Synthesis, Characterization and Photophysical properties of Lanthanide (III) Complexes with dicyandiamide in 2-ethoxyethanol

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ABSTRACT

Five novel lanthanide (Tb^{3+}, Eu^{3+}, Gd^{3+}, Sm^{3+} and Dy^{3+}) complexes with dicyandiamide in 2-ethoxyethanol were synthesized and characterized. The spectroscopic studies indicate the formation of lanthanide complexes. The thermal analysis data indicate a series of wt. loss of the ligand at different temperatures. The photophysical properties of these complexes were studied using ultraviolet-visible absorption spectra, fluorescence excitation and emission, and phosphorescence spectra. The ligand acts as the main energy donor and luminescence sensitizer of the Ln^{3+} ions. The luminescence intensities of Tb^{3+}complex show the strongest luminescence and Sm^{3+} species show the weakest emission. Life-time studies on (Tb^{3+} and Eu^{3+}) complexes indicate biexponential nature of the luminescence decay.

Keywords: Lanthanide complexes, Luminescence, Terbium, Dicyandiamide, biexponential.
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INTRODUCTION

In recent years, there has been a growing interest in the photophysical properties of lanthanide coordination compounds with organic ligands because these complex systems can be used as active centres of luminescent materials [1-3] or the structural and functional probes for chemicals or biological macromolecule systems [4-6]. Effective shielding of the 4f orbitals of the lanthanide ions by the $5s^2 5p^6$ octet precludes the existence of strongly covalent cation-ligand interaction and accounts for the substantially electrostatic bonding indicated by the recorded magnetic, spectral, and rapid ligand-exchange properties of these complex species. Of the ligands forming complexes with the lanthanide ions, the majority, by a wide margin, contain oxygen-atom donor sites in their molecular structures. Nitrogen donors are well characterized

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only in association with oxygen donors in anionic species such as the polyamine polycarboxylates and 8-quinolinolates [7] or, to a more limited extent, in cationic species such as the pyramidine chelates [8].

The report of J. H. Forsberg and T. Moellar [9] indicated that the direct reaction of ethylenediamine with a lanthanide (III) salt in acetonitrile resulted solid compound of the stoichiometric composition $Ln(en)_3X_3$ and $Ln(en)_4X_2$, where $X = NO_3$, Cl, Br or ClO_4. Recently, S-Prope et.al [10] reported the synthesis and the luminescence properties of dinuclear lanthanide complexes derived from co-valently linked macrocyclic ligands and all the complexes gave characteristic emission spectra incorporation of the lanthanide ions with metal binding sites. A variety of research works were also reported on the energy transfer and luminescence of lanthanide complexes with β-diketones, aromatic carboxylic acids, and some macrocyclic compounds which have good energy match and are suitable for the luminescence of lanthanide ions [11-14]. Spectroscopic and antimicrobial properties of new lanthanide (III) complexes derived from Coumarin Schiff base [15], some new lanthanide complexes derived from 2,4 and 2,5-dihydroxyacetophenones [16] and also synthesis of lanthanones complexes with beta diketones [17] have also been reporte. In this paper, we synthesized the corresponding complexes of lanthanide ions (Eu^{3+}, Tb^{3+}, Gd^{3+}, Dy^{3+} and Sm^{3+}) with dicyandiamide in 2-ethoxyethanol and characterized. The photo physical properties of these complexes were discussed in detail using ultraviolet absorption spectra, phosphorescence spectrum, fluorescence excitation and emission spectra. The life-time measurements on two complexes (Eu^{3+} and Tb^{3+}) have also been investigated.

EXPERIMENTAL SECTION

Materials and measurements:
All chemicals and solvents used were of reagent grade. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C elemental analyzer. Infrared spectroscopy with KBr pellets was performed on a Shimadzu FT-IR-8400s model spectrophotometer in the 4000-400 cm^{-1}. Thermal analyses of the compounds were carried in an air atmosphere with a Perkin-Elmer STA 6000. Ultraviolet absorption spectra of the ligand and its five lanthanide complexes were recorded on a Perkin Elmer UV-Vis Lambda 35 spectrophotometer. All the luminescence spectra and lifetime of the complexes were determined with Perkin-Elmer LS-55 spectrophotometer in phosphorescence mode equipped with source of Xenon discharge lamp. Excitation slit width = 10 nm, emission slit width = 5nm. For the lifetime measurement gate time is fixed at 0.05 ms and the delay time varies from 0.1 ms onwards.

