Applicability of Reddish Orange Light Emitting Samarium (III) Complexes For Biomedical and Multifunctional Optoelectronic Devices

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Abstract

Six crimson samarium (III) complexes based on β -ketone carboxylic acid and ancillary ligands were synthesized by adopting grinding technique. All synthesized complexes were investigated via employing elemental analysis, infrared, UV-Vis, NMR, TG/DTG and photoluminescence studies. Optical properties of these photostimulated samarium (III) complexes exhibit reddish-orange luminescence due to $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition at 606 nm of samarium (III) ions. Further, energy band gap, color purity, CIE color coordinates, CCT and quantum yield of all complexes were determined accurately. Replacement of water molecules by ancillary ligands enriched the complexes (S2-S6) with decay time, quantum yield, luminescence, energy band gap and biological properties than parent complex (S1). Interestingly, these efficient properties of complexes may find their applications in optoelectronic and lighting systems. In addition to these the antioxidant and antimicrobial assays were also investigated to explore the application in biological assays.

Introduction

From last few decades, lanthanide materials gathered the special attention due to their versatile applications in various fields like lasers[1], OLEDs[2], display devices[3], LED bulbs [4] and biological systems[5]. Hence, synthesis of lanthanides complexes with prominent high quantum yield, large stock shifts and long luminescence decay time has become a hot research topic at present time. Lanthanide complexes possess luminescence due to 4f-4f transitions, which are Laporte forbidden according to spin parity rule [6]. Hence, direct excitation in lanthanides is not beneficial as it results in low molar absorptivity and weak luminescence[7, 8]. In order to overcome this catastrophe, a light harvesting chromophore was incorporated in coordination sphere which absorb energy from external source and transfer to lanthanides via antenna effect[9]. Generally, β -hydroxy ketone, β -keteocarboxylic acid and aromatic carboxylic acid are vigilantly studied due to their significant ability to transfer the absorbed energy from external source to lanthanides[10, 11]. However, β -keteocarboxylic acid is an excellent chromophore to generated excellent reddish orange emission for display devices and other applications. Further, specially Eu (III), Tb (III) and Sm (III) having unique optical properties such as narrow emission bands, long decay time, large stock shifts and high luminescence due to electronic transitions in emission spectra[12]. Out of these, samarium (III) complexes grab significant attention due to their ability to emit reddish orange (606 nm) emission utilized in high quality display devices.

Currently, six scarlet samarium (III) complexes have been prepared by utilizing 1-cyclopropyl-6-fluro-4-oxo-7-piperazin-1-ylquinoline-3-carboxylic acid (L), bathophenanthroline (batho), 1,10-phenanthroline (phen), neocuproine (neo), 2,2'-bipyridyl (bipy) and 5,6-dimethyl-1,10-phenanthroline (dmph) ligands via grinding technique. All synthesized complexes were investigated via utilizing UV-Vis, ^{13}C -NMR, ^1H -NMR and IR spectroscopy. The information regarding elemental composition and thermal stability can be achieved by using elemental and thermogravimetric analysis. The photoluminescent spectra and decay time are executed effectively for reporting the photoluminescent aspects of samarium (III) complexes. The emitting color of complexes is confirmed by colorimetric parameters (color purity and CIE) of complexes. The sensitization of samarium ion by ligand can be well illustrated by investigation of energy transfer process in detail. To assess the antioxidant and antimicrobial activities, complexes are screened for DPPH and tube dilution techniques respectively.

Experimental

2.1 Reagents and instruments

All solvents and chemicals were of analytical reagent grade with a stated purity 99% acquired from commercial source named Sigma Aldrich and used as such without further purification. The photoluminescence spectra were executed on spectrophotometer (Hitachi F-7000) equipped with xenon lamp. The elemental analyses enquired on Perkin Elmer 2400 CHN elemental analyser. Thermal stability was checked up to 800°C temperature on SDT Q 600 analyzer with 20°C/min in nitrogen atmosphere. ^1H and ^{13}C NMR spectra were performed on Bruker Avance II spectrophotometer in DMSO at 400 MHz frequency. IR spectra were obtained by perkin Elmer 400 spectrophotometer using KBr pellet in 4000 cm^{-1} to 400 cm^{-1} . The decay time value was determined via the FL solutions software F-7000 by monitoring $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ emission line of Sm^{3+} in solid state. The UV-Vis absorption spectra were executed on Shimadzu-2450 spectrophotometer. DPPH and tube dilution technique were used to investigate the antioxidant and antimicrobial activities respectively.

2.2 Preparation of complexes

To synthesize the complex S1, ligand (0.498 g) and samarium nitrate hexahydrate (0.222 g) were placed in mortar and grinded properly. In order to mix all contents appropriately few drops of water added and pH of solution was adjusted at 7 with the help of NaOH (0.01 M) solution. Resulting paste was purified by dissolving in 10 mL water and centrifuged for 2 minutes, moreover, same procedure was repeated for 2-3 times and dried the resultant sample in oven at 50 °C. Same steps were repeated by adding ancillary ligands such as bipy (0.078 g) S 2, neo (0.104 g) S 3, dmph (0.104 g) S 4, batho (0.161 g) S 5 and phen (0.09 g) S 6 supplemented to the mortar having L and $\text{Sm}(\text{NO}_3)_6 \cdot 6\text{H}_2\text{O}$. To portray the energy transfer dynamics triplet state of ligands were considered, for which same procedure repeated to prepare corresponding gadolinium complexes. The synthetic route and structure of all samarium complexes via utilizing grinding technique was displayed in scheme 1[13].

