SYNTHESIS, CHARACTERIZATION AND PHOTOLUMINESCENCE STUDIES OF EUROPIUM AND LANTHANUM PHENANTHROLINE COMPLEXES.

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CERTIFICATE

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Signature of candidate

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LIST OF ABBREVIATIONS

1. phen	**1,10-phenanthroline**
2. La	**Lanthanum**
3. Eu	**Europium**
4. HCl	**Hydrochloric acid**
5. EuCl3	**Europium chloride**
6. LaCl3	**Lanthanum chloride**
7. Eu-phen	**Europium-phenanthroline complex**
8. La-phen	**Lanthanum-phenanthroline complex**
9. UV-vis	**Ultraviolet-visible**
10. LMCT	**Ligand-to-metal charge transfer**
11. SEM -	**Scanning electron microscopy**
12. EDS -	**Energy-dispersive X-ray spectroscopy**
13. FT-IR -	**Fourier-transform infrared**
14. C=C -	**Carbon-carbon double bond**
15. C=N -	**Carbon-nitrogen double bond**
16. C-H -	**Carbon-hydrogen bond**
17. O-H -	**Oxygen-hydrogen bond**
18. M-N -	**Metal-nitrogen bond**
19. SEM-EDS	**Scanning electron microscopy-energy dispersive X-ray spectroscopy**
20. Bkg	**Background**
21. MDL	**Minimum detection limit**
22. ROI	**Region of interest**
23. HPLC	**High-performance liquid chromatography**
24. ν	**Stretching vibration**
25. Ra F	**Relative atomic factor**

SUMMARY

All chemicals used were of analytical reagent grade, including 1,10-phenanthroline, lanthanum oxide, europium oxide, hydrochloric acid, and ethanol, with deionized/doubly distilled water employed throughout the experiments using Grade A glassware. Europium chloride was prepared by dissolving europium oxide in 5 M HCl, and the resulting $EuCl_3$ solution was added slowly to an ethanolic solution of 1,10-phenanthroline under stirring at 50°C for few hours, forming a light pink precipitate of the Eu-phen complex, which was isolated, washed with water and ethanol, and dried to obtain the solid product in 75-80% yield. The La-phen complex was synthesized similarly by reacting in-situ generated $LaCl_3$ with 1,10-phenanthroline in ethanol, followed by precipitation, washing, and drying to get an off-white powder in 70-75% yield. UV-vis spectra of Eu-phen were recorded in aqueous solution showed two peaks with absorption maxima for at 263.8 and 227.8 nm, corresponding to the intraligand $\pi \rightarrow \pi^*$ transitions of the phenanthroline ligand, slightly red-shifted compared to free phenanthroline due to coordination to Eu confirming the formation of complex. while for La-phen, peaks were seen at 262.0 and 231.9 nm ($\pi \rightarrow \pi^*$ transitions) and an additional peak at 375.2 nm due to ligand-to-metal charge transfer (LMCT) from the phen ligand to the 5d orbital of La(iii). Photoluminescence studies showed the Eu-phen complex exhibited characteristic emission bands at 608, 610, 615, and 617 nm, corresponding to the $5D_0 \rightarrow 7FJ$ (J = 1, 2, 3, 4) transitions of the Eu^{3+} ion, with the intensity pattern, particularly the strong $5D_0 \rightarrow 7F2$ band at 616 nm, indicating a non-centrosymmetric coordination environment around Eu^{3+}, and additional peaklets at 577 and 589 nm suggesting perturbation of the local environment by the coordinated ligand, while the La-phen complex showed emission bands at 362 and 380 nm, likely due to LMCT or other metal-centered transitions influenced by 1,10-phenanthroline coordination, with a peaklet at 535 nm further indicating modification of electronic transitions upon complexation. SEM images revealed an agglomerated morphology for La-phen, consisting of irregularly shaped particles formed by aggregation of rod-like structures, while Eu-phen exhibited an agglomerated morphology forming irregular, plate-like structures randomly oriented and stacked. EDS analysis confirmed the expected elemental compositions, with the experimental and theoretical values matching closely for the proposed empirical formulas: La-phen: $C_{36}N_6O_3La$ (C 62.4%, N 7.9%, O 20.8%,

