RESEARCH ARTICLE



Synthesis of cool white light emitting novel dysprosium (Dy³⁺) complexes with tetradentate β -ketoamide and heterocyclic auxiliary ligands

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Abstract

To improve current multiphase white light emitting diodes (WLEDs), a novel series of five complexes consisting of one binary and four ternary complexes that emitted cool white light was successfully synthesized using a chelating tetradentate ligand and auxiliary ligands, i.e. 5,6-dimethyl-1,10-phenanthroline, 1,10-phenanthroline, 4,4'dimethyl-2,2'-bipyridyl, and 2,2'-bipyridyl. The series was examined structurally using elemental analysis, Fourier transform infrared spectroscopy, energy dispersive X-ray analysis, ultraviolet-visible spectroscopy, and proton nuclear magnetic resonance spectroscopy. These complexes had the appropriate thermal stability required for the generation of white organic LEDs (WOLEDs). Dysprosium (III) (Dy³⁺) ion complexes demonstrated the characteristic emission peaks of blue colour at 482 nm and yellow colour at 572 nm, respectively, when excited using near ultraviolet light. Band gap, refractive index, and decay lifetime of the optimized samples were recorded as 2.68 eV, 2.12, and 1.601 ms, respectively. Correlated colour temperature value (7875 K), Commission International de l'Eclairage coordinates (0.300, 0.294), and colour purity (21.04×10^{-2}) of the optimized complex were near to those of white illuminants as defined by the National Television System Committee. These complexes had promise as commercial LEDs for the advanced optoelectronics devices, especially as WOLEDs for illumination applications.

KEYWORDS

β-ketoamide tetradentate ligand, dysprosium, luminescence, spectral analysis, WOLED

1 | INTRODUCTION

In the illumination science and technology field, white light-emitting organic material has been an unambiguous illuminant and is used, for example, in fluorescence and incandescence lamps.^[1-4] Researchers have been interested in white organic light emitting diodes (WOLEDs) because of their many benefits such as high productivity, long lifetime, reliability, low energy consumption, and environment friendly characteristics. At this time, luminescence systems in the bioanalysis and material sciences fields are encouraging. Many applications have been established such as in lighting devices, lasers, sensor devices, optical

communication, luminescence thermometry, and for display devices, bioimaging, and bio-labels. $^{\left[5-7\right] }$

For most lanthanide ions, metal-centred luminescence arises in the near infrared (near-IR), visible, and ultraviolet (UV) light regions of the electromagnetic spectrum due to intraconfigurational f-f transitions. The 4f subshell energy levels are affected by the chemical environment of organic ligands around the lanthanide ions due to shielding of the 4f subshell by 5s and 5p subshells. This results in intense emission peaks from the lanthanide ions.^[8] Conversely, lanthanide ions show weak emission intensity due to the Laporte forbidden rule for f-f transitions. Intensity of lanthanide-mediated luminescence can be increased by incorporating the ions within a framework of chromophoric organic ligands.^[9-12] Using photosensitizer energy transfer processes, organic ligands with large absorption coefficients (K) absorb UV-visible light and then transfer it to the metal ion.^[13,14] Therefore, suitable organic ligands have been synthesized that have strong binding sites and that efficiently sensitize metal ions. Further enhancement of emission intensity, radiative lifetime, and internal quantum yield are possible by creating a mixed coordinated environment in which f-f transitions are no longer forbid-den.^[15-17] A mixed environment has been obtained using heteroatoms containing ligands as ancillary ligands.

In the present work, a β -ketoamide tetradentate ligand, i.e. ethylenediamine-*N*,*N'*-bis(acetoacetamide) (L), was prepared and had a strong binding site. Using the one pot chemical reaction method, a new series of organic complexes was synthesized using Dy(III) ions and based on ligand L and auxiliary ligands, i.e. 5,6-dimethyl-1,10-phenanthroline (dmph), 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridyl (dmbipy), and 2,2-bipyridyl (bipy). The structural framework and thermal behaviour of the organic complexes were characterized using nuclear magnetic resonance (NMR), elemental analysis (EA), energy dispersive X-ray analysis (EDAX), IR radiation, and thermogravimetric (TG) analyses. The optical features of the complexes were explored using diffuse reflectance (DR), UVvisible light absorbance, and photoluminescence (PL) analysis.

