complex 1**, when excited at 270 nm and slit width 5 nm. Figure 2 consists of three characteristics transition as follows  $^4G_{5/2} \rightarrow ^6H_{5/2}$  at 564 nm,  $^4G_{5/2} \rightarrow ^6H_{7/2}$  at 602 nm,  $^4G_{5/2} \rightarrow ^6H_{9/2}$  at 645 nm. The intensity of all peak were found to be very low. In the present study it was observed that 645 nm corresponds to  $^4G_{5/2} \rightarrow ^6H_{9/2}$



**Fig. 1** Absorption spectra for **Complexes 1–4** were obtained in  $1.0 \times 10^{-5}$  mol/L ethanolic solution

transition, showing better intensity as compared to other two transitions, that may be due to the sensitivity of Sm(III) towards the asymmetric environment and also agrees for the magnetic dipole transition [19].

The emission spectrum of **Complex 2**, Fig. 3 composed of prominent transitions, arises from  $^5D_0 \rightarrow ^7F_J$  ( $J=0,1,2$ ) at 579 nm, at 592 nm and at 613 nm respectively excited at 270.2 nm and slit width of 5 nm. The strongest emission at  $^5D_0 \rightarrow ^7F_2$  and  $^5D_0 \rightarrow ^7F_1$  are very sensitive to the structure of ligand. However, the  $^5D_0 \rightarrow ^7F_2$  indicates the hypersensitive transition which strictly depends on the nature of ligand [20]. It can be conclude from luminescence intensity that there is an optimum energy difference between the triplet state of the ligand and excited state of the Eu(III) ion. The emission spectrum for **Complex 3**, Fig. 4 is composed of characteristics emission bands for Tb(III) which arises from excited state  $^5D_4$  when excited at 271 nm and slit width of 5 nm. The peak obtained at 489 nm corresponds to  $^5D_4 \rightarrow ^7F_6$ . The most intense peak obtained at 545 nm belongs to  $^5D_4 \rightarrow ^7F_5$  transition [21]. Other two peaks  $^5D_4 \rightarrow ^7F_4$  and  $^5D_4 \rightarrow ^7F_3$  at 585 and 620 nm respectively have lesser intensity. **Complex 3** shows better results for luminescence among all complexes.

The luminescence intensity of other three complexes were found to be weak which may be due to partial energy absorption by the both ligand molecules before being transferred to the Ln(III) ion.

The emission spectrum of **Complex 4**, Fig. 5 obtained has excitation at 272 nm with slit width of 5 nm is composed of two peaks at 485 nm and 578 nm corresponding to  $^4F_{9/2} \rightarrow ^6H_{15/2}$ ,  $^4F_{9/2} \rightarrow ^6H_{13/2}$  transitions respectively. The intensity of luminescence spectra of Sm (III) and Dy (III) were

**Table 2**  $\lambda_{max}$  values for absorption spectra

Compounds	$\lambda_{max}$ values
<i>o</i> -phenanthroline	264 nm
<i>p</i> -NBA	254 nm
[Sm <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> (Phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	269.2 nm
[Eu <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> (Phen) <sub>2</sub> ].4H <sub>2</sub> O	272.4 nm
[Tb <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> (Phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	270 nm
[Dy <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> (Phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ].2H <sub>2</sub> O	269.3 nm

**Table 3** IR Spectral data for synthesized **Complexes 1–4** in (cm<sup>-1</sup>)

Complexes	C=N	C-H	COO <sup>-</sup>	-OH	Ln-N	Ln-O
<i>v</i> <sub>sym</sub> <i>v</i> <sub>asym</sub>						
<i>p</i> -Nitrobenzoic acid( <i>p</i> -NBA)	–	–	1695	3113	–	–
<i>o</i> -phenanthroline( <i>o</i> -phen)	1572	3064	–	–	–	–
[Sm <sub>2</sub> (Phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ·2H <sub>2</sub> O]	1460	2880	1436,1608	3346	420	551
[Eu <sub>2</sub> (Phen) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ·4H <sub>2</sub> O]	1480	2895	1438,1610	3348	439	574
[Tb <sub>2</sub> (Phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ·2H <sub>2</sub> O]	1492	2904	1440,1615	3350	432	577
[Dy <sub>2</sub> (Phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ·2H <sub>2</sub> O]	1525	2908	1450,1625	3355	441	586

found to be very weak as compared to Tb(III) and Eu(III) complexes. It may be inferred that the energy difference between the ligand triplet state and emitting level of Sm (III) and Dy (III) are not favorable for energy transfer [22]. The coordinated water molecules are responsible for decreasing the luminescence intensity of these complexes, as the partial energy absorbed by the ligand as a result of thermal vibrations of water molecules. However, presence of –OH causes quenching effect and facilitates the radiationless de-excitation of Ln (III) ion [23].