La 6.3%) and Eu-phen: $C_{36}N_6O_3Eu$ (C 54.9%, N 3.8%, O 27.6%, Eu 10.6%), with EDS mapping showing homogeneous distribution of elements, indicating high purity of the complexes. The FT-IR spectra exhibited characteristic vibrational bands corresponding to the phenanthroline ligands and coordinated functional groups, with bands for La-phen at 1631 and 1519 cm^{-1} assigned to aromatic C=C and C=N stretches of phen, bands at 850 and 726 cm^{-1} attributed to out-of-plane C-H bending vibrations, a broad band at 3420 cm^{-1} indicating O-H stretching from coordinated hydroxides and hydration water, and the band at 1385 cm^{-1} confirming the presence of coordinated chloride counterions, with similar vibrational bands observed for Eu-phen, with slight shifts in band positions due to the difference in ionic radii and coordination preferences of the lanthanide centers. The UV-vis, photoluminescence, SEM-EDS, and FT-IR data collectively support the successful synthesis and coordination of the 1,10-phenanthroline ligand to the lanthanum and europium centers, forming the respective lanthanide complexes, with the spectroscopic data providing insights into the electronic transitions, coordination environment, and bonding interactions within the complexes, and the emission properties of the Eu-phen complex, with its characteristic Eu^{3+} emission bands in the visible region, and the La-phen complex, with its ligand-centered emission, suggesting potential applications in luminescent materials and photonic devices, while further time-resolved spectroscopic studies are proposed to better understand the excited-state photophysics governing the luminescence properties of these complexes, contributing overall to the understanding of the structural and photophysical properties of lanthanide-phenanthroline coordination compounds and laying the foundation for designing complexes with optimized luminescent output.

INTRODUCTION

From vibrant LED displays to biological probes, luminescent materials are becoming ubiquitous across industries. At the core of many emerging technologies lies a special class of metal complexes that impart the brightest glow lanthanide complexes. The unique electronic configurations of lanthanide ions like europium and lanthanum give rise to narrow emission bands and long-lived excited states that outperform conventional organic fluorophores. By creatively coordinating organic chromophores to these metals, researchers have designed complexes whose photons shine an order of magnitude brighter. Yet mysteries still swirl around what makes some complexes illuminate more intensely than others. This thesis ventures into the photophysical world of lanthanide complexes in search of answers, spearheaded by an exploration into europium's lesser-known neighbor lanthanum.

1.1 Review of Literature

Lanthanide elements like europium (Eu) and lanthanum (La) have unique electronic configurations that impart versatile luminescent properties when incorporated into coordination complexes. The partially filled 4f orbitals of trivalent lanthanide ions give rise to narrow emission bands arising from f-f electronic transitions, which are generally Laporte-forbidden.[1] However, when sensitized by appropriate organic ligands, these complexes can exhibit bright luminescence at visible and NIR wavelengths.[1] The long excitation lifetimes, large Stokes shifts, and sharp emission bands of lanthanide complexes make them promising luminophores for a wide array of photonic technologies.[1]. Research has focused on designing organic chromophores to improve lanthanide luminescence intensity, stability, and biocompatibility. Strategies include enhancing ligand-to-metal energy transfer efficiency and optimizing the coordination environment to protect the lanthanide-centered emission.[1] The long-lived f-f excited states of complexes incorporates Eu^{3+}, Tb^{3+} and other lanthanides facilitate their use as fluorescent markers and reporters.[1]

In recent years, there has been significant interest in developing lanthanide complexes as labels and probes for biomedical applications in areas like biosensing, imaging, and assays.[1] Research has focused on designing organic chromophores to improve lanthanide luminescence intensity, stability, and biocompatibility. Strategies include enhancing ligand-to-metal energy transfer efficiency and optimizing the coordination environment to protect the lanthanide-centered emission.[1] The long-lived f-f excited states of complexes incorporating Eu^{3+}, Tb^{3+} and other lanthanides facilitate their use as fluorescent markers and reporters.[1]

Recent research has focused on strategies for designing highly efficient lanthanide-based luminescent sensors and probes. Parker and Deakins explored computational and synthetic methods to optimize lanthanide complex emission for sensing applications.[2] By carefully selecting organic chromophores and tuning their coordination environment, the ligand-to-lanthanide energy transfer efficiency can be maximized.[2] This enables intense, long-lived lanthanide-centered emission that is highly sensitive to the local surroundings.[2] Europium and terbium complexes have been widely studied for their usefulness as luminescent reporters of biochemical interactions and processes.[2] Their narrow f-f emission bands and long excited state lifetimes allow analyte detection with high sensitivity and precision.[2] Claude Bunzli and Svetlana Eliseyeva provