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PHOTOPHYSICAL PROPERTIES AND LUMINESCENCE BEHAVIOUR OF LANTHANIDE COMPLEXES

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Abstract

A series of lanthanide elements from ranging from Lanthanum (La): Z=57 to Lutetium (Lu): Z=71 shows the interesting photophysical or optical properties like high luminescence efficiency, long luminescent decay time, low molar absorbance, large stokes shift, high range of color purity and line-like emission. These properties can be achieved by formation of coordination complexes of metal ion (lanthanides) with organic ligands (to form binary complex) which sensitize the energy levels of metal ions. There are various kinds of ligands utilized for the synthesis of these types of complexes, such as β -hydroxy ketones, aromatic carboxylic acids, β -diketones and β -ketones amides etc, these ligands exhibit the strong power of bonding with metal ion as well as possess suitable energy levels which are compatible with energy levels of metal ion. In addition to these ligands, some second type of auxiliary ligands (2,2-bipyridine: bipy, 1,10-phenanthroline: phen, bathophenanthroline: batho and 5,6-dimethyl-1,10-phenanthroline: dmph etc.) are bonded to metal ion in coordination sphere (to form ternary complexes), which further improves the photophysical features of these complexes. The photophysical properties display the various processes such as absorption, excitation and emission, absorption shown by absorption of light by the ligand from the source of light, then it is excited from lower energy level S_n (singlet) to excited (higher energy) levels S_1 . After that, S_1 level of ligand transmit energy to T_1 (triplet) state of it, then it transfers energy to resonating (higher energy) levels of metal ion and it relaxes to lower level by energy or light emission in visible region of electromagnetic spectrum. By this process, the most of lanthanide ions emit light in visible range and confirm the different types of characteristic color or luminescence while some of lanthanides like Praseodymium, Neodymium and Holmium etc. do not emit light in visible range. Therefore, these synthesized complexes are luminescent in nature and these complexes play a great role in various fascinating applications solar technology, solid light emitting devices, telecommunication, laser technology, bioimaging and light emitting diodes (LEDs).

Keyword: Europium; Terbium; Luminescence; Sensitization; Lanthanide ions.

Introduction

Photophysical properties are described by the behaviour of material towards interaction of light which involves the absorption, emission and scattering of light. Lanthanide elements are also known as f-block elements due to presence of outer most electrons in f-subshell. A series of lanthanide consists of 14 elements starting from La (Lanthanum): Z=57 to Lu (Lutetium): Z=71 [1]. The general representation of lanthanide element is shown by Ln . These properties of lanthanides arise from the particular type of electronic configuration $4f^n 5d^{0-1} 6s^2$ ($n=1-14$). The most of lanthanides exhibit two types of oxidation state, +2 and +3. Lanthanides reveal the photophysical properties by electronic transition in $4f-4f$ orbital which is shielded by $5d$ & $6s$ orbital, hence, the electrons in $4f$ orbital are not affected by the surrounding environment and $4f$ level is split into different types of electronic levels [2]. This result into production of $4f-4f$ sharp emission in visible range of electromagnetic spectra. But this transition ($4f-4f$) is not allowed according to Laporte selection rule result into production of low molar absorbance, obtaining low luminescence efficiency on account of direct $4f-4f$ photo-excitation of lanthanide ions [3-4]. The most common photophysical or optical properties are low molar absorptivity, large stokes shift, sharp emission bands, long luminescence life time, high color purity and wide range of internal quantum efficiency etc [5]. In order to procured the best photophysical performance or luminescence efficiency (absorption of light by an element, then emission of light), lanthanide ions form coordination compound with the suitable chromophoric ligands by antenna effect by which ligands transfer the absorbed light (excited triplet state) to the $4f$ level of Ln^{n+} (Ln^{3+}) ion after that, light is emitted in visible range of electromagnetic spectra [6-7]. This emission reflects a special type of luminescence of Ln^{n+} ions, red: Eu^{3+} (europium), green: Tb^{3+} (terbium): green, Tm^{3+} (thulium): blue, Sm^{3+} (samarium): orange and so on [8-9].

In this way, the antenna effect or photosensitized effect enhance the luminescence power of lanthanide ion. Hence, there are various kinds of organic ligands such as aromatic carboxylic acid, β -ketoamides, β -diketones, β -hydroxy ketones and

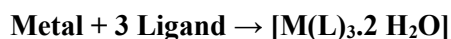


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macrocyclic ligands etc. which form coordination complexes with Ln^{3+} ions and improve the luminescence of lanthanide ions [10]. The binding organic ligands have the suitable energy levels as well as strong bonding tendency which in turn enhance the luminescence [11-12]. On the other hand, coordination complex (containing metal and ligands) of Ln^{3+} ion having water molecules as a solvent (in binary complex) which diminishes the luminescence of complex by high energy O-H oscillators. These oscillators lower down the energy of lanthanide centred excited state through non-radiative decay process resulting into shorter life time of excited state and decreases the luminescence of complexes [13]. This lower luminescence can be improved by replacement of solvent molecules by some other type of ligands known as auxiliary ligands (batho, phen, dmph, bipy etc.) which complete the coordination number of complex as well as provide rigid structure to the coordination complex (ternary complex) so that other ligand cannot bind with the metal ion and further increase the photoluminescence of lanthanide ion [14]. Now a days, research of lanthanide complexes becomes a hot topic in research field owing to advanced applications in scientific fields such as security ink [15], probes for bioimaging [16-19], display devices [20], laser and sensor technology [21-22], solar energy conversion [23-24], probes for bioimaging [16-19], organic light emitting diodes (OLEDs) and biological sensors [25-27] etc.

1. General Route of lanthanide complexes:



Binary complex



Ternary complex

2. Mechanism of photoluminescence phenomenon

Photoluminescence occurs by two main processes: first one is absorption & excitation and second is emission process, which are follows as:

2.1. Absorption and excitation mechanism

Photoluminescence can be shown by absorption of UV-light by atoms present in the particular element from the source of light. The element constitutes discrete energy levels possessing electrons with opposite spin. The electron in lower energy creating a vacancy in this level on excitation (with time limit of 10^{-14} - 10^{-15} s) into higher energy level through absorption of energy. The amount of energy absorbed by the electron depends upon the difference of energy between lower energy and higher energy levels. Out of total applied light by the source, some light is re-emitted of higher wavelength and some of light is absorbed by the electron. The absorption is the result of electronic transitions between rotational (R_n) and vibration (V_n) levels within a single electronic level (E_n), henceforth, a broad absorption band is obtained.

The intensities of absorption and excitation bands are quietly different because absorption depends upon the excitation of electron from ground state to excited state while excitation mainly depends on the amount of light which can be absorbed by the atom, hence, both peaks are of different intensities. The absorption band of a complex is recorded in solid form on a UV-spectrophotometer in the range of 200-400 nm while excitation spectrum is recorded on Photoluminescence spectrophotometer ranging from 200-500 nm [28] as shown in **Fig. 1**. The excitation spectrum of Eu^{3+} and Tb^{3+} ion complexes consists of a broad band at the range of 200-400 nm (**Fig. 1**), vary with the types of organic ligands used in coordination compounds.

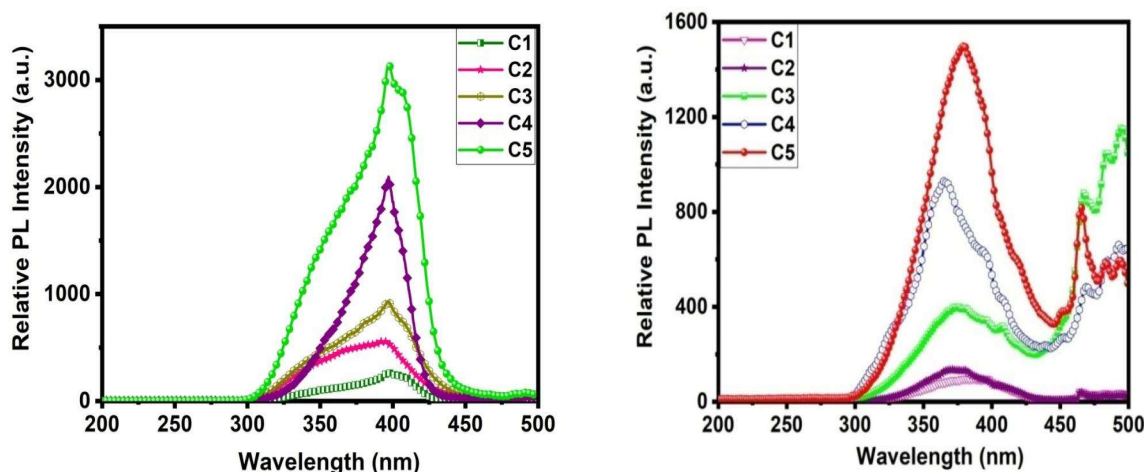


Fig. 1. Excitation spectra of europium (M= Eu: left) and terbium (M= Tb: right) complexes showing C1 complex: $[M(L)_3 \cdot 2H_2O]$, C2: $[M(L)_3 \cdot batho]$, C3: $[M(L)_3 \cdot dmph]$, C4: $[M(L)_3 \cdot phen]$ & C5: $[M(L)_3 \cdot bipy]$

2.2. Emission mechanism

Emission is defined as de-excitation of electrons from higher energy to lower energy level by releasing radiations within a time limit, this time is called as decay time. The emission spectrum is noted on photoluminescence spectrophotometer in the range of 400-800 nm. The absorption or excitation spectra both are mirror images of emission spectrum but the emission band obtained is noted at higher wavelength than that of absorption or excitation band, known as Stokes shift as demonstrated in Fig. 2. The emitted light displays the characteristics type of luminescence.

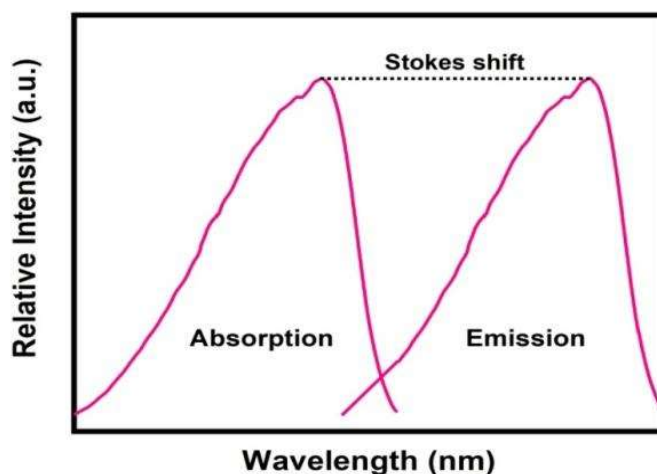


Fig. 2. Representation of wavelength of emission and absorption spectra by gap of energy of Stokes shift.



Table 1: The various electronic energy levels (ground and excited) and type of emission shown by lanthanide ions.

Lanthanides	Ln	Ln ³⁺	Excited level	Ground level	Luminescence type	Emission
Praseodymium	Pr	[Xe] 4f ²	¹ G ₄	³ H _J	P	NIR
			¹ D ₂	³ F _J	P	NIR
			³ P ₀	³ H _J	F	Orange
Neodymium	Nd	[Xe] 4f ³	⁴ F _{3/2}	⁴ I _J	F	NIR
Samarium	Sm	[Xe] 4f ⁵	⁴ G _{5/2}	⁶ H _J	P	Orange
Europium	Eu	[Xe] 4f ⁶	⁵ D ₀	⁷ F _J	P	Red
Gadolinium	Gd	[Xe] 4f ⁷	⁶ P _{7/2}	⁸ S _{7/2}	P	UV
Terbium	Tb	[Xe] 4f ⁸	⁵ D ₄	⁷ F _J	P	Green
			⁴ F _{9/2}	⁶ H _J	P	Yellow
Dysprosium	Dy	[Xe] 4f ⁹				Orange
			⁵ F ₅	⁵ I _J	F	NIR
			⁵ S ₂	⁵ I _J	F	Green
Erbium	Er	[Xe] 4f ¹¹	⁴ S _{3/2}	⁴ I _J	F	Green
			⁴ I _{13/2}	⁴ I _{15/2}	F	NIR
Thulium	Tm	[Xe] 4f ¹²	¹ G ₄	³ H _J	P	Blue, NIR
Ytterbium	Yb	[Xe] 4f ¹³	² F _{5/2}	² F _{7/2}	F	NIR

The emission spectrum exhibit the different types of finger or line-like peaks due to different types of electronic transition (within ground and excited electronic levels as shown in **Table 1**) depends upon the type of luminescent centre such as Sm³⁺ ion: ⁴G_{5/2}→⁶H_J, Eu³⁺ ion: ⁵D₀→⁷F_{0, 1, 2, 3, 4, 5, 6} (⁵D₀: ground energy level & ⁷F_J: excited level), Tb³⁺ ion: ⁵D₄→⁷F_{J=6, 5, 4, 3, 2, 1, 0} and Gd³⁺ ion: ⁶P_{7/2}→⁸S_{7/2} [29] as intensified in **Fig. 3**.

The transitions of terbium and europium ion are recorded in **Table 2**. The surrounding ligands in coordination sphere decide the emission intensities or luminescence efficiencies of these lanthanide complexes. For europium ion, ⁵D₀→⁷F₂ type of transition is electric dipole (more intense) transition at 615 nm and responsible for red emission while terbium ion displays the green emission due to ⁵D₄→⁷F₅ transition produces a peak at wavelength of 545 nm approx. (highly intense). On the other hand, ⁵D₀→⁷F₁ and ⁵D₄→⁷F₃ are magnetically allowed (less intense) transition for Eu³⁺ and Tb³⁺ ion, respectively [30-31]. These different types of emission peaks for both europium and terbium ion are demonstrated in **Fig. 4**. The other weak emission for Europium ion (⁵D₁, ⁵D₂, and ⁵D₃ higher levels to ground levels) and terbium ion are manifested in **Fig. 4**. The intensities ratio for electric dipole and magnetic dipole transition decides the luminescence performance.

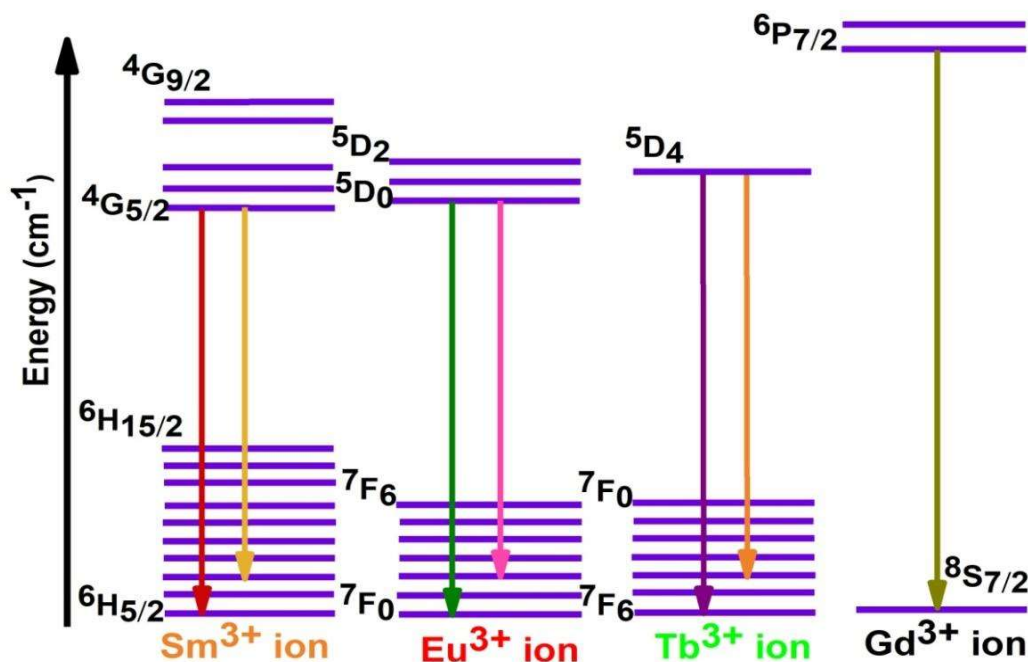


Fig. 3. Representing the different types of electronic 4f-4f transitions in case of Eu^{3+} , Tb^{3+} , Sm^{3+} and Gd^{3+} ions.

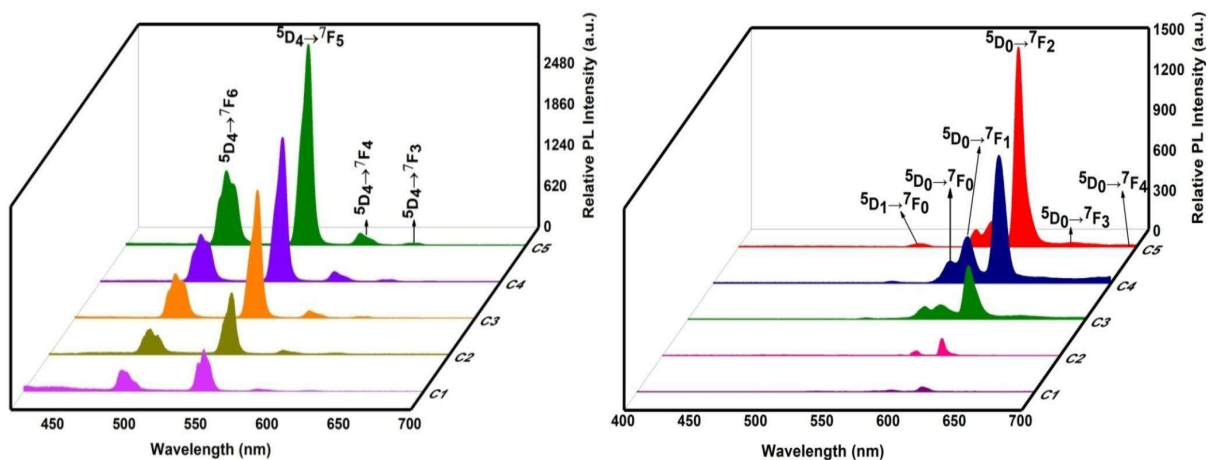


Fig. 4. Emission spectra of europium ($M = \text{Eu}$: Left) and terbium ($M = \text{Tb}$: right) complexes showing C1 complex: $[\text{M}(\text{L})_3 \cdot 2\text{H}_2\text{O}]$, C2: $[\text{M}(\text{L})_3 \cdot \text{batho}]$, C3: $[\text{M}(\text{L})_3 \cdot \text{dmp}]$, C4: $[\text{M}(\text{L})_3 \cdot \text{phen}]$ & C5: $[\text{M}(\text{L})_3 \cdot \text{bipy}]$.



Table 2: The various types of electronic transitions for terbium and europium ion.

Eu ³⁺ ion		Tb ³⁺ ion	
Transitions	Wavelength (nm)	Transition	Wavelength (nm)
⁵ D ₀ → ⁷ F ₀	580	⁵ D ₄ → ⁷ F ₆	490
⁵ D ₀ → ⁷ F ₁	592	⁵ D ₄ → ⁷ F ₅	545
⁵ D ₀ → ⁷ F ₂	615	⁵ D ₄ → ⁷ F ₄	585
⁵ D ₀ → ⁷ F ₃	652	⁵ D ₄ → ⁷ F ₃	620
⁵ D ₀ → ⁷ F ₄	697	⁵ D ₄ → ⁷ F ₂	647
		⁵ D ₄ → ⁷ F ₁	660
		⁵ D ₄ → ⁷ F ₀	695

⁵D_J and ⁷F_J: lower and higher energy levels of terbium and europium ion

3. Sensitization process or energy transfer phenomenon

The energy transfer process involves the transfer of energy from bonding organic ligand to central metal ion and occurs through two main mechanisms: first ligand transfer energy from its singlet state S₁ and second is through triplet T₁ state. The second pathway of energy transfer is found to be slow process and not favourable for intersystem crossing process ISC, hence, ligand transfer energy through triplet state [32-34]. The sensitization defines as feeding of excited or resonating levels of metal ion by energy transfer from ligands. The ligands absorb light from source, electron is excited to higher energy singlet state S_n from its ground singlet state S₀, then it relaxes to lower energy singlet state S₁, known as internal conversion (IC) through non-radiative decay process [35-36]. After that, excited triplet state T₁ feeds by S₁ state on account of heavy atom effect of lanthanide ions, by the process of intersystem crossing (ISC) on requirement of energy gap of 0.62 eV (ΔE_{S₁-T₁}) stated by Reinhoudt's rule between these two states [34]. Lastly, the resonating levels (⁵D₄: Tb³⁺ & ⁵D₂ and ⁵D₀: Eu³⁺ ion) of metal ion are sensitized by this triplet state of ligands (organic as well as auxiliary), which is favoured by difference of energy (0.31-0.62 eV) between these states for Eu(III) ion and 0.23-0.49 eV (for terbium ion), confirmed by Latva empirical rule [35]. If T₁ state transfer energy back to ground singlet state S₀ by non-radiative decay then it is known as phosphorescence process.

There is another condition for energy transfer efficiently that the triplet state of ligand must be located at higher energy state as compared to energy levels of metal ions. But for most of lanthanide ions i.e. La³⁺ & Gd³⁺ ions T₁ states are positioned at lower energy position than that of resonating levels of these metal ions, hence, energy transfer mechanism from ligand, L→La³⁺ or Gd³⁺ is strictly hindered and do not show the luminescence in visible region. Therefore, we should select the ligand with appropriate energy levels which are compatible with levels of metal ion in coordination compounds as well as bonding ligands should possess the strong capacity for bonding with metal ion. Thus, ligands selecting for coordination compounds should be compatible in energy for metal ion and it is best for energy transfer and obtaining high luminescence efficiency.

The feeding of higher energy (resonating) levels of metal ions by T₁ state of ligand is confirmed by two main mechanisms, Dexter energy transfer [36] and Foster energy transfer [37] mechanism. Dexter energy transfer mechanism involves the acceptance of electron by acceptor (resonating level of metal ion) molecule from donor (T₁ state of ligand) molecule then electrical neutrality is maintained by back transfer of electron from acceptor to donor molecule, it requires close interaction between acceptor and donor molecule (up to 10 Å) and this complete process is called as double electron substitution process



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[36]. On the contrary, Foster energy transfer process occurs by producing dipole-dipole interaction between acceptor and donor, which is induced by excited ligand on the metal ion and this process proceeds without close interaction between two interacting molecules, hence, it can be completed with a large distance ($\sim 30\text{-}100 \text{ \AA}$) between donor & acceptor [37]. The Foster energy transfer mechanism is dominated for energy transfer phenomenon in case of lanthanide complexes. The energy transfer or sensitization mechanism for mainly europium and terbium ion is manifested in **Fig. 5**.

4. Radiative and non-radiative pathway

Radiative type of process involves the relaxing of resonating levels of metal ions to lower energy levels by releasing light in the form of radiations by two pathways: phosphorescence and fluorescence pathway.

4.1. Phosphorescence

Phosphorescence is a radiative type of pathway in which electron gets excited to S1 state on absorption of light, then it decays to excited triplet state T1 via ISC anisole (non-radiative pathway) and it finally relaxes to ground state singlet state S0 by releasing radiations as manifested in **Fig. 5**. In this type of photoluminescence, the materials are continue glowing for some time as the source of radiations is cut off, it occurs through parity forbidden type of transition because S1 and T1 states possess different multiplicity and proceeds very slowly, hence, it is known as delayed fluorescence. Phosphorescence is found to be temperature dependent pathway.

4.2. Fluorescence

This type of relaxation pathway displays the relaxing of excited singlet S1 state to ground S0 state. It is spin allowed transition due to same singlet multiplicity of ground and excited state. It involves the excitation of electron from S0 state to S1 state, then S1 state relaxes to S0 state by emission of photon to surrounding (**Fig. 5**). In this type of luminescence, materials stop glow as the radiation source is removed and it occurs very rapidly and find potential applications in time-resolved fluorescence & fluorescence resonance energy transfer spectroscopy. If emitted and absorbed energy are of similar magnitude then fluorescence is known as resonance fluorescence. The fluorescence intensity can be diminished either of quenching or bleaching. The quenching defines the decomposition of fluorescent irreversibly by light with the use of oxygen molecule while bleaching involves the fluorescence intensity reduction in presence of heavy metals salts. The fluorescence is temperature independent pathway.

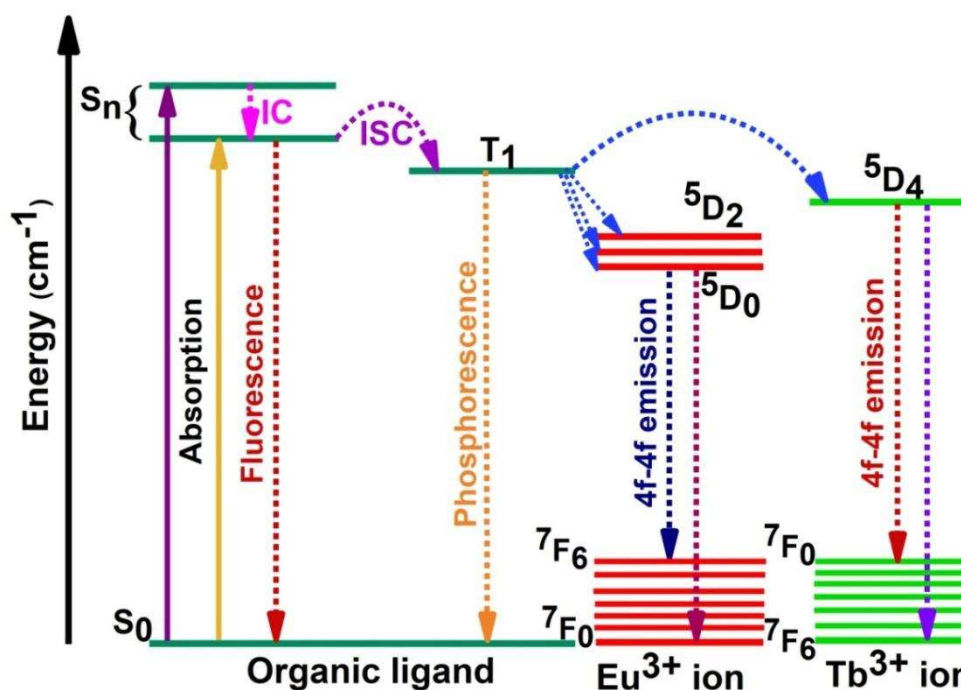


Fig. 5. Sensitization process between organic ligand and metal ion (Tb^{3+} & Eu^{3+} ion).

4.3. Non-radiative type of pathway

The non-radiative pathway defines as the emission of light by relaxing excited levels to lower energy levels in the form of heat. For luminescent complexes, non-radiative type of pathway is more favourable than that of radiative pathway. The non-radiative route can be occurred through intersystem crossing, internal conversion & vibrational relaxation, which are explained as:

4.3.1. Intersystem crossing

This type of pathway explains the feeding of excited triplet state by excited singlet state on releasing heat in time period of 10^{-8} s and it is named as spin forbidden type of transition owing to different type of spin multiplicity of both states. Therefore, Intersystem crossing (ISC) is more acceptable route than that of internal conversion (IC). The organic luminescent complexes containing heavy atoms mainly follow the ISC pathway.

4.3.2. Internal conversion

In this pathway, the excited singlet S_n state relaxes to lower energy excited singlet S_1 state by emission of heat within a time period of 10^{-12} s. This is represented by $S_n \rightarrow S_1$ in which spin multiplicity of both states remain conserved.

4.3.3. Vibrational relaxation

There are various types of vibrational levels within the electronic levels, the excited vibrational level gets relax to lower level by releasing light in the form of heat in time period range of 10^{-14} - 10^{-12} seconds. This process is a fast process and takes shorter time as compared to luminescent decay time.



Conclusion

The efficient photophysical properties of lanthanides mainly europium and terbium ion become a cornerstone for researchers in field of research. The most common photophysical properties are high range of quantum efficiency, sharp emission bands, low molar absorptivity, large stokes shift, high color purity and high luminescent decay time. The photophysical properties consist of absorption, excitation and emission. The excitation band is a broad band in the range of 200-400 nm due to 4f-4f electronic transition is case of Eu^{3+} , Tb^{3+} & Sm^{3+} ions etc. After excitation of electron from ground state to excited state, the life time of excited state and it decays back to ground state by emission of light in visible region & emit different types of luminescent color according to their light absorbed (Sm^{3+} : orange, Tb^{3+} : green and Eu^{3+} : red or pink etc.), which is represented by emission spectrum. The emission spectra display the various kinds of emission peaks (finger like) on account of different electronic transitions from higher energy levels of metal ion to ground energy level, $^5\text{D}_0 \rightarrow ^7\text{F}_0, 1, 2, 3, 4, 5, 6$ for Eu^{3+} ion and $^5\text{D}_4 \rightarrow ^7\text{F}_{6,5,4,3,2,1,0}$ for Tb^{3+} ion. The luminescence phenomenon confirms by the transfer of energy from ligand to metal ion and high luminescence efficiency of metal ion is attained by coordination of organic ligand exhibiting the strong bonding efficiency and favourable energy level for energy transfer to metal ion. This luminescence efficacy is further improved by binding of auxiliary ligand to $[\text{M}(\text{L})(\text{Auxiliary ligand})]$ coordination sphere. Therefore, these luminescent complexes having interesting applications in research area such as Laser technology, telecommunication, bioimaging, display devices, security ink, amplifier and OLEDs (organic light emitting diodes) etc.

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