The luminescence quantum yields for **Complexes 1–4** were calculated by comparative method using standard with known quantum yield. In present study we used Rhodamine101 as standard whose quantum yield is 0.96 in ethanolic solution. The following relation is used for calculation of Quantum yield

$$Q_x = Q_s \times A_x/A_s \times E_x/E_s \times (\eta_x/\eta_s)^2$$

Where  $Q_x$ ,  $Q_s$  are quantum yield for sample and standard respectively,  $E$  being the integrated and corrected emission spectrum,  $A_x$  and  $A_s$  are the absorbance at the excitation wavelength for sample and standard respectively, and  $\eta$  is the refractive index.

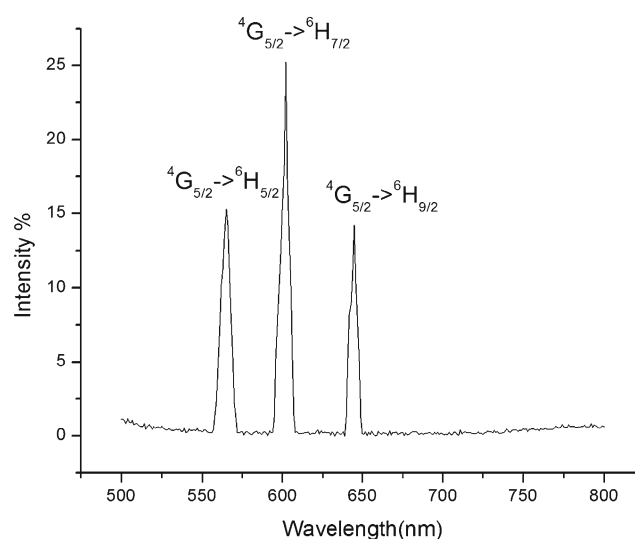
### Electronic Spectral Studies

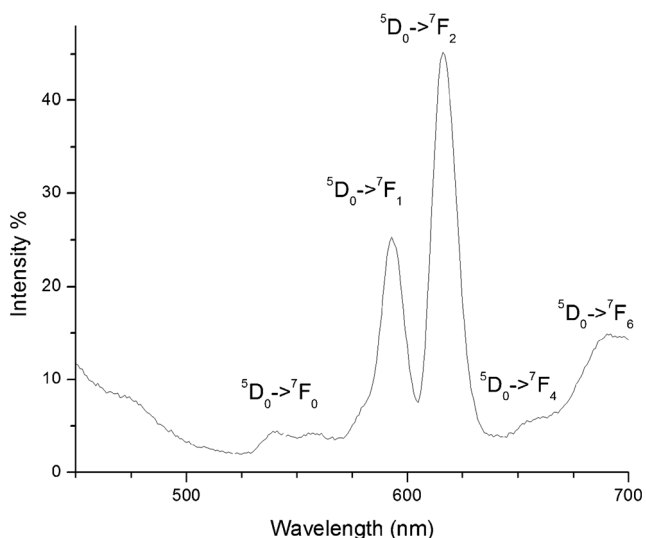
The shielding of  $-4f$  orbital takes place due to the larger radial expansion of the  $5s^2 5p^6$  subshells, which makes them to behave as “inner orbital”. The transition takes place between states with in configuration. They are parity forbidden and consist of mainly electric and magnetic dipole transition.

**Table 4** Quantum yield values for **Complexes 1–4**

Complexes	Quantum yield (%)
[Sm <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ( <i>o</i> -phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O]	14.37
[Eu <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ( <i>o</i> -phen) <sub>2</sub> ·4H <sub>2</sub> O]	55.33
[Tb <sub>2</sub> ( <i>p</i> -NBA) <sub>2</sub> ( <i>o</i> -phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O]	47.79
[Dy <sub>2</sub> ( <i>p</i> -NBA) <sub>3</sub> ( <i>o</i> -phen) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O]	2.94