Synthesis of Complexes
The complexes were prepared by refluxing corresponding lanthanide (Eu^{3+}, Tb^{3+}, Gd^{3+}, Sm^{3+}, Dy^{3+}) nitrates (0.01mole) with dicyandiamide (0.03moles) in 2-ethoxyethanol on a steam bath for 10-12 hrs. Colorless solid complexes were formed. They were filtered off, washed several times with acetone and dried in air. The yield exceeded 80% in all cases (88% for Tb, 85% for Eu and Gd, 82% for Sm and Dy). The compositions of the complex systems were confirmed by elemental analysis and are presented in Table 1.

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Table 1: Elemental analysis (C, H, and N) data of the complexes

Compound	%C		%H		%N	
	Calcd	Found	Calcd	Found	Calcd	Found
$TbC_{18}H_{42}N_{15}O_{12}$	26.37	26.47	5.12	4.99	25.64	25.26
$EuC_{18}H_{42}N_{15}O_{12}$	26.60	26.05	5.17	4.89	25.86	25.95
$GdC_{18}H_{42}N_{15}O_{12}$	26.41	26.01	5.13	5.35	25.68	25.33
$SmC_{18}H_{42}N_{15}O_{12}$	26.67	26.24	5.18	5.23	25.92	25.22
$DyC_{18}H_{42}N_{15}O_{12}$	26.27	26.55	5.10	5.01	25.54	25.14

RESULTS AND DISCUSSION

Infrared Spectra:

The IR spectrum of dicyandiamide shows a $\nu(C\equiv N)$ band at 2167 cm^{-1} and a band at 1656 cm^{-1} for the azomethine $\nu(C=N)$ group. When complexation occurs there is absence of band ca. 2167 cm^{-1} suggesting that free nitrile group is completely absent in all the complexes. In all the complexes the presence of $\nu(C=N)$ band in the range 1571-1596 cm^{-1} indicates coordination through C=N of the amidine part. The appearance of IR bands in the range 963-970 cm^{-1} and in the range 1226-1240 cm^{-1} may be assigned to $\nu_s(C-O-C)$ and $\nu_a(C-O-C)$, respectively. A strong band at ca. 1384 cm^{-1} suggests the presence of ionic nitrate in the complexes. The presence of the stretching frequencies in the range 3100-3400 cm^{-1} is suggestive of the $\nu(N-H)$ stretching region of the complexes [9]. On the basis of our experimental evidence, we suggest the most probable structure of the Ln (III) complexes as shown in Fig 1.
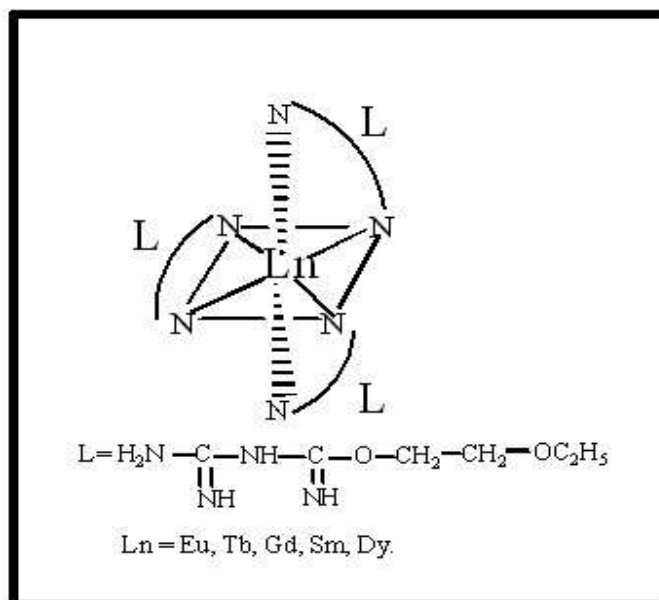
Fig. 1. The most probable coordination structure of the complexes