2 | EXPERIMENTAL

In this research work, pure lanthanide nitrates $(Dy(NO_3)_3.5H_2O)$ and gadolinium Gd(NO₃)₃.6H₂O) of Sigma Aldrich company was utilized to prepare complexes. Other high purity chemicals were also used as received.

2.1 | Synthesis of ligand

The ligand ethylenediamine-*N*,*N*′-bis (acetoacetamide) **L** was synthesized as a crude solid by mixing ethane-1,2-diamine and tert-butyl acetoacetate in xylene and refluxing for 2 h, followed by the subsequent removal of xylene by vacuum evaporation. To prepare white precipitates, the solution of the crude solid in hexane and ethyl acetate was left overnight and then collected by filtration and dried in vacuum desiccators.^[18] Analysis: Fourier transform infrared (FT-IR): cm⁻¹ 3282 (s), 3094 (s), 2948 (m), 1722 (s), 1641 (s), 1564 (s), 1423 (m), 1418 (w), 1240 (w), 1164 (w), 941 (w), 737 (w), 621 (s), 539 (s), 397 (s). Proton NMR (¹H-NMR) (D₂O, 400 MHz): chemical shift on the delta scale (δ) 8.10 (t, 2H, NH), 4.70 (s, 4H, -CH₂-), 3.24 (d, 4H, -CH₂-), 2.14 (s, 6H, -CH₃) parts per million (ppm).

2.2 | Synthesis of complexes C1-C5

An aqueous solution of ligand L (2×10^{-3} mol) was added slowly into a stirred solution of dysprosium nitrate (Dy(NO₃)₃.6H₂O) (1×10^{-3} mol)

in water, supervised by careful heating of the mixture on a hot plate at 150°C. A dark yellow solid, the C5 complex, was collected from the beaker, after complete evaporation of the liquid.^[19] The resultant solid was washed with cold water and dried under reduced pressure. A similar mechanism was followed to synthesize C1–C4 complexes using Dy(NO₃)₃.6H₂O, ligand L and ancillary ligands at a molar ratio of 1:1:2, respectively. The aqueous solution of Dy(NO₃)₃.6H₂O (1 ×10⁻³mol) and ligand L (1 ×10⁻³mol) was mixed with an ethanolic solution of ancillary ligands, dmph (2×10⁻³ mol), phen (2×10⁻³ mol), dmbipy (2×10⁻³ mol), and bipy (2 ×10⁻³ mol) to synthesize the C1–C4 ternary complexes, respectively. To obtain the position of the triplet state of ligand L, the complex (Gd(L)(H₂O)₄).3NO₃ (G1) was also synthesized following the above-mentioned method. Scheme 1 shows a summary of the synthesis pathway and chemical structures of ligand L and the Dy(III) complexes (C1–C5).

- (Dy(L)(dmph)₂).3NO₃ (C1): light yellow; FT-IR: cm⁻¹ 3281 (s), 3096 (m), 2943(m, b), 2361 (m), 1709 (m), 1642 (s), 1556 (m), 1490 (b), 1385 (s), 1299 (s), 1171 (m), 1142 (w), 1077(w), 1038 (s), 950 (m), 809 (s), 732 (s), 670 (w), 618 (m), 542 (m), 420 (m);); ¹H-NMR (dimethyl sulphoxide (DMSO), 400 MHz): δ 9.051 (t, 1H, NH), 8.47 (t, 1H, NH), 8.29 (d, 4 H, Ar-H), 7.79 (m, 12 H, Ar-H), 4.91 (s, 2H, -CH₂-), 3.34 (s, 2H, -CH₂-), 3.12 (t, 2H, -CH₂-), 3.09 (t, 2H, -CH₂-), 2.65 (s, 6H, -CH₃), 2.50 (s, 6H, -CH₃), 2.47 (s, 3H, -CH₃), 1.79 (s, 3H, -CH₃), ppm.
- (Dy(L)(phen)₂).3NO₃ (C2): pinkish; FT-IR: cm⁻¹ 3286 (s), 3096 (s), 2953 (m, b), 2357 (m, b), 1718 (s), 1642 (s), 1562 (m), 1499 (b), 1380 (s), 1304 (s), 1116 (m), 1038 (s), 814 (s), 732 (s), 623 (m), 542 (m), 418 (m); ¹H-NMR (DMSO, 400 MHz): δ 9.11 (t, 1H, NH), 8.52 (t, 1H, NH), 8.32 (d, 4 H, Ar-H), 7.80 (m, 12 H, Ar-H), 4.94 (s, 2H, -CH₂-), 3.36 (s, 2H, -CH₂-), 3.14 (t, 2H, -CH₂-), 3.13 (t, 2H, -CH₂-), 2.50 (s, 3H, -CH₃), 1.82 (s, 3H, -CH₃), ppm.
- (Dy(L)(dmbipy)₂).3NO₃ (C3): pinkish; FT-IR: cm⁻¹ 3374 (b), 2393 (m, b), 1704 (w), 1638 (s), 1538 (w), 1490 (w), 1381 (s, sh), 1175 (w), 1031 (w), 940 (w), 830 (w),671 (b) 543 (m), 438(w); ¹H-NMR (DMSO, 400 MHz): δ 9.12 (t, 1H, NH), 8.61 (t, 1H, NH), 7.67 (d, 4 H, Ar-H), 7.68 (m, 12 H, Ar-H), 4.91 (s, 2H, -CH₂-), 4.11 (s, 2H, -CH₂-), 3.61 (t, 2H, -CH₂-), 3.47 (t, 2H, -CH₂-), 2.61 (s, 6H, -CH₃), 2.52 (s, 6H, -CH₃), 2.49 (s, 3H, -CH₃), 1.80 (s, 3H, -CH₃), ppm.
- (Dy(L)(bipy)₂).3NO₃ (C4): pinkish; FT-IR: cm⁻¹ 3376 (b), 2390 (m, b), 1709 (w), 1642 (s), 1542 (m), 1442 (w), 1385 (s, sh), 1185 (w), 1038 (w), 951 (w), 823 (w),666 (b), 575 (w) 427 (w); ¹H-NMR (DMSO, 400 MHz): δ 9.16 (t, 1H, NH), 8.63 (t, 1H, NH), 7.89 (d, 4H, Ar-H), 7.72 (m, 12H, Ar-H), 4.93 (s, 2H, -CH₂-), 4.21 (s, 2H, -CH₂-), 3.64 (t, 2H, -CH₂-), 3.51 (t, 2H, -CH₂-), 2.59 (s, 3H, -CH₃), 1.91 (s, 3H, -CH₃), ppm.
- (Dy(L)₂).3NO₃ (C5): dark yellow; FT-IR: cm⁻¹ 3329 (b), 2357 (w) 1652 (s), 1544 (m), 1487 (s), 1386 (s), 1293 (w), 1172 (w), 1031 (m), 845 (m), 743 (m), 653 (w), 433 (m); ¹H-NMR (DMSO, 400 MHz): δ 9.04 (t, 2H, NH), δ 8.53 (t,1H, NH), δ 8.11 (t, 1H, NH), 4.95 (s, 4H, -CH₂-), 4.74 (s, 4H, -CH₂-), 3.39 (t, 4H, -CH₂-), 3.11 (t, 4H, -CH₂-), 2.49 (s, 6H, -CH₃), 2.13 (s, 6H, -CH₃), ppm.

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SCHEME 1 Synthesis route and chemical structures of ligand L and the Dy(III) complexes (C1–C5)



TABLE 1	Analytical data for ligand (L)
and C1-C5 d	ysprosium (III) complexes

Complex	C (%) found (cal)	H (%) found (cal)	N (%) found (cal)	Dy (%) found (cal)
L	52.61 (52.63)	7.02 (7.01)	12.30 (12.28)	-
C1	45.94 (45.92)	4.03 (4.01)	12.69 (12.67)	16.37 (16.35)
C2	43.56 (43.53)	3.41 (3.39)	13.45 (13.43)	17.35 (17.33)
C3	43.02 (43.01)	4.63 (4.61)	13.28 (13.26)	17.13 (17.11)
C4	40.51 (40.50)	3.61 (3.60)	14.18 (14.17)	18.28 (18.26)
C5	29.83 (29.82)	3.97 (3.95)	12.18 (12.16)	20.19 (20.13)

3 | RESULTS AND DISCUSSION

3.1 | Elemental composition

EDAX spectroscopy results were obtained using an Ametek EDAX system; measurements for carbon, hydrogen, and nitrogen (CHN) EA were carried out on a Perkin Elmer CHN 2400 elemental analyzer, to authenticate the elements present in the complexes. Agreement of the CHN and EDAX findings accurately demonstrated that the percentage elemental compositions of samples were in accordance with their suggested formulae. The composition data are listed in Table 1. EDAX spectra were also used to determine the quantitative elemental

composition (C, O, N, and Dy) of the synthesized complexes with the help of peak analysis (Figure 1). $^{[20-22]}$

3.2 | FT-IR spectral analysis

FT-IR spectra of powder samples were measured using an Alpha Bruker spectrophotometer, over the wavelength range $400-4000 \text{ cm}^{-1}$.

The peak at 3282 cm⁻¹ in the ligand **L** spectra corresponded to the stretching vibrations of the amide groups N-H bonds. This band was also found in spectra of the complexes at *c*. 3300 cm⁻¹ with

EDAX spectrum of optimized

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variation in intensity and shape. These findings suggested that binding of ligand L to dysprosium ions occurred without deprotonation. Peaks at 1722 cm⁻¹ and 1641 cm⁻¹ were attributed to the stretching vibrations of >C=O bonds of keto and amide groups, respectively. In the spectra for the complexes, the transition frequency as well as intensity of these two bands varied, and represented binding of ligand L to Dv metal ions through carbonyl groups. Moreover, the band assigned to vibrations of Dy-O bonds was obtained at c. 418 cm⁻¹, as discussed in a previous publication.^[23] The peaks associated with bending vibrations of N-H bonds and stretching vibrations of C-N bonds were shifted towards lower and higher frequencies, respectively. These shifts also showed consistency of binding in carbonyl groups and metal ions. The peaks displayed in the spectra of ternary complexes at 542 cm⁻¹ were present due to the stretching vibrations of Dy-N bonds and indicated binding between secondary ligand and metal ion through nitrogen atoms.^[24] The peak present at 1380 cm⁻¹ was related to the free nitrate group.^[25] Analogous IR spectra of the dysprosium complexes C1-C5 indicated that they had almost the same chemical environment around the dysprosium ions. Spectra for ligand L and complex C2, as a representative of all the complexes, are presented in Figure 2(a, b). The significant IR spectral data of complexes (C1-C5) and ligand (L) are listed in Table 2.

¹H-NMR spectral analysis 3.3

A Bruker Avance II 400 NMR spectrometer with tetramethylsilane as the internal reference was used to obtain ¹H-NMR spectral data.

The ¹H-NMR spectra of Dy³⁺ complexes and ligand were recorded at room temperature in DMSO solvent. The ¹H-NMR spectrum of the ligand displayed significant variation compared with the spectra of the Dy³⁺ complexes. In the proton NMR spectrum of the ligand (Figure 3a), the signal for the amide protons was located at δ 8.10 ppm, methylene group protons bound to NH groups were located at δ 3.24 and those bound to carbonyl groups were positioned at δ 4.70 ppm. The peak for the terminal methyl protons was situated at δ 2.14 ppm. In the spectra of the complexes, the signal for the amide protons revealed splitting as well as downfield shifting. On complexation of the metal ion with ligand L, splitting may be attributed to nonequivalence protons of two amide groups. Due to the involvement of neighbouring carbonyl groups in bond formation, the



FIGURF 1

(C5) sample

FIGURE 2 (a) IR spectra of ligand (L). (b) IR spectra of complex (Dy(L)(phen)₂).3NO₃ (C2)

electron density around the amide protons decreased and led to downfield shifting in the range δ 8.11–9.11 ppm and the intensity of the complexes diminished. Moreover, in the inner coordination sphere of the complexes, the C1-C4 ternary complexes showed peaks in the

LUMINESCENCE_WILEY 5

TABLE 2	Main infrared spectral data
for the uncoc	ordinated ligand L and its
dysprosium (I	II) complexes C1-C5

Compound	ν_{N-H}	VCONH	$\nu_{C=O}$	δ_{N-H}	ν_{C-N}	ν _{Dy-N}	$\nu_{\rm Dy-O}$
L	3282 (s, sh)	1722 (s)	1641 (s)	1565 (m)	1423 (m)	-	-
C1	3281 (s)	1709 (m)	1642 (s)	1556 (m)	1490 (b)	540 (m)	420 (m)
C2	3286 (s)	1718 (m)	1642 (s)	1563 (m)	1499 (b)	542 (m)	418 (m)
C3	3374 (b)	1704 (w)	1638 (s)	1538 (w)	1490 (w)	543 (m)	438 (w)
C4	3376 (b)	1709 (w)	1642 (s)	1542 (m)	1442 (w)	575 (w)	427 (w)
C5	3329 (b)	1719 (w)	1652 (s)	1544 (m)	1487 (s)	-	433 (m)

b, broad; m, medium; s, strong; w, weak; ν , frequency.