Electric dipole selection rules forbid such transitions but these rules are relaxed by several mechanisms. An important one is the coupling with vibrational states, where a molecular vibration temporarily changes the geometric arrangement around the metal ion, therefore, affect its symmetry. Other mechanisms which cause a breakdown of the selection rules are the  $J$ -mixing and the mixing with opposite-parity wavefunctions, such as  $-5d$  orbitals, ligand orbitals or charge transfer states. The coupling between these vibrational and electronic states and the  $-4f$  wavefunctions depends on the strength of the interaction between the  $-4f$  orbitals and the surrounding ligands; in view of the shielding of the  $-4f$  orbitals, the degree of mixing remains small, and so are calculated as the oscillator strengths of  $f-f$  transitions. However, these forbidden transitions become allowed as magnetic dipole (MD) and induced electric dipole (ED) transition. The intensities of MD transitions are usually very weak and independent of the chemical environment whereas ED transitions are sensitive to the chemical environment. When lanthanide ion is under the influence of a ligand-field, non-centrosymmetric interactions allow the mixing of electronic states of opposite parity into the

**Fig. 2** Emission spectra for **Complex 1** is obtained in  $1.0 \times 10^{-5}$  mol/L ethanolic solution.



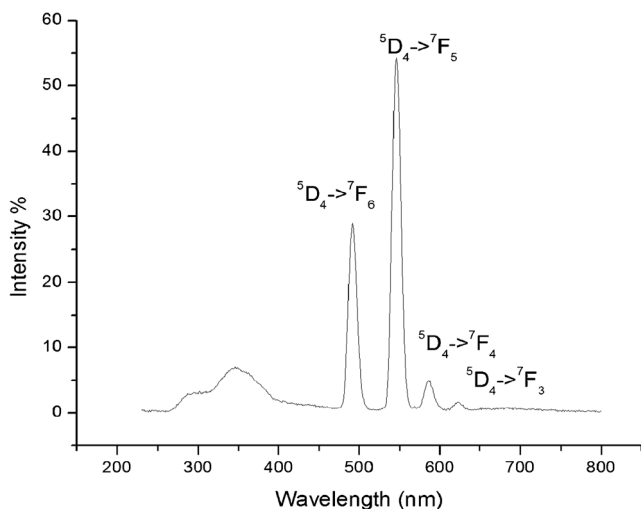
**Fig. 3** Emission spectrum for **Complex 2** is obtained in  $1.0 \times 10^{-5}$  mol/L ethanolic solution

–4f wave functions. Judd –Ofelt theory is important for predicting the spectral intensity of these transitions [24].

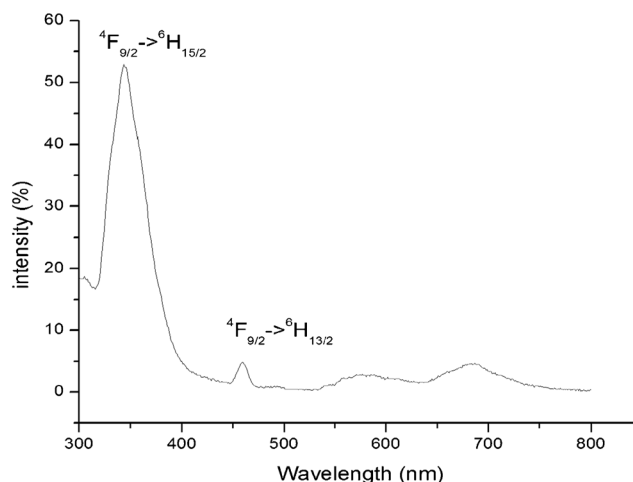
In present work electronic spectral parameters for Eu(III) emission spectrum is carried out by using Judd- Ofelt theory. The oscillator strength, ( $f_{exp}$ ) an informative parameter of intensity and susceptibility of specific electronic transitions which can be calculated by using the following relation:

$$f_{exp} = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu \tag{1}$$

where,  $\epsilon$  is the molar extinction coefficient which corresponds to energy ( $\text{cm}^{-1}$ ).



**Fig. 4** Emission spectrum for **Complex 3** is obtained in  $1.0 \times 10^{-5}$  mol/L ethanolic solution



**Fig. 5** Emission spectrum for **Complex 4** is obtained in  $1.0 \times 10^{-5}$  mol/L ethanolic solution

$$f_{cal} = \left[ \frac{8\pi^2 m c \nu}{3h(2J+1)} \right] \times \left[ n(n^2+2)^2/9 \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle J || U^{\lambda} || J' \rangle| \right] \tag{2}$$

Where,  $n$  is the refractive index of the medium,  $h$  is Plank’s constant.

The Oscillator strength ( $f$ ) is calculated by using Eq. 1, is a better agreement between calculated and experimental values presented in Table 5.