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Thermal Studies:

Thermal studies on two lanthanide (III) complexes (Gd and Tb) were studied.The thermal analysis of the Gd (III) complex indicates decomposition of the complex in four steps (~10% wt loss in the temp. 100-200°C; ~9% wt loss at 300°C; ~6% wt loss at 410 and 13% wt loss at 630°C) and Tb(III) complex shows four stages of wt loss, 4.5% in the range 70-80°C; ~5.2% wt loss at 190-210°C; 3% wt loss at 330-350°C and 4.1% wt loss at 490-510°C. There is poor evidence for the presence of H_2O molecules in the complexes based on their thermal data.

Surface morphological studies

To give a typical idea about the single phasic nature of the compounds, the X-ray diffraction powder studies for Tb (III) complex was studied using XPERT-PRO Diffractometer with Cu-Kα radiation of wavelength 1.54056Å operating at a voltage of 40kV and a current of 20mA.The scanning rate was maintained at 1.6^o/min over a 2θ range of 10-80° employing the reflection mode for scanning. Parameters of crystal lattice were determined using a set of programs, called P-INDEX, which are based on least-squares approach. X-ray powder diffraction (XRD) of the complex and dicyandiamide are depicted in (Fig 2). The observed diffraction data of complex is given in Table 2.The complex crystallizes in monoclinic structures with unit cell dimensions a = 12.613 Å, b = 3.637 Å, c = 8.775 Å, β = 93.102^o, and cell volume V = 402.04 Å^3 respectively. To evaluate the crystallite size of the synthesized complex, D is determined using Debye-Scherer formula [18, 19] given by D = 0.94λ/β cosθ, where β is the full width at half maximum of the predominant peak and θ is the diffraction angle and λ is the wavelength of light. The size of the crystallites of the complex is found to be 23nm.

Table 2: Powder X-ray diffraction data of Tb (III) complex

Peak number	d-spacing (Å)		2θ values		Δ 2θ	(h k l)
	Observed	Calculated	Observed	Calculated		
1	6.2976	6.2976	14.064	14.051	0.013	(2 0 0)
2	5.2469	5.2504	16.884	16.873	0.011	(2 0 -1)
3	3.6903	3.6915	24.096	24.088	0.008	(2 0 -2)
4	3.3593	3.3593	26.512	26.512	0.000	(0 1 1)
5	3.1176	3.1168	28.609	28.617	-0.008	(3 0 -2)
6	3.0167	3.6157	29.588	29.598	-0.010	(4 0 -1)
7	3.9117	2.9135	30.680	30.660	0.020	(4 0 1)
8	2.3873	2.3869	37.648	37.654	-0.006	(5 0 1)
9	2.1349	2.1345	42.299	42.308	-0.009	(5 0 2)
10	1.7966	1.7970	50.777	50.763	0.014	(6 1 -1)