2.3 Evaluation of biological Activities

2.3.1 Antioxidant activities

DPPH (2,2-diphenyl-1-picrylhydrazyl) protocol was adopted to compute the antioxidant activities of all referred complexes. The stable free radical DPPH lost its violet color and change into pale yellow due to association with antioxidants moiety, which results a significant drop in absorption at 517 nm on spectrophotometer. In order to prepare numerous concentrations such as 25, 50, 75 and 100 $\mu\text{g/mL}$, dimethylsulfoxide (DMSO) was used as a solvent. Further, 1 mL DPPH solution was added to the 1mL solution of each test samples in their corresponding flasks. The absorbance was recorded after 30 minute incubation in dark at 25°C by taking ascorbic acid as a standard. All tests were performed in triplicate to get concordant values and the scavenging activity of DPPH is expressed in IC_{50} (50% of maximum scavenging activity) values. The IC_{50} value was determined by graph plotting between scavenging activity (SCA) and numerous concentrations of test samples. By using equation 1 the DPPH scavenging activity of all test samples was determined[14]:

$$\text{DPPH scavenge activity (\%)} = \frac{A_c - A_t}{A_c} \quad (1)$$

Where A_t and A_c refers to the absorbance test samples and control reaction respectively.

2.3.2 Antimicrobial activities

Antimicrobial assays were executed for all title complexes by employing tube dilution protocol[15]. Antibacterial activities of these samples were carried out against the following in vitro gram negative bacteria: *Pseudomonas aeruginosa* (MTCC1688), *Escherichia coli* (MTCC 443) and in vitro gram positive bacteria: *Streptococcus pyogenes*

(MTCC442), *Staphylococcus aureus* (MTCC 96). Antifungal activities of these complexes were screened against the fungal strain takes *Candida albicans* (MTCC 227), *Aspergillus clavatus* (MTCC 1323) and *Aspergillus niger* (MTCC 282). The reference drugs norfloxacin and greseofulvin were used for antibacterial and antifungal activities respectively.

All samples (reference + ligand + complexes) were dissolved in DMSO to give concentration of 200µg/mL. The incubation period for antibacterial activities is 24h at 37°C and for antifungal activities is 7 days at 24°C for *Aspergillus avatus* and *Candida albicans* but 48h at 37°C for *Aspergillus niger*[16]. The zone of inhibition of antimicrobial activities has been recorded in MIC values.

Results And Discussion

3.1 Elemental analysis

Table 1 displays the elemental analytic data from CHN elemental analyser, which had been estimated to be in complete harmony with the calculated values and recommend $[Sm(L)_3.(H_2O)_2].6H_2O$ (S1), $[Sm(L)_3.bipy].6H_2O$ (S2), $[Sm(L)_3.neo].6H_2O$ (S3), $[Sm(L)_3.dmph].6H_2O$ (S4), $[Sm(L)_3.batho].6H_2O$ (S5) and $[Sm(L)_3.phen].6H_2O$ (S6) respectively as the proposed formula.

Table 1
The elemental analytical data for all S1-S6 Samarium (III) complexes.

Complexes	C (%) found (cal.)	H (%) found (cal.)	N (%) found (cal.)	Sm(%) found(cal.)
S 1	42.74 (42.76)	5.98 (6.01)	8.78 (8.80)	10.46 (10.48)
S 2	47.42 (47.46)	5.72 (5.77)	9.58 (9.66)	9.40 (9.41)
S 3	47.64 (46.65)	5.84 (5.86)	9.79 (9.81)	9.54 (9.56)
S 4	51.56 (1.57)	5.70 (5.73)	8.79 (8.82)	8.58 (8.59)
S 5	48.09 (48.11)	5.90 (5.92)	9.47 (9.50)	9.23 (9.25)
S 6	48.03 (48.11)	5.89 (5.92)	9.48 (9.50)	9.22 (9.25)

3.2 Spectral analysis

Figure 1 represents the infrared spectrum of complex S1 and free ligand (L), to evaluate the chelation site in bonding. The IR spectra of S 2- S 6 complexes show that all complexes have almost identical IR spectra as displayed in Figure S1 in supplementary file. The position and intensity of some guide peaks are changed from ligand to complexes, which help to find the binding site in complexes. The broad band scrutinized at 3410 cm^{-1} depicts the presence of aqua molecule in all synthesized (S1-S6) complexes[17]. In ligand spectra the band noted at 1711 cm^{-1} and 1625 cm^{-1} reflects the existence of carboxylic and ketonic group respectively. It is important to note that the band due to carboxylic acid (1711 cm^{-1}) completely disappeared in synthesized complexes, peak in all S1-S6 complexes signalize the chelation through carboxylato group. Additionally, bands due to ketonic group (1625 cm^{-1}) shift in all S1-S6 complexes (Table 2) revealing that the second chelation site is through ketonic oxygen. The asymmetric and symmetric vibrations of carboxylato group appears at $1585\text{-}1592\text{ cm}^{-1}$ and $1370\text{-}1375\text{ cm}^{-1}$ respectively which are absent in ligand spectra[18]. Further, carboxylate group is a bidentate ligand, hence, can bind either as unidentate or as bidentate by producing change in relative vibrational positions of asymmetric and symmetric stretching.

Complexes exhibits $\Delta\nu > 200\text{ cm}^{-1}$ [$\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$], this demonstrates the unidentate linkage of carboxylic group[19]. The observed $\Delta\nu$ values for all synthesized S1-S6 complexes are found to be 210-220 cm^{-1} as enlisted in Table2, suggesting the unidentate attraction of carboxylato group. Further, the new band appeared at 459-464 cm^{-1} , 539-548 cm^{-1} and 1481-1486 cm^{-1} in S2-S6 complexes assigned for stretching vibrations of $\nu_{\text{Sm-O}}$, $\nu_{\text{Sm-N}}$ and $\nu_{\text{C-N}}$ respectively in all synthesized complexes as elucidated in Table 2.

Table 2

The characteristic IR bands (cm^{-1}) for ligand and its samarium (III) complexes.

Compounds	$\nu_{\text{O-H}}$	$\nu_{\text{-COOH}}$	$\nu_{\text{Sm-O}}$	$\nu_{\text{Sm-N}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$	ν_{as} (COO^-)	ν_{s} (COO^-)	$\Delta\nu_{\text{COO}^-}$ ($\nu_{\text{as}}-\nu_{\text{s}}$)
L	-	3530(S)	-	-	-	1625(S)	-	-	-
S 1	3410(B)	-	464(W)	-	-	1624(S)	1590(S)	1370(S)	220
S 2	3410(B)	-	463(W)	548(W)	1483(W)	1620(S)	1588(S)	1372(S)	216
S 3	3410(B)	-	462(W)	547(W)	1481(W)	1622(S)	1589(S)	1374(S)	215
S 4	3410(B)	-	459(W)	539(W)	1482(W)	1623(S)	1585(S)	1375(S)	210
S 5	3410(B)	-	460(W)	545(W)	1486(W)	1622(S)	1590(S)	1372(S)	218
S 6	3410(B)	-	461(W)	546(W)	1484(W)	1623(S)	1592(S)	1373(S)	219
B = broad, S = strong, W = weak									

Figure 2 represents the $^1\text{H-NMR}$ spectrum of free ligand and synthesized complex (S1) carried out in DMSO as a solvent. It is evident from the figure that some significant changes take place when the spectrum of complex is compared with the ligand. The anisotropic property of samarium ions is responsible for upfield and downfield shifts in complexes [20]. The peak observed at 15 ppm manifest the presence of carboxylic group in ligand, which completely disappeared in synthesized complexes, confirming the chelation of ligand through deprotonated carboxylic acid[21]. In the ligand spectra the peaks observed at 7.56 - 9.39 ppm (aromatic $-\text{CH}_2-$), 3.26-3.98 ppm (aliphatic $-\text{CH}_2-$) and 1.19-1.33 ppm ($-\text{CH}_3$) are shifted to 7.54 – 8.66 ppm (upfield), 2.39-2.90 ppm (upfield) and 1.18-1.31 ppm (upfield) in complexes respectively. The paramagnetism nature of samarium (III) ions causes upfield shifting of all protons in complexes[22].

Figure S2 in supplementary file portrays the $^{13}\text{C-NMR}$ spectrum of L and S1 complex, the carbon values noticed at 176.33 (C=O), 165.81(COOH), 139-153 (aromatic C=C), 106-118 (aromatic C-C) and 35.93-46.26 ($-\text{C}-\text{C}-\text{C}-$) shifted upfield in corresponding samarium (III) complexes due to paramagnetism of Sm^{3+} ion. It is evident from the figure that the peak of carboxylic group in ligand was completely disappeared in complex and the peak of ketonic group in ligand shifts by 7.74 - 7.86 in all synthesized complexes, which depicts that chelation of L in complexes through ketonic (C=O) and carboxylic group (COO^-) respectively[23].

Figure 3 depicts the UV-Vis absorption spectra of all S1-S6 synthesized complexes and L (1×10^{-5} mol/L) by taking DMSO as a solvent. Ligand acts as key absorption for all S1-S6 complexes because absorption displayed by these complexes is weak in 200-500 cm^{-1} region. It is evident from the figure that absorption maxima observed at 280 nm

wavelength is assigned to $\pi - \pi^*$ electronic transitions[24]. Further, the encapsulation of ancillary ligand in S2-S6 complexes upsurge the absorbance as well as saturates the coordination framework.

All results observed from spectroscopic measurements are in good agreement with each other and certifies that the chelation of ligand with samarium (III) ions through carboxylato (COO^-) and ketone groups in the coordination.

3.3 Thermal analysis

Figure 4 reveal the thermal decomposition pattern for S1 complex, since thermal decomposition pattern exhibited by all synthesized complexes are in similar nature, so, S1 was taken as a representative. The complex S1 exhibits 18% mass loss attributed to decomposition of 15 water molecules present outside of coordination sphere up to 88°C. The next loss in mass is 71% accredited to collapsing of complex and removal of two water molecules and three ligand molecules up to 242°C to 557°C present in coordination sphere (i.e. complex start decomposing) [25]. At last, the oxide of samarium (III) ion remains as residue, which was further confirmed through analysis of DTG curves. Theoretical and computed values are in good agreement with total loss of mass in complex. The complexes posses' optimum stability, hence, can be employed as luminescent materials in optoelectronic devices.

3.4 Optical band gap & refractive index

Figure 5 (a) and (b) describe the plot between photon energy and absorption coefficient of all samples (L, S1-S6) and the inset denotes the diffused reflectance (DR) spectra of L and corresponding complexes in their respective figures. Kubelka and Munk states that the optical band gap (E_g) for solid samples can be calculated by transformation of DR[26]. The equation 2 denotes the relationship between Kubelka and Munk ($F(R_\infty)$) and energy band gap as given below:

$$[F(R_\infty) h\nu]^n = C (h\nu - E_g) \quad (2)$$

Where, E_g represent energy band gap, $h\nu$ shows energy of incident photon and values of n are variable having values 3, 2, 1.5 and 0.5 assigned for indirect forbidden transitions, direct allowed transitions, direct forbidden transitions and indirect allowed transitions respectively. Herein, the value of n is equals to 2 for direct allowed transition and the equation is written as follows:

$$[F(R_\infty) h\nu]^2 = C (h\nu - E_g) \quad (3)$$

$F(R_\infty)$ denotes the Kubelka-Munk function and can be derived as follows:

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \quad (4)$$

Where, S denotes scattering coefficient, K represents absorption coefficient and R_∞ refers to ratio of R_{normal} to R_{standard} . The optical band gap values for L and all synthesized samarium (III) complexes are determined by extrapolation of a tangent up to x-axis in Tauc plot. The observed values for all S1-S6 complexes and L are catalogued in Table 3. As the table illustrate that the value of energy band gap is less for complexes in comparison to the ligands, resulting a number of extra electronic states between samarium (III) ions, hence reinforcement of energy transfer increases, so photoluminescence also increase[27]. Therefore, the property of large energy band gap values makes them a promising candidate for semiconductor power appliance.