The strength of all induced electric dipole transition  $S'_{ED}$  (emission) of lanthanide ion of certain matrix can be calculated on the basis of three phenomenological parameters  $\Omega_{\lambda} (\lambda = 2, 4, 6)$  which belongs to particular lanthanide ion and its environment. The squared reduced matrix element  $|\langle J || U^{\lambda} || J' \rangle|^2$  whose values [25] are independent of the chemical environment surrounding the Ln (III) ion. The transition from  ${}^5D_0 \rightarrow {}^7F_J$  ( $J = 2, 4, 6$ ) are purely induced electric dipole nature.

$$S'_{ED} = \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle J || U^{\lambda} || J' \rangle|^2 \tag{3}$$

The spontaneous emission probability  $A(\psi J \rightarrow \psi' J')$  for a particular induced electric dipole transition is obtained from

$$A(\psi J \rightarrow \psi' J') = [64\pi^4 \nu^3 / 3h(2J+1)] [n(n^2+2)^2/9] S'_{ED} \tag{4}$$

**Table 5** Oscillator Strength values for some transition from  ${}^5D_0 \rightarrow$

${}^5D_0 \rightarrow$	Energy ( $\text{cm}^{-1}$ )	$f_{cal}$	$f_{exp}$
${}^7F_6$	14492.75	0.0421	0.042
${}^7F_4$	15284.68	0.304	0.305
${}^7F_2$	16207.46	10.372	10.376

**Table 6** Judd–Ofelt intensity parameters  $\Omega_2, \Omega_4, \Omega_6$ 

Complex 2	$\Omega_2 \times 10^{-20} \text{ cm}^2$	$\Omega_4 \times 10^{-20} \text{ cm}^2$	$\Omega_6 \times 10^{-20} \text{ cm}^2$
	4.080935	0.183642	0.285665

The total transition probability  $A_T$  is calculated by the summation of all transition to the final  $\psi'J'$  is given by

$$A_T = \sum A(\psi J \rightarrow \psi' J') \quad (5)$$

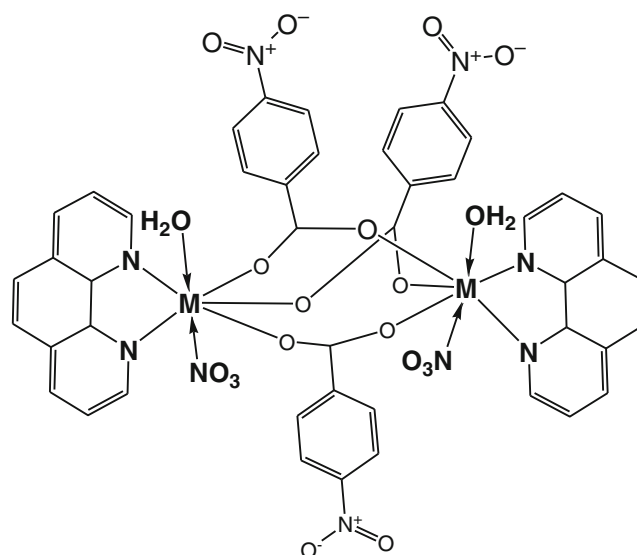
The value of branching ratio  $\beta_R$  is calculated using  $A(\psi J \rightarrow \psi' J')$  and  $A_T$  for fluorescence spectrum

$$\beta_R = \frac{A(\psi J \rightarrow \psi' J')}{A_T} \quad (6)$$

Radiative lifetime  $T_R$  for excited state can be calculated by using this relation

$$T_R = \frac{1}{A_T} \quad (7)$$

The oscillator strength depends upon the concentration of ion. The transition occurs around  $16207.46 \text{ cm}^{-1}$  corresponds to hypersensitive transition. This transition is induced when an atom is considered as an oscillating electric dipole and it interacts with the electric field of electromagnetic radiation and due to the crystal field perturbation. [26]. The oscillator strength of these transitions  $S'_{ED}$  can be calculated by using Eq. 3. Judd–Ofelt intensity parameters are denoted by  $\Omega_\lambda$  ( $\lambda=2, 4, 6$ ) and applicable for calculating the intensity of these transitions  $S'_{ED}$  occurring in both solution and solid lanthanides. J-O parameters consider refractive index of the medium and radial wave function of the state (of interacting orbitals). It is suggested that  $\Omega_2$  parameter is strongly affected by the covalency or covalent nature of bonding. To explain  $\Omega_2$ , it is significant to consider the nature and size of ligand taking part in the bond formation, a particular atom (O-, N-) directly forming bond with the Ln (III) ion [27]. It get affected due to change in partial charge on respective atom. Considering the size of ligand it can be said that larger size of ligand alter the value of  $\Omega_2$  because these ligands gather around the metal ion and thus shows variation in covalency. Covalency assists formation of asymmetric