Luminescence properties

The absorption spectra of the complexes (around 270 nm) show a slight red shift, the shape and intensity being similar to that for the ligand. This implies that the absorption depends mainly on the ligand and is the main energy donor and luminescence sensitizer of Ln^{3+} ion. The effective energy absorption mainly takes place in the narrow ultraviolet region of 200-280nm. The excitation bands for Tb (III) complex under the green emission of 546nm posses four main peaks at 236nm, 251nm 266nm, and 272nm, respectively. The excitation bands for Eu (III) complex under the red emission of 618 nm show peaks at 223, 242, 265nm, 271nm.
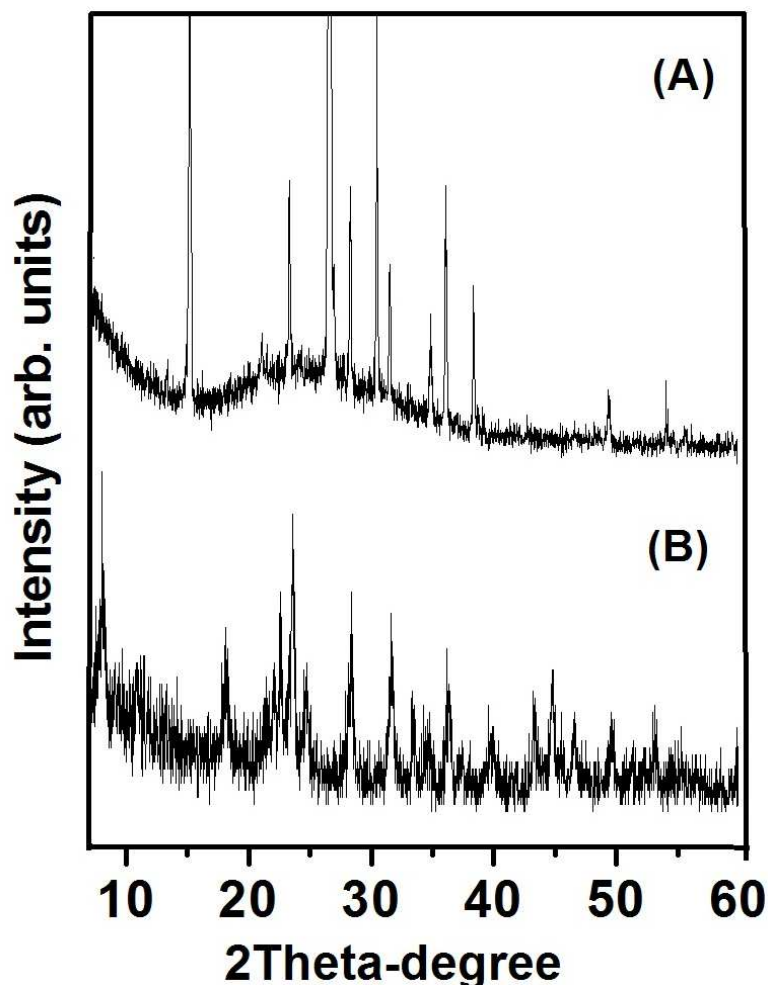
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Fig. 2. XRD spectrum of (A) free ligand (dicyandiamide); (B) Terbium (III) complex.

The excitation intensity of Tb (III) complex is stronger than that of the Eu (III) complex. The excitation bands for Sm (III) complex under the emission of 596 nm show four main peaks at 223nm, 242nm, 256 nm, 271 nm. The Dy (III) complex under the emission of 484 nm exhibit three main peaks at 223,242 and 259 nm. Further, the corresponding emission spectra were recorded with the four different excitation wavelengths, and they show similar emission position except for different luminescent intensities which suggests that the four excitation bands are all the effective energy sensitizers for the luminescence of lanthanide ions. Fig 3- 6 show the emission spectra for Tb (III), Eu (III), Sm (III) and Dy (III) complexes respectively.
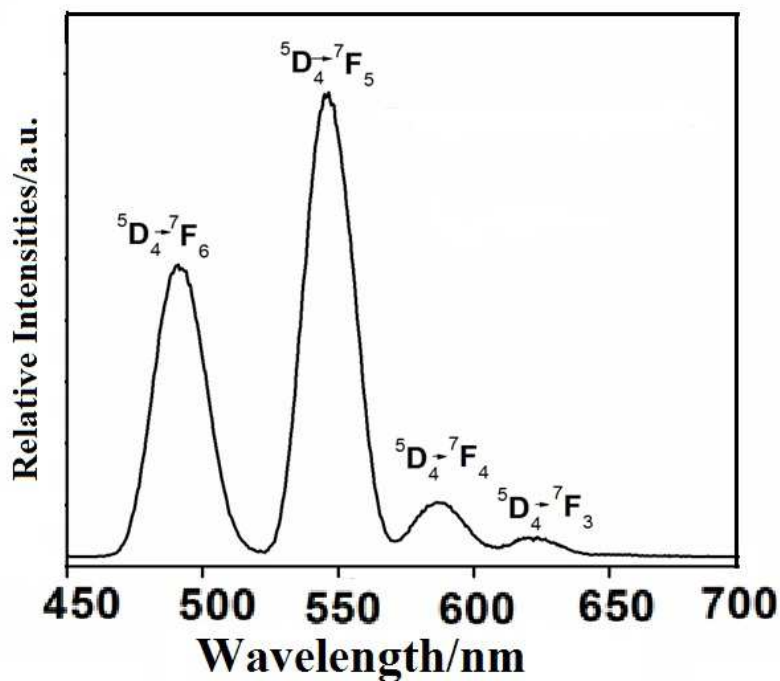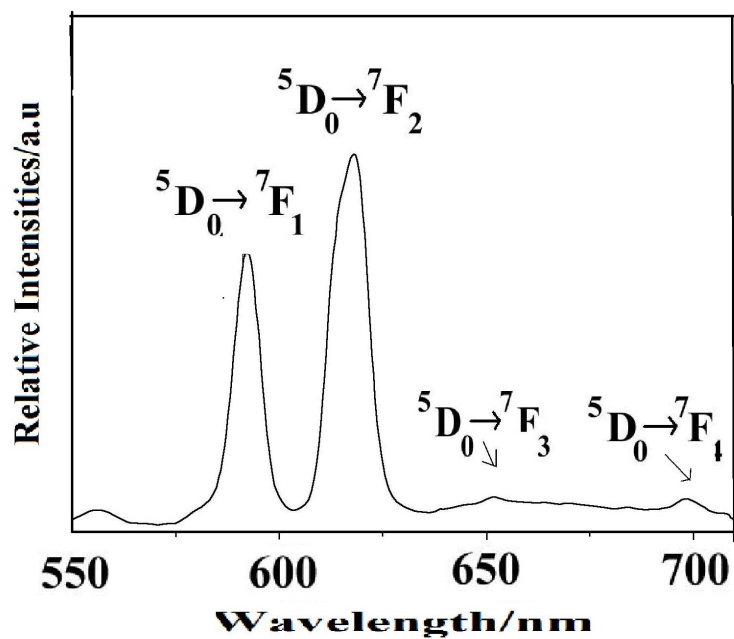
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Fig. 3: Emission spectrum of Tb (III) complex

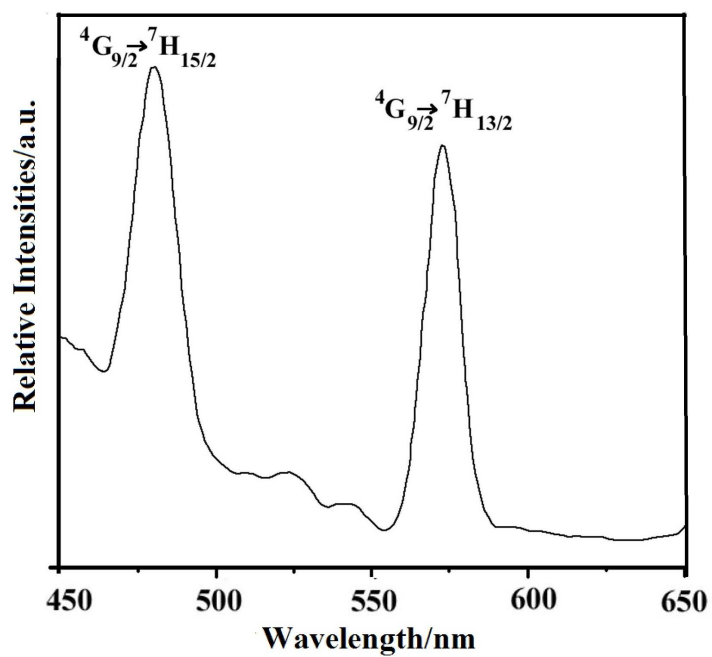**Fig. 4: Emission spectrum of Eu (III) complex**

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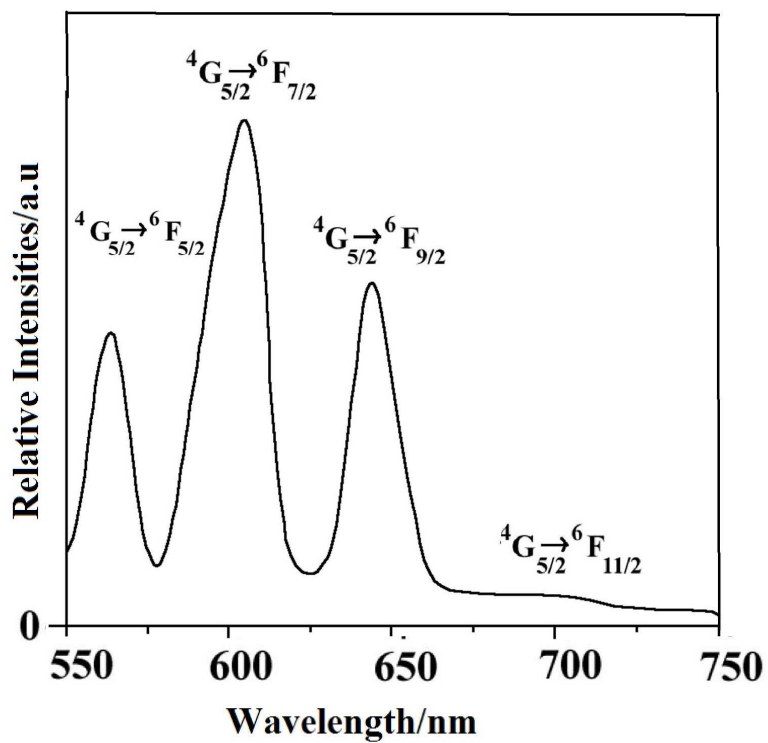**Fig. 5: Emission spectrum of Dy (III) complex**

Fig. 6: Emission spectrum of Sm (III) complex

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For the Tb (III) complex, the emission spectra show four emission peaks under the excitation of 236nm: at 491nm, 546nm, 588nm, 623nm attributed to be the characteristic emission for $^5D_4 \rightarrow ^7F_J$(6, 5, 4, 3)transition of Tb^{3+} ion . Among them $^5D_4 \rightarrow ^7F_5$ transition exhibits the strongest green emission, and $^5D_4 \rightarrow ^7F_6$ transition shows the second blue emission. Eu (III) complex shows four emission peaks under the excitation of 265nm: at 592nm, 618nm, 652nm, and 697nm, corresponding with the characteristic emission $^5D_0 \rightarrow ^7F_J$ transitions (J = 1, 2, 3, 4) of Eu^{3+} ion. For Dy(III) complex, the luminescence spectra show two apparent emission peaks at 483 nm and 574 nm under the excitation of 256 nm, which corresponds to the characteristic emission for the $^4F_{9/2} \rightarrow ^6H_J$ (J = 15/2, 13/2) transitions of Dy^{3+} ion. The Sm (III) complex shows four emission peaks under the excitation of 259 nm: at 561 nm, 596 nm, 643 nm, and 721 nm, attributed to be the characteristic emission for the $^4G_{5/2} \rightarrow ^6H_J$ (J = 5/2, 7/2, 9/2, 11/2).The luminescence intensities of terbium complex shows stronger luminescence than those of other lanthanide systems. Europium and Samarium complex show weaker luminescence than terbium complex but stronger than samarium which indicates that the triplet state energy is more suitable for the luminescence of terbium ion than europium and dysprosium ions. Gd^{3+} complex was selected as model complex for the determination of the triplet state energies of the organic ligand owing to their high phosphorescence-fluorescence ratio compared to those of the other Ln^{3+} complexes and Gd^{3+} can sensitize the phosphorescence emission of ligand. According to the luminescence principle of rare earth complexes with organic ligands [20], intramolecular energy transfer efficiency depends mainly on two energy transfer processes [21]: (a) the energy transfer from the lowest triplet energy level of the ligand to the resonant energy level of the Ln^{3+} ion by Dexter's resonant exchange interaction and (b) the inverse energy transfer from Ln^{3+} to organic ligand by a thermal deactivation mechanism. Both energy transfer rate constants depend on the energy difference between the lowest triplet level energy of the ligand and the resonant energy level of the lanthanide.