range δ 7.80–8.52 ppm in $^1\text{H-NMR}$ spectra that were attributed to aryl protons of secondary ligands.^[26] All the complexes of the dysprosium ions demonstrated similar spectral behaviour, therefore the spectrum for C2 complex is depicted in Figure 3(b) as a representative of the complexes.

Thermal analysis 3.4

The HiRes 1000 TG analysis system was used to perform TG analysis in the temperature range 30-600°C with a 10°C/min increase in temperature under an inert atmosphere of nitrogen gas.

The breakdown behaviour of all dysprosium (III) complexes was almost similar and was clearly concluded by their resulting thermograms. The decomposition of only one complex, i.e. the C2 complex, was excellent, and is given as a representative of all the complexes. The TG curve for C2 is depicted in Figure 4 and described in detail. Decomposition of the C2 complex proceeded in three steps, and was concluded by its TG curve; initial weight loss of *c*. 6.7% over temperature range 160–180°C resembled the elimination of one nitrate ion. Subsequent loss in weight of *c*. 13.3% over the range 190–210°C was attributed to exclusion of the remaining two nitrate ions from outside the coordination sphere. Next, 63% loss of weight in the third step from 260 to 420°C was endorsed by the removal of a ligand molecule and two ancillary ligand molecules (i.e. phen).

Finally, the curve beyond 420°C was attributed to the remaining final residue of the dysprosium oxide. These thermal studies suggested that stability of the PL entity occurred up to 200°C, and confirmed the use of these complexes as promising materials for WOLEDs.^[27]

3.5 | UV-visible absorption and diffuse reflectance analysis

A Shimadzu UV-3600 plus spectrophotometer with $BaSO_4$ as the reference material was used to measure the liquid state absorption and solid-state DR spectra of the samples in the wavelength range 200–700 nm.

The UV-visible spectra of the Dy complexes (C1-C5) and free ligand (L) consisted of one band with ranges 250–335 nm and 250–400 nm, respectively, as shown in Figure 5. The band was assigned to $\pi \rightarrow \pi^*$ electron transitions of the ligand due to formation of conjugated chelated rings.^[28,29] The maxima of ligand and complexes were measured at 284 nm (for L) and for C1-C5, respectively, at 298 nm, 302 nm, 310 nm, 311 nm, and 314 nm. These shifts (14–30 nm) in absorption spectra of the complexes (C1-C5) in the direction of increasing wavelengths was due to coordination.^[30–32] The main



FIGURE 4 TGA curve of complex $(Dy(L)(phen)_2)$.3NO₃ (C2) under an inert N₂ atmosphere



FIGURE 5 UV-visible absorption spectra of ligand (L) and Dy³ ⁺ complexes (C1–C5)

TABLE 3 Optical band gap values, lifetime values, and refractive index values (n) for the Dy(III) complexes (C1–C5)

Complexes	Band gap (eV)	τ (ms)	n
C1	3.42	1.168	1.96
C2	3.25	1.428	1.99
C3	3.17	1.468	2.01
C4	2.71	1.491	2.11
C5	2.68	1.601	2.12

contribution to the absorption spectra of the complexes came from ligand centred transitions, which were shown by the similarity between the absorption spectra of dysprosium (III) complexes and the spectrum of ligand L.

Optical properties of the ligand and complexes were obtained using UV-visible spectroscopy. Band gap values of the complexes and ligand as listed in Table 3 were determined using the Kubelka-Munk function (F(R_∞)) and h_ν (energy of photon) as given in Equation (1):^[33,34]

$$\left\{hv F(R_{\infty})\right\}^{m} = C(hv - E_{g})$$
(1)

where C, ν , h, and E_g represent, respectively, the proportionality constant, energy of incident radiation, Plank's constant, and the energy band gap. The exponent m values were different under different conditions, i.e. for direct allowed (m = 2), direct forbidden (m = 1.5), indirect forbidden (m = 3), and indirect allowed (m = 0.5). Kubelka–Munk function, F(R_∞), was associated with the observed reflectance (R_∞ = R_{normal}/R_{standard}) of the samples through scattering coefficient (S) and absorption coefficient (K) as:^[34]