Table 3
The energy band gap and refractive indices for ligand and all S1-S6 complexes.

Compounds	Energy band gap (E_g)	Refractive Index
L	3.14	2.012
S 1	3.04	2.035
S 2	2.81	2.081
S 3	2.93	2.056
S 4	2.97	2.048
S 5	2.91	2.061
S 6	2.94	2.054

Further, in order to find out the refractive index (n) of all S1-S6 complexes precisely, the energy band values are employed by the following relation [28]:

$$\frac{(n^2 - 1)}{(n^2 + 1)} = 1 - \sqrt{\frac{E_g}{20}} \quad (5)$$

Where, n represent the refractive index and E_g signifies energy band gap values, the estimated value for all synthesized are epitomized in Table 3. The refractive index values enable these complexes as a promising candidate in optoelectronic devices.

3.7 Photoluminescence features

Figure 6(a) indicates the excitation spectra of all S1-S6 complexes by monitoring the ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ electronic transition at 606 nm. Formation of complex extend the π - conjugation, hence, the intramolecular energy transfer from L to Sm^{3+} increases by antenna effect, this results in broadening of excitation spectra. The peak found at 360 nm, 374 nm, 404 nm, 453 nm, 472 nm and 495 nm attributed to the electronic transitions arising from ground state ${}^6H_{5/2}$ to excited state ${}^4F_{9/2}$, ${}^4D_{5/2}$, ${}^6P_{7/2}$, ${}^4F_{5/2}+{}^4I_{13/2}$, ${}^4G_{7/2}$, ${}^4I_{7/2} + {}^4M_{15/2}$ in samarium (III) ions respectively[29, 30]

Figure 6(b) represents the three dimensional emission spectra of all S1-S6 complexes monitored at excitation wavelength (356 nm) in solid state. The luminescence spectra displays mainly three peaks at 566 nm, 606 nm and 651 nm which belongs to ${}^4G_{5/2} \rightarrow {}^6H_j$ (where $j = 5/2, 7/2, 9/2$) electronic transition of samarium (III) ions in all synthesized complexes respectively. Out of these, first transition, ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$, is magnetic dipole transition, which follows the selection rule of $\Delta J = 0$, where J is total angular momentum, hence intensity of this peak does not depend on coordination environment around Sm^{3+} . ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ is mixed transition with (partly magnetic and partly electric dipole) but has dominating electric dipole character whereas ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$ is purely electric dipole transitions. The most intense peak of spectra at 606 nm due to hypersensitive ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition is responsible for vermilion emission of complexes and makes them suitable for orange light emitting devices. This transition complies with the selection rule of $\Delta J = \pm 1$, The electric dipole transition at 651 nm represent immensely asymmetrical surroundings around Sm^{3+} ion[31, 32]. The upsurge the photoluminescence from S1 complex to S2-S6 complexes is explained by

introduction of ancillary ligands in place of water which results increase in radiative rate by diminished the vibrational quenching caused by water molecules.

3.8 Luminescence decay curves and quantum yield

The average environment surrounding samarium (III) ion is investigated by observing decay time curves under 356 nm excitation and 606 nm emission wavelengths respectively as depicted in Figure 6(c). The luminescence decay time curves are well fitted by monoexponential function and it is derived from the equation given [33]:

$$I = I_0 \exp (-t/\tau) \quad (6)$$

Herein, τ represents the decay time for radiative transitions while I_0 and I represent the integrated intensity of peaks at time 0 and t , respectively. Luminescence decay time curves are best fitted in mono-exponential function, which specifies the homogenous environment around samarium (III) ion in complexes. Further, the total decay time depends upon both radiative and nonradiative as given by the following relation:

$$A_{\text{total}} = 1/\tau = (A_{\text{rad}} + A_{\text{nrad}}) \quad (7)$$

The observed values of decay time for S 1 (0.72), S 2(1.40), S 3(1.78), S4 (2.02), S 5 (2.41) and S 6 (2.15) are embodied in Table 4. The observed order for decay time in complexes is found to be S1<S2<S3<S4<S6<S5, the higher value of decay time in S2-S6 complexes than that of S1 was credited to extended conjugation by introduction of ancillary ligands. The decay time of complexes pursues single exponential behaviour which is responsible for homogenous coordination environment and single luminescent centre around central metal ion.

Table 4
Estimated quantum yield, decay time values, CIE color coordinates, color purity and CCT of all samarium (III) complexes.

Complexes	Quantum yield	τ (ms)	CIE coordinates (x, y)	% Color purity	CCT(K)
S 1	22.22	0.72	0.5542, 0.4447	98.01	2002.15
S 2	43.20	1.40	0.5560, 0.4430	98.53	1980.13
S 3	54.93	1.78	0.5702, 0.4288	98.28	1836.01
S 4	62.34	2.02	0.5521, 0.4468	98.89	2027.39
S 5	74.38	2.41	0.5558, 0.4432	98.44	1984.02
S 6	66.35	2.15	0.5573, 0.4417	99.04	1966.83

Quantum yield is an important parameter, utilized to observe the luminescence of samarium (III) ion in complexes[34]. It can be described as the ratio of numerical quantity of photons emitted to photons absorbed. However it can be calculated using following equation:

$$\Phi (\%) = \frac{\tau}{\tau_{\text{rad}}} \times 100 \quad (8)$$

Where, Φ represent quantum yield, τ and τ_{rad} represent the total decay time and decay time for radiative transition. The decay time for radiative transition (τ_{rad}) of samarium (III) complexes was found to be 3.24ms for transition $^6G_{5/2}$ manifold for Sm^{3+} . The observed values reveal increase in quantum yield for S2 – S6, relative to S1. This can be interpreted due to synergistic effect of ancillary ligand and lesser nonradiative transition which leads to increase in luminescence. It is noteworthy to emphasise that the luminescence decay time of the synthesised complexes is higher

than most of the reported- [Sm(ligand)₃.ancillary] complexes in literature, while life time was fetched by observing ⁴G_{5/2} → ⁶H_{7/2} emissive transition, as mentioned in Table 5.

Table 5
Comparison of decay time of our synthesized complexes with other [Sm(ligand)₃.ancillary] complexes when decay time was calculated by monitoring ⁴G_{5/2}→⁶H_{7/2} electronic transition

Complex	Decay time (ms)	Reference
Sm(L) ₃ .2H ₂ O	0.72	This work
[Sm(L) ₃ .bipy]	1.40	This work
[Sm(L) ₃ .neo]	1.78	This work
[Sm(L) ₃ .dmph]	2.02	This work
[Sm(L) ₃ .batho]	2.41	This work
[Sm(L) ₃ .phen]	2.15	This work
[Sm(HDMPE) ₃ .phen]	0.99	[35]
[Sm(HDMPE) ₃ .biq]	0.90	[36]
[Sm(L) ₃ .mphen]	0.56	[37]
Sm(L) ₃ .2H ₂ O	0.44	[38]

3.7 Colorimetric analysis

The emission spectra of luminescence investigation used to determine the color coordinates (x, y) of all S1-S6 complexes by utilizing MATLAB software. CIE (Commission International de l'Elclairge) color coordinates of all S1-S6 complexes are found to be 0.5542, 0.4447 (S1), 0.5560, 0.4430 (S2), 0.5702, 0.4288 (S3), 0.5521, 0.4468 (S4), 0.5558, 0.4432 (S5) and 0.5573, 0.4417 (S6) respectively, enlisted in Table 4. CIE color triangle (Figure 7), displays the observed color coordinates of all S1-S6 complexes, which authenticate the effective sensitization of Sm³⁺ ions by the L in reddish-orange zone [39]. Amazingly, these bright reddish-orange colors of complexes can be explored in color indicator diodes.

Color purity (CP) of all complexes is ascertained by employing CIE color coordinates with respect to white light, which shows how actively a meticulous complex act as reddish orange color emitter. CP of all complexes was calculated by using the following relation:

$$CP = \sqrt{\frac{(x_s - x_i)^2 + (y_s - y_i)^2}{(x_d - x_i)^2 + (y_d - y_i)^2}} \quad (9)$$

In aforementioned equation, (x_s, y_s) represents color coordinates of S1-S6 complexes, (x_i, y_i) refers to white light color coordinates (x_i = 0.33, y_i = 0.33) and (x_d, y_d) represents the dominated color coordinates. CP determined by equation 9 is reported in Table 4, which specify that the color purity of S2-S6 is significantly higher as compared to S1. This fact

is explained on the basis of synergic effect of ancillary ligands in place of solvent molecules. Hence, these complexes are proved to be bright orange color emitting materials to be utilized in OLEDs.

Further, an important parameter CCT (correlated color temperature) helps to investigation the quality and nature of light emitted from a light source. Depending on their CCT values, the complexes are cool light source (above 4000K), warm light source (below 3200K) and neutral light source (3200-4000K)[34]. The CCT can be evaluated by applying the Mc-Camy equation:

$$\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5514.31 \quad (10)$$

Where n can be written as:

$$n = \frac{x - x_e}{y - y_e} \quad (11)$$

Here, (x, y) displays the CIE color coordinates of all S1-S6 complexes and (x_e, y_e) stands for chromaticity epicentre (0.3320, 0.1858). Observed values of CCT for all S1-S6 complexes are found to be below 3200K (Table 4) indicating the applicability of these complexes in home appliances as a warm light source.

3.8 Energy transfer dynamics

The photosensitization is a multistep phenomenon that manifest the excitation of L from ground state to singlet excited state, thereafter energy is transferred to triplet state by intersystem crossing and then to emitting levels of samarium (III) ions via nonradiative process. Further, energy transfer from emitting levels to ground levels of samarium (III) ions is responsible for luminescence as portrayed in Figure 8. It is important to note that there must be suitable energy gap between ligands and metal ions for effective sensitization, the smaller or larger energy gap leads to weak luminescence due to either back energy transfers or inadequate overlaps among acceptor energy levels. The overlap between the absorption spectrum of ligand and excitation spectrum of complex (S1) displayed in Figure S3 put in supplementary file, which indicates the effective sensitization of samarium (III) ions by the L. In order to investigate the energy transfer mechanism the singlet and triplet state of ligand and ancillary ligands are calculated by referring the edge wavelength of absorption spectrum and shortest emission of phosphorescence spectrum of gadolinium complexes respectively. The absorbance spectrum of dmph and neo is shown in Figure S4 and S5 in supplementary file and their inset represent phosphorescence spectra of gadolinium complexes respectively. The absorbance spectrum of L is displayed in Figure 9 and phosphorescence spectrum of gadolinium complex of ligand is shown in inset of this figures. The photoluminescence acquired by gadolinium complexes is $32,000 \text{ cm}^{-1}$ (lowest possible excitation), which is much higher than the photoluminescence of ligands, hence the peak due to gadolinium complex is not observed in spectrum. The energy difference between singlet and triplet state of L is found to be 3320 cm^{-1} , hence intersystem crossing is not much effective (Empirical rule), which results in internal conversion of energy from ligand to metal ion [40]. Further, Latva's rule state that the energy difference between ligand and lanthanides ions must be $2000\text{-}5000 \text{ cm}^{-1}$ for effective energy transfer[41]. Energy difference between singlet and triplet states of ligand and ancillary ligands are found to be 4719 cm^{-1} (L), 4433 cm^{-1} (phen), 5233 cm^{-1} (bipy), 3430 cm^{-1} (dmph), 4957 cm^{-1} (neo) and 3333 cm^{-1} (batho) as tabulated in Table 6 with respect to samarium ion, which as optimum to efficient transfer of energy.

Table 6
The energies of L, phen, bipy, dmph, neo and batho ancillary ligands.

Ligands	Energy levels		$\Delta E (S_1 \rightarrow T_1) (cm^{-1})$	$\Delta E (T_1 \rightarrow ^4G_{5/2}) (cm^{-1})$
	Singlet (cm^{-1})	Triplet (cm^{-1})		
L	25,706	22,386	3320	4719
Phen	31,000	22,100	8900	4433
Bipy	29,900	22,900	7000	5233
Dmph	31,250	21,097	10154	3430
Neo	30,750	22,624	8126	4957
Bathophen	29,000	21,000	8000	3333

3.9 Evaluation of Biological properties

3.9.1 Antioxidant features

Figure 10(a) represents the percentage scavenging activities of all title complexes with respect to the standard ascorbic acid at 517nm. The IC_{50} values are observed from the plot between scavenging activity (SCA) and different concentration of samples are portrayed in figure 10(b) and enlisted in Table 7. Larger value of SCA leads to lower value of IC_{50} , results higher antioxidant capacity of synthesized complexes. The stable free radical of DPPH adopt diamagnetic character by accepting a proton from antioxidant moiety, hence show decrease in absorbance so scavenging activity increases[36]. The antioxidant activities of all S1-S6 complexes are good as compared to ligand, due to donation of electrons from $L \rightarrow Sm^{3+}$, which increase the capability of complexes to oxidise. Further, it is evident from the table that the antioxidant activities of S2 - S6 complexes are higher than S1, explained on the basis of synergic effect produced by ancillary ligands. These complexes have excellent antioxidant activities so can be used as antioxidant agent in pharmaceutical field.

Table 7
 IC_{50} values for antioxidant activities of L and all S1-S6 samarium (III) complexes

Compounds	Concentration ($\mu g/mL$)				
	100	50	25	12.25	IC_{50}
L	86.20	69.25	55.59	36.35	44.42
S 1	88.00	69.40	57.00	40.32	40.61
S 2	88.62	70.67	56.46	41.21	39.79
S 3	88.73	72.34	56.43	42.72	38.09
S 4	89.36	71.07	57.42	43.41	37.35
S 5	89.57	74.02	59.13	44.98	34.05
S 6	87.01	70.33	57.59	43.07	37.49
STD	88.79	76.22	64.49	52.89	19.39

3.9.2 Antimicrobial activities

Figure 10(c) symbolize the antibacterial activities of all S1-S6 complexes in their corresponding minimum inhibitory concentration (MIC) values against both in vitro gram positive or in vitro gram negative bacteria. Further, Table 8 embodied the results observed from antimicrobial (antibacterial and antifungal) activities of all test samples with respect to standard by using tube dilution technique[35]. The antimicrobial activities of all synthesized complexes are higher than that of ligand due to delocalization of π electrons, which results to increase in lipid attraction tendency of L towards Sm^{3+} ion. So, Sm^{3+} ion can access to deeper extent of microorganism cell and improve the antimicrobial activities by slow down the growth of microorganism [42]. On the basis of this fact, one can easily see that these complexes employed as good bactericidal and fungicidal agent in pharmaceutical field.

Table 8
Antimicrobial activities of L and all S1-S6 samarium (III) complexes.

Compounds	Anti bacterial activities in term of their MIC values				Antifungal activities in term of their MIC values		
	<i>E. Coli</i>	<i>P. Aeruginosa</i>	<i>S. Aureus</i>	<i>S. Pyogenus</i>	<i>C. Albicans</i>	<i>A. Niger</i>	<i>A. Clavatus</i>
L	145	270	180	260	200	800	800
S 1	115	220	120	180	150	210	220
S 2	105	190	115	150	150	220	180
S 3	90	130	125	100	150	180	190
S 4	80	120	62.5	90	140	220	120
S 5	50	90	40	70	120	130	180
S 6	65	110	50	80	130	140	90
STD	10	10	10	10	500	1000	1000

Conclusions

Six ternary complexes of samarium (III) ions by utilizing ketocarboxylic acid and ancillary ligands were synthesized and characterized. The proposed composition of complexes is confirmed by elemental analysis and TGA/DTG investigation of complexes. Investigation of IR, UV-visible and NMR (^1H & ^{13}C) spectra of ligand and complexes in details confirm the formation of complexes. Besides, photoluminescence spectral studies shows that under 356 nm excitation, all synthesized complex exhibits the characteristics peaks at 566 nm, 606nm and 651 nm which can be credited to ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$), ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$) and ($^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$) electronic transitions of Sm^{3+} respectively. The energy band gap and refractive index of all complexes and ligand are determined precisely, which enables the applicability of them in semiconductor devices. Investigation of luminescence decay time in detail provide the homogenous environment around samarium (III) ion with excellent intrinsic lifetime (0.7 2-2.42) of all synthesized complexes. CIE colors coordinates, quantum yield (22.22-74.38) and color purity (98.01-99.04) of all S1-S6 complexes were determined accurately. According to CCT, these complexes are warm in appearance. Energy transfer dynamics validates the successful transfer of energy from ligand (triplet energy state) to samarium (III) ion (resonating energy states). Biological activities of these complexes display the potential use of these complexes in pharmaceutical field.

All results validate that these samarium (III) complexes can be utilized in lasers, display devices, OLED's, semiconductors and biological assays.

Declarations

Authors Declarations

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Data Availability

All data analysed during this study are included in this article and its supplementary information.

Code Availability

No software or any computational study was not used for this study.

Authors' contributions

Pooja Hooda performed experimental works, data collection, analysis, validation, interpretation and wrote the original manuscript. Savita Khatri and Poonam Kumari contributed to the experimental, reviewed and edited manuscript. V. B. Taxak, R. K. Malik, S. P. Khatkar, and Rajesh Kumar contribute to supervision, technical support, editing functions and manuscript review.

Ethics Declarations

Ethics Approval/Declarations

Not Applicable

Consent to Participate

Not Applicable

Consent for Publication

Not Applicable

Conflicts of Interest/Competing Interests

The authors say no conflicts of interest regarding this research work.

References

1. Khatkar SP, Kumar R, Khatkar A, Taxak VB (2015) Synthesis, characterization, enhanced photoluminescence and biological activity of Eu (III) complexes with organic ligands. *J Mater Sci Mater Electron* 26:7086–7095
2. Khanagwal J, Khatkar SP, Dhankhar P et al (2020) Synthesis and photoluminescence analysis of europium (III) complexes with pyrazole acid and nitrogen containing auxiliary ligands. *Spectrosc Lett* 53:625–647
3. Liu Y, Tu D, Zhu H, Chen X (2013) Lanthanide-doped luminescent nanoprobes: controlled synthesis, optical spectroscopy, and bioapplications. *Chem Soc Rev* 42:6924–6958
4. Wang D, Zheng C, Fan L et al (2014) Photoluminescence behavior of europium (III) complexes containing 1-(4-tert-butylphenyl)-3-(2-naphthyl)-propane-1, 3-dione ligand. *Spectrochim Acta Part A Mol Biomol Spectrosc* 117:245–249
5. Refat MS, El-Hawary WF, Moussa MAA (2011) IR, ¹H NMR, mass, XRD and TGA/DTA investigations on the ciprofloxacin/iodine charge-transfer complex. *Spectrochim Acta Part A Mol Biomol Spectrosc* 78:1356–1363
6. Taxak VB, Khatkar SP (2012) Synthesis and Luminescent Properties of M₂V₂O₇: Eu (M= Sr, Ba) Nanophosphors. *J Fluoresc* 22:891–897
7. Leonzio M, Melchior A, Faura G et al (2018) A chiral lactate reporter based on total and circularly polarized Tb (III) luminescence. *New J Chem* 42:7931–7939
8. Devi R, Chahar S, Khatkar SP et al (2017) Relative study of luminescent properties with Judd-Ofelt characterization in trivalent europium complexes comprising ethyl-(4-fluorobenzoyl) acetate. *J Fluoresc* 27:1349–1358
9. Chahar S, Taxak VB, Dalal M et al (2016) Structural and photoluminescence investigations of Sm³⁺ doped BaY₂ZnO₅ nanophosphors. *Mater Res Bull* 77:91–100
10. Zhang Z, Tang R (2012) Synthesis and fluorescence properties of Tb (III) complex with a novel β-diketone ligand as well as spectroscopic studies on the interaction between Tb (III) complex and bovine serum albumin. *J Mol Struct* 1010:116–122
11. Kumar R, Boora P, Khatkar A et al (2016) Synthesis, photoluminescence and biological properties of terbium (III) complexes with hydroxyketone and nitrogen containing heterocyclic ligands. *Spectrochim Acta Part A Mol Biomol Spectrosc* 152:304–310
12. Sarioğlu AO, Yalçın ŞP, Ceylan Ü et al (2020) Photoluminescence properties of samarium (III)-based complexes: Synthesis, characterization and single crystal X-ray. *J Lumin* 227:117537
13. Kumar R, Makrandi JK, Singh I, Khatkar SP (2008) Preparation and photoluminescent properties of europium complexes with methoxy derivatives of 2'-hydroxy-2-phenylacetophenones. *J Lumin* 128:1297–1302
14. Kassim NK, Lim PC, Ismail A, Awang K (2019) Isolation of antioxidative compounds from *Micromelum minutum* guided by preparative thin layer chromatography-2, 2-diphenyl-1-picrylhydrazyl (PTLC-DPPH) bioautography method. *Food Chem* 272:185–191
15. Rieckmann KH, Sax LJ, Campbell GH, Mrema JE (1978) Drug sensitivity of *P. falciparum*. An in vitro microtechnique. *Lancet* 1:22–23
16. Hooda P, Taxak VB, Malik RK et al (2021) Designing of emerald terbium (III) ions with β-ketocarboxylic acid and heterocyclic ancillary ligands for biological and optoelectronic applications. *Luminescence*
17. Perkampus H (1976) LJ Bellamy: The Infrared Spectra of Complex Molecules, Vol. 1, 3. Auflage, Chapman and Hall Ltd., London 1975, 433 Seiten, 32 Abb., 22 Tabellen, Preis:£ 8.—

18. Khanagwal J, Kumar R, Hooda P et al (2021) Designing of luminescent complexes of europium (III) ion with hydroxyl ketone and nitrogen donor secondary ligands for improving the luminescence performance and biological actions. *Inorganica Chim Acta* 525:120463
19. Refat MS (2007) Synthesis and characterization of norfloxacin-transition metal complexes (group 11, IB): spectroscopic, thermal, kinetic measurements and biological activity. *Spectrochim Acta Part A Mol Biomol Spectrosc* 68:1393–1405
20. Bala M, Kumar S, Chahar S et al (2020) Synthesis, NMR and optical features of intense green color terbium (III) complexes. *Optik (Stuttg)* 202:163636
21. Al-Omar MA (2005) Ciprofloxacin: analytical profile. *Profiles of Drug Substances, Excipients and Related Methodology*. Elsevier
22. Skauge T, Turel I, Sletten E (2002) Interaction between ciprofloxacin and DNA mediated by Mg²⁺-ions. *Inorganica Chim Acta* 339:239–247
23. Bala M, Kumar S, Devi R et al (2018) Synthesis and photoluminescence properties of europium (III) complexes sensitized with β -diketonato and N, N-donors ancillary ligands. *Spectrochim Acta Part A Mol Biomol Spectrosc* 196:67–75
24. Khanagwal J, Kumar R, Devi R et al (2021) Photoluminescence performance of green light emitting terbium (III) complexes with β -hydroxy ketone and nitrogen donor ancillary ligands. *Luminescence* 36:742–754
25. Sadeek SA, El-Shwiniy WH, Zordok WA, El-Didamony AM (2011) Spectroscopic, structure and antimicrobial activity of new Y (III) and Zr (IV) ciprofloxacin. *Spectrochim Acta Part A Mol Biomol Spectrosc* 78:854–867
26. Phogat P, Khatkar SP, Malik RK et al (2021) Crystal chemistry and photoluminescent investigation of novel white light emanating Dy³⁺ doped Ca₉Bi (VO₄)₇ nanophosphor for ultraviolet based white LEDs. *Mater Chem Phys* 124828
27. Sehrawat P, Khatkar A, Boora P et al (2020) Tailoring the tunable luminescence from novel Sm³⁺ doped SLAO nanomaterials for NUV-excited WLEDs. *Chem Phys Lett* 755:137758
28. Khanagwal J, Kumar R, Bedi M et al (2021) Enhanced Optoelectronic and Biological Potential of Virescent-Glowing Terbium (III) Complexes with Pyrazole Acid. *J Electron Mater* 50:2656–2668
29. Bedyal AK, Kumar V, Ntwaeaborwa OM, Swart HC (2014) A promising orange-red emitting nanocrystalline NaCaBO₃: Sm³⁺ phosphor for solid state lightning. *Mater Res Express* 1:15006
30. Devi S, Khatkar A, Taxak VB et al (2018) Optical properties of trivalent samarium-doped Ba₅Zn₄Y₈O₂₁ nanodiametric rods excitable by NUV light. *J Alloys Compd* 767:409–418
31. Hooda A, Khatkar SP, Khatkar A et al (2019) Crystal structure, synthesis and photoluminescent properties of a reddish-orange light emitting SrGdAlO₄: Sm³⁺ nanophosphor. *Mater Chem Phys* 232:39–48
32. Yan B, Song YS (2004) Spectroscopic study on the photophysical properties of lanthanide complexes with 2, 2'-bipyridine-N, N'-dioxide. *J Fluoresc* 14:289–294
33. Parker D (2000) Luminescent lanthanide sensors for pH, pO₂ and selected anions. *Coord Chem Rev* 205:109–130
34. Chauhan A, Langyan R (2020) Preparation and optical features of samarium (III) complexes introducing bidentate fluorinate and secondary ligands. *J Mater Sci Mater Electron* 31:22085–22097
35. Nandal P, Kumar R, Khatkar A et al (2016) Synthesis, characterization, enhanced photoluminescence, antimicrobial and antioxidant activities of novel Sm (III) complexes containing 1-(2-hydroxy-4, 6-dimethoxyphenyl) ethanone and nitrogen containing ancillary ligands. *J Mater Sci Mater Electron* 27:878–885
36. Nandal P, Kumar R, Sheetal SP, Taxak VB (2018) Preparation, Photoluminescent Behaviour, Antimicrobial and Antioxidant Properties of New Orange Light Emitting Sm (III) Complex, Sm (CHME) 3. Dmphen

37. Chauhan A, Malik RK, Lohra S, Langyan R (2021) Investigation of photophysical properties of ternary Sm (III) complexes. *Optik (Stuttg)*242:167078
38. Chauhan A, Langyan R (2021) Preparation, characterization and luminescence behavior of some samarium complexes. *Rare Met*40:2618–2626
39. Dar WA, Ganaie AB, Iftikhar K (2018) Synthesis and photoluminescence study of two new complexes [Sm (hfaa) 3 (impy) 2] and [Eu (hfaa) 3 (impy) 2] and their PMMA based hybrid films. *J Lumin*202:438–449
40. Räsänen M, Takalo H, Rosenberg J et al (2014) Study on photophysical properties of Eu (III) complexes with aromatic β -diketones–Role of charge transfer states in the energy migration. *J Lumin*146:211–217
41. Latva M, Takalo H, Mukkala V-M et al (1997) Correlation between the lowest triplet state energy level of the ligand and lanthanide (III) luminescence quantum yield. *J Lumin*75:149–169
42. Liu J-Y, Ren N, Zhang J-J, Zhang C-Y (2013) Preparation, thermodynamic property and antimicrobial activity of some rare-earth (III) complexes with 3-bromo-5-iodobenzoic acid and 1, 10-phenanthroline. *Thermochim Acta*570:51–58

Figures

Figure 1

The IR spectra of L and S1 complex.

Figure 2

The ^1H -NMR spectrum of ligand L and its S1 complex.

Figure 3

UV-Vis absorption spectra of ligand and all synthesized S1-S6 complexes.

Figure 4

TG/DTG curve of S1 complex of samarium in nitrogen atmosphere.

Figure 5

(a) The diffused reflectance spectrum of ligand and inset represent the corresponding reflectance spectrum. (b) The diffused reflectance spectra of S1-S6 complexes and inset displays its corresponding reflectance spectra.

Figure 6

(a) The excitation spectra of all S1-S6 complexes monitored at 606 nm. (b) the emission spectra of all S1-S6 complexes monitored at 356 nm. (c) Luminescence decay curves for all S1-S6 complexes monitored at $\lambda_{EM} = 606 \text{ nm}$ and $\lambda_{EX} = 356 \text{ nm}$.

Figure 7

CIE color coordinates representation of all S1-S6 complexes.

Figure 8

The systematic energy transfer pathway for [Sm(L)3.bipy].6H2O complex.

Figure 9

The absorbance of ligand spectrum and inset represent the phosphorescence spectrum of corresponding gadolinium complex.

Figure 10

(a) Percentage scavenging activity of L and S1-S6 complexes with respect to standard drugs. (b) The IC₅₀ values of ligand and all synthesized complexes with respect to standard drugs. (c) The antibacterial activities of L and all S1-S6 complexes with respect to standard drugs.

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