Intramolecular energy transfer in rare earth complexes conforms to Dexter's exchange energy transfer theory [22, 23]:

$$k_{ET} = (2\pi Z^2/R) \exp(-2rl) \int F_d(E) \, F_a(E) \, dE \qquad\qquad (1)$$

k_{ET} is the rate constant of energy transfer, r is the intermolecular distance between the energy donor and acceptor atoms, l is the *van der Waals* radius, the integral represents the overlap between the luminescence spectrum of the ligands and the spectrum of Ln^{3+} ($F_d(E)$: the luminescence spectrum of energy donor (ligand), $F_a(E)$: absorption spectrum of energy acceptor (Ln^{3+}), and $2\pi Z^2/R$ is a constant relating to the mutual distance between Ln^{3+} and coordinated atom, r and l are both considered to be constant for intramolecular energy transfer processes.

From Eq. (1), k_{ET} increases with decreasing energy difference ΔE (Tr-Ln^{3+}) between the triplet state energy of ligand and the resonance emission energy of Eu^{3+} and Tb^{3+}. Thus ligand with a larger energy difference cannot sensitize rare earth ions effectively. On the other hand, there exists an inverse energy transfer process which affects luminescence intensity by temperature [24] (k (T): rate constant of inverse energy transfer process (thermal deactivation process), A: preexponential factor):

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$$K (T) = A exp (-\Delta E(Tr-Ln^{3+})/RT \qquad\qquad (2)$$

It can be seen that in the inverse energy transfer process the activation energy is approximately equal to ΔE (Tr-Ln^{3+}); therefore, a decreasing energy difference increase k (T).

The value of the lowest triplet energy state of the ligand is determined to be 24,000 cm^{-1}, calculated from the phosphorescence emission of Gd (III) complex. The energy differences between the triplet state of ligand and the resonance energy level of Eu^{3+} ($^5D_0$, 17264 cm^{-1}), Tb^{3+}($^5D_4$, 20,500 cm^{-1}), Sm^{3+}($^4G_{5/2}$, 17900 cm^{-1}) and Dy^{3+} ($^4F_{9/2}$, 20900 cm^{-1}) can be calculated to be 6736 cm^{-1}, 3500 cm^{-1}, 6100 $cm^{-1}$and 3100 cm^{-1}, respectively. It can be seen that the ligand can sensitize the lanthanide ions effectively. There exists a lot of energy gap between the lowest excited state level ($^4G_{5/2}$) and the highest ground state level ($^6F_{11/2}$) of Sm^{3+}, causing readily some nonradiative energy transfer process to lose the excited energy, resulting the weakest luminescence of Sm^{3+} complex.

Lifetime study:
Fig. 7(a) shows the typical decay curve of $^5D_0 \rightarrow ^7F_2$ (618nm) emission for Eu(III) complex when excited at 265 nm and Fig. 7(b) shows the typical decay curve for $^5D_4 \rightarrow ^7F_5$(546 nm) emission for Tb(III) complex when excited 236 nm. The solid line indicates the biexponential fitting to data and biexponential decay equation is expressed as

$$I_t = I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}}$$

Where I_1 and I_2 are intensities at different times, τ_1 and τ_2 are their corresponding lifetimes. The average lifetime (τ_{av}) can be calculated using the equation

$$\tau_{ave} = \frac{I_1\tau_1^2 + I_2\tau_2^2}{I_1\tau_1 + I_2\tau_2}$$

This fitting clearly shows that the complexes are well fitted with biexponential fitting. The biexponential decay behavior depends on the number of different luminescent centre, energy transfer, defects and impurities in host. The average life- time of Tb(III) is τ_{av} = 6.46ms and for Eu(III) τ_{av} = 0.226ms complexes where Eu(III) complex has shorter life-time. Life-time study indicates biexponential nature of the luminescence decay.