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

On tangential extrapolation of $(h\nu F(R_{\infty}))^2$ versus the $h\nu$ curve to zero in Tauc plots, the band gap values were calculated as 3.97 eV for ligand and 2.68 eV for the optimized complex. The E_g value of the ligand L (3.97 eV) was higher compared with that of complexes C1–C5 (3.42–2.68 eV). This decrease in energy band gap between conduction band and valence band was due to the extended structural framework of the Dy³⁺ complexes.^[35–37] The optical band gap values for complexes were in the range for wide band gap (WBG) semiconductors and demonstrated the better luminescence properties of the samples and the application of these complexes in OLEDs, laser technologies, military radars, and especially WOLEDs. Figure 6(a, b) represents the Tauc plots for ligand L and the C5 complex, whereas their DR spectra are shown in the insets.

Using the band gap values, the refractive index (n) of the samples could be calculated, as shown in Equation 3:^[38]



$$\frac{n^2 - 1}{n^2 + 1} = 1 - \sqrt{\frac{E_g}{20}}$$
(3)

FIGURE 6 (a) Tauc plots of ligand **L**. Inset shows the resultant DR spectra. (b) Tauc plots of Dy^{3+} complex ((DyL₂).3NO₃) (C5). Inset shows the resultant DR spectra

The refractive index values for ligand (1.87) and complexes (1.96–2.31) were comparable, as presented in Table 3, with zinc oxide (n = 2.0) and zirconium dioxide (n = 2.1). Therefore, this increased presentation of the complexes for use in photonic crystal fibres and optoelectronic devices.^[39,40]

3.6 | Photoluminescence spectra

The PL spectral properties of the complexes were studied using an Hitachi F-7000 fluorescence spectrophotometer, in which a xenon lamp was used as the radiation source. Slit width and voltage of the spectrophotometer were fixed at 2.5 nm and 700 photomultiplier tube (PMT) voltage, respectively.

The excitation spectra for the Dy^{3+} complexes were measured in the range 200–500 nm, with emission wavelengths of 482 and 572 nm (Figure 7a). In the spectra, a broad, intense band from 300 nm to 400 nm was attributed to ligand transitions.^[41–43] This band showed that the dysprosium ion was predominantly excited by ligand **L**. Excitation maxima for the complexes were situated at 344 nm wavelength and were close to the UV-vis absorption maxima.

For the wavelength range 400-700 nm, the emission spectra of the five C1-C5 complexes were generated at room temperature, with 344 nm as excitation wavelength. The sharp, well separated spectra agreed with the precise transitions of the dysprosium ion from the resonating level of the dysprosium (III) ion, ${}^{4}F_{9/2} \rightarrow {}^{6}H_{1}$ (where J = 15/2, 13/2).^[44] The emission spectra of the Dv³⁺ complexes consisted of two emission peaks: one peak was located in the blue region of the visible spectrum at 482 nm and was due to magnetic dipole (MD) transitions and other peak was located in the vellow region at 572 nm and was due to electric dipole (ED) transitions, which were dominant.^[45,46] A wide band range of 400-550 nm was observed in the spectra from the C1-C4 complexes and could be assigned to the residual emission of ancillary ligands. The spectra for the five complexes (C1-C5) were different in terms of intensity, but similar in shape. The magnitude of intensity for these complexes was in decreasing order from C5 to C1, as depicted in Figure 7(b). The spectrum of the C5 complex was most intense because:

- Participation of water molecules was inhibited by the presence of two molecules of ligand L that completed the coordination sphere of complex C5, thereby enhancing the luminescence intensity of the complex. Vibronic coupling of high-energy O-H oscillators of H₂O can quench luminescence intensity if they are present in coordination sphere.^[47–49]
- A stronger, stable structure was formed in the complex due to the total chelated nature of the C5 complex that shielded it from lattice vibrations.
- 3. There was effective overlap of the resonance energy state of the dysprosium ion and the excited triplet energy state of ligand L.

To examine the uniformity around the dysprosium ion, at room temperature, the decay time (τ) profiles of the Dy³⁺ complexes were



Complex	Colour coordinates (x, y)	СР	u′, v′	CCT (K)
C1	0.275, 0.239	45.48×10 ⁻²	0.207, 0.405	17 603
C2	0.284, 0.249	40.04×10 ⁻²	0.209, 0.414	13 026
C3	0.279, 0.302	25.64×10 ⁻²	0.184, 0.448	9442
C4	0.268, 0.272	36.71×10 ⁻²	0.187, 0.427	12 795
C5	0.300, 0.294	21.04×10^{-2}	0.202, 0.446	7875

 TABLE 4
 Calculated colour

 coordinates, colour purity, (u, v), and CCT

 values for the C1-C5 complexes

recorded by fitting both excitation (344 nm) and emission (482 nm, 572 nm) wavelengths. The monoexponential decay curve for the complexes suggested that dysprosium ions were situated at same equivalence sites (Figure 7c). The lifetime values (τ) for the C1–C5 complexes were calculated using a single exponential curve fitting program and were 1.168, 1.428, 1.468, 1.491, and 1.601, respectively^[50] (Table 3). The higher lifetime value of the C5 complex was attributed to the solvent free and complete chelation.

3.7 | Chromaticity analysis

Commission Internationale de l'Eclairage (CIE), 1931 chromaticity colour coordinates (x, y) were used to analyze the performance of the prepared complexes. Using MATLAB software, the CIE coordinates of the synthesized samples were calculated by introducing emission spectral data. The calculated colour coordinates for C1–C5 as listed in Table 4 were (0.275, 0.239), (0.284, 0.249), (0.279, 0.302), (0.268, 0.272), and (0.300, 0.294), respectively. These values were close to those of white illuminants as defined by the National Television System Committee (NTSC). The given coordinates were in close agreement with the coordinates reported by Sehrawat *et al.*^[50] A photograph of an optimized sample under UV lamp is shown in the inset in the CIE diagram. Coordinates were plotted (Figure 8a), and lay in the white region of the colour map, therefore demonstrating their widespread use in solid illumination, mainly in WOLEDs.^[34,35]

The colour purity (CP) of the complexes is listed in Table 4. The optimized complex gives the lowest value of CP (21.04×10^{-2}), suggesting the purity of the white light.

In addition, the correlated colour temperature (CCT) was determined to assess the excellence of the white light, and to illustrate the nature of the emitted light (coolness as well as warmth) in affinities of temperature. CCT values less than 3200 K are termed 'warm', whereas values above 4000 K are characterized as 'cool'.^[35] The calculated values for u', v', and CCT are listed in Table 4.

Furthermore, Figure 8(b) shows the CCT diagram of the best sample. CCT values for all the synthesized complexes were between 5516 and 17 603 K, which demonstrated their cool white light quality. These complexes could therefore be used to great effect in WOLEDs for outdoor lighting.^[31–35]

3.8 Photosensitized energy transfer process

The photosensitized energy transfer process for the complexes was interpreted using emission spectral data. The process of energy transfer

PUNIA ET AL.



FIGURE 8 (a) CIE chromaticity diagram for the Dy³⁺ complexes. Inset displays the UV lamp image of the optimized complex (C5). (b) CCT diagram of the optimized complex (C5)

in the Dy³⁺ complexes involved photoexcitation of ligands from the ground singlet state (S_0) to the excited singlet state (S_1) by absorption of UV-visible light. These excited ligands transferred energy to emissive excited states of the dysprosium ion through their triplet state by intersystem crossing. Then, the excited emitting energy level of the dysprosium ion showed emission characteristics in the visible region through multiphoton relaxation. The energy value of the excited singlet state of ligand was calculated using its UV-visible absorption spectrum. The phosphorescence spectra of the $(Gd(L)(H_2O)_4)$ (G1) complex are shown in Figure 9 and were used to determine the triplet state of the ligand with the lowest emission wavelength. The lowest energy level for the G1 complex was at c. 32 000 cm⁻¹ and was much above the triplet state of ligand. Therefore, energy transfer was not permitted from the triplet state of ligand to the Gd³⁺ ion.^[51] According to Reinhoudt, an energy gap of c. 5000-8000 cm^{-1} is required for efficient transition from singlet to triplet states in a ligand. Furthermore, the difference in energy between the triplet states of the ligand and emissive level of the dysprosium ion should also be in the range c. 2000-



FIGURE 9 Phosphorescence spectrum of the gadolinium complex (Gd(L)(H₂O)₄).3NO₃ (G1)

TABLE 5 Energy parameters of main ligand L and secondary ligands (bipy and phen) in cm⁻¹ for the sensitization phenomenon

Ligands	S ₁	T ₁	$\Delta E_0 (S_1 - T_1)$	∆E (T ₁ - ⁴ F _{9/2})
L	30 581	23 474	7107	2474
bipy	29 900	22 900	7000	1900
phen	31 000	22 100	8900	1100

 ΔE_0 , energy gap between excited singlet and triplet state; ΔE_1 , energy gap between excited triplet state and resonating level.

5000 cm^{-1[52-54]} If the excited states are close enough together, the luminosity of the complexes reduces and peaks also show wide, weak characteristics in addition to a narrow, sharp profile, due to the back energy transfer process.^[55] Our explanation, for emission spectra of the complexes is that, unlike the binary (C5) complex, the slightly weak, wide band range 400-550 nm observed for the spectra of the ternary (C1-C4) complexes may attributed to residual emission of ancillary ligands. This was because the energy gap between the triplet state of the ancillary ligands and emitting state of the dysprosium metal ion was less than 2000 cm⁻¹. The energy difference between the triplet state of ancillary ligands (bipy and phen) and the ${}^{4}F_{9/2}$ excited level of the dysprosium ion was 1900 and 1100 cm⁻¹, respectively, leading to comparatively less energy transfer. Some transferred energy was transferred back to the triplet state of the ancillary ligand and was emitted as a wide band in the range 400-550 nm. The excited singlet (S₁) and triplet (T1) states of the secondary ligands were taken from previous publications and energy transfer-related parameters are summarized in Table 5. The S₁ and T₁ states of ligand **L** were positioned, respectively, at 30 581 and 23 474 cm⁻¹. The excited level (${}^{4}F_{9/2}$) of the dysprosium ion was positioned at 21 000 cm⁻¹.^[56] The singlet and triplet states of the main ligand L had an optimum energy gap of 7107 cm⁻¹ for effective intersystem crossing. The difference in energy between the T_1 excited level of ligand L and the ${}^{4}F_{9/2}$ excited level of the dysprosium ion was 2474 cm⁻¹. The ⁴F_{9/2} excited level decayed to the ⁶H_{13/2} emissive excited level through a nonradiative decay process. This signified that ligand L had the capacity to sensitize the dysprosium ion. The C5



FIGURE 10 Energy transfer mechanism of the dysprosium (III) complex ((DyL₂).3NO₃) (C5)

complex contains, in their coordination sphere, two tetradentate ligands for **L** as an antenna ligand. This C5 complex had high intensity due to the presence of the most suitable energy gap (2747 cm⁻¹) for transferring energy from the triplet state of ligand to the resonance level of the dysprosium ion. Furthermore, a stronger, stable structure for the complex was formed due to the total chelated nature of the C5 complex that shielded it from lattice vibrations. The process of energy transfer for the C5 complex is presented in Figure 10.

4 | CONCLUSION

Here, a new series of five dysprosium complexes (C1-C5) were synthesized by mixing tetradentate ligand (L) as the main ligand and heterocyclic auxiliary ligands as secondary ligands with dysprosium metal ions. The characteristics of these complexes were investigated using EA (CHN and EDAX), IR and NMR spectroscopy, and TG analysis. The ancillary ligand bound through nitrogen atoms and the main ligand bound through carbonyl oxygen atoms in keto and amide groups, respectively. EDAX spectra detected guantitatively the elemental composition of the synthesized sample. Emission spectra of the Dy³⁺ complexes consisted of two emission peaks: one peak was located in the blue region of the visible spectrum at 482 nm and was due to MD transitions and other peak was located in the yellow region at 572 nm and was due to ED transitions under excitation in the UV region, i.e. 344 nm. The complexes were thermally stable up to 200°C, which was clearly represented by the TG curve of the C2 complex. The E_g values of the complexes were in the range for WBG semiconductors, indicating that these complexes were suitable for application in LEDs, signal processing, and laser technology. Finally, CIE coordinates and the CP of the complexes proposed an emission of cool white light, because they were near to the white coordinates of NTSC and commercial LEDs. Based on these interesting results, these complexes could be used as multifunctional photoluminescent materials in applications such as lighting, laser technology, semiconductors, and display devices.^[35,57]

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