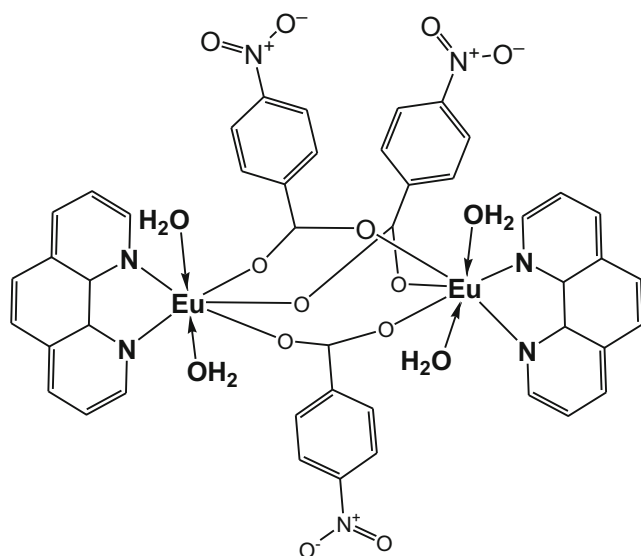
**Fig. 6** Probable structure for **Complexes 1, 3, 4** where  $M = \text{Sm(III), Tb(III), Dy(III)}$  respectively

environment around the Eu (III) ion. Hence, the distribution of dipole is reflected by  $\Omega_2$  parameter.  $\Omega_4$  and  $\Omega_6$  are structure dependent parameter and shows rigidity of host ion. The trend obtained for J-O intensity parameters in the present study as follows  $\Omega_2 > \Omega_6 > \Omega_4$  which is similar as obtained by Mehta et al. [28] in their studies are tabulated in Table 6. In light of screening and shielding of  $-4f$  orbital from outer lying  $6s-5d$  orbitals the degree of covalence is found to be more. As regard the physical significance of the  $\Omega_2$  parameter is the indication of covalence of the first order orbital interaction equivalent near LCAO model for Ln (III) interaction whereas  $\Omega_4$  and  $\Omega_6$  are the indicative of symmetry perturbation.

Radiative relaxation process occurs from an excited state  $\psi J$  of a lanthanide ion to usually lower lying states  $\psi' J'$ , gives rise to several lines in the emission spectrum of any complex. Using JO theory  $\Omega_\lambda$  ( $\lambda=2,4,6$ ), further radiative parameters viz., spontaneous emission probability  $A(\psi J \rightarrow \psi' J')$ , the total emission probability  $A_T$  involving all the intermediate terms of fluorescent transitions, the fluorescent branching ratio  $\beta_R$ , radiative lifetime  $T_R$  of various emission processes originating from excited state  $^5D_0$  have been evaluated using the standard formulae and presented in Table 7 and (Figs. 6 and 7).

**Table 7** The peak energy ( $\text{cm}^{-1}$ ), radiative transition probability ( $A(\psi J \rightarrow \psi' J')$ ), total radiative transition probability ( $A_T$ ), branching ratio ( $\beta_R$ ), radiative life time ( $T_R$ )

$^5D_0 \rightarrow$	Energy ( $\text{cm}^{-1}$ )	$S_{ED}$	$(A(\psi J \rightarrow \psi' J'))(s^{-1})$	$A_T (s^{-1})$	$\beta_R$ (%)	$T_R (ms^{-1})$
$^7F_6$	14493	2.24E-05	142.8273		0.00304	
$^7F_4$	15285	0.000166	1238.64		0.02633	
$^7F_2$	16207	0.00512	45652.66	47034.13	0.97063	2.126



**Fig. 7** Probable structure for **Complex 2**

## Conclusion

The **Complexes 1–4** were successfully synthesized; it was found that *p*-nitrobenzoic acid and *o*-phenanthroline are better ligands for transferring the absorbed energy to the Ln (III) ion which give rises to luminescence. All the complexes have shown their characteristics emission. Furthermore, calculation of J–O parameters recommends the nature of bonding between the Eu (III) and donating atom of the ligand. In these series of electronic spectral parameters calculation, the radiative lifetime is the most informative term. The branching ratios are evaluated for each probable lasing transition of Eu (III) ion. The efficiency of luminescent complexes can be achieved by  $T_R$ . The presence of water molecules causes the quenching, tends to decrease the quantum yield. Such ligands which are responsible for increase the non-radiative decay can be easily accomplished, however, it is also helpful for designing or selecting the organic ligands to achieve high radiative lifetime.

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