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(a)   (b)
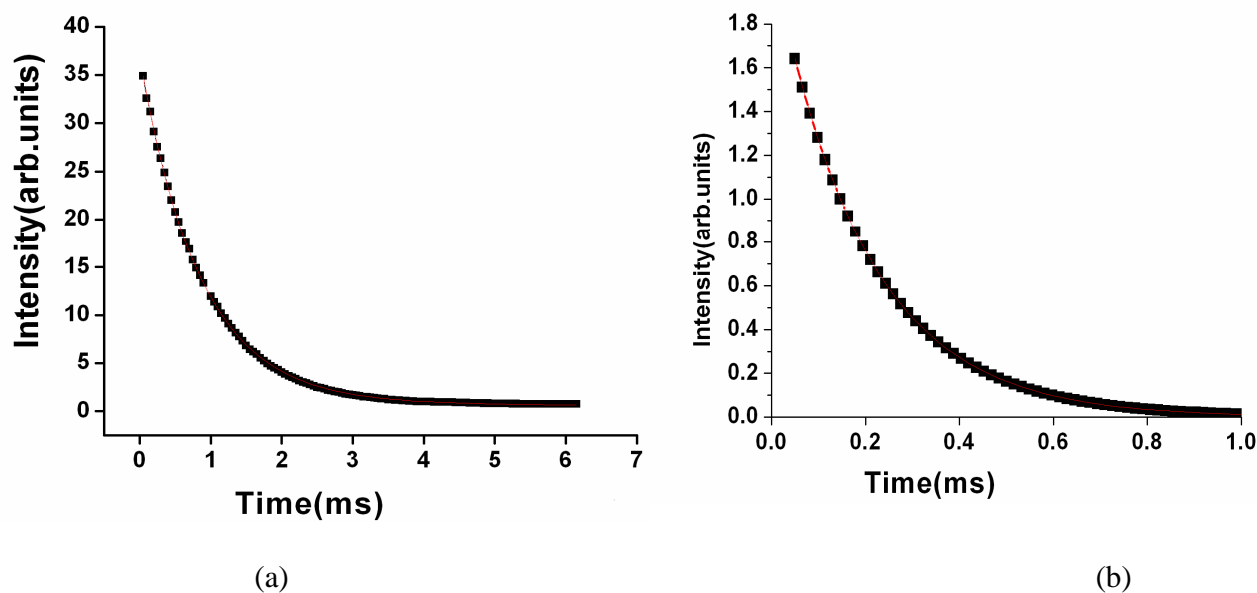
Fig. 6: Decay life-time curve of (a) Tb (III) and (b) Eu (III) complex

Table 3: Luminescence data and life-time measurement of Tb (III) and Eu (III) complexes

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Assignment	τ_{av} (ms)
Tb(III)complex	236	491	$^5D_4 \rightarrow {}^7F_6$	6.46
		546	$^5D_4 \rightarrow {}^7F_5$	
		588	$^5D_4 \rightarrow {}^7F_4$	
		623	$^5D_4 \rightarrow {}^7F_3$	
Eu(III)complex	265	592	$^5D_0 \rightarrow {}^7F_0$	0.226
		618	$^5D_0 \rightarrow {}^7F_1$	
		652	$^5D_0 \rightarrow {}^7F_1$	
		697	$^5D_0 \rightarrow {}^7F_4$	

CONCLUSION

Five lanthanide complexes of Eu, Tb, Gd, Sm and Dy with dicyandiamide in 2-ethoxyethanol have been synthesized and characterized. Their photo physical properties have been studied. The excitation and emission spectra of four complexes were discussed in detail, and terbium complex shows the strongest luminescence compared to those of other lanthanide systems. Life-time study on Tb (III) and Eu (III) complexes indicate biexponential nature of luminescence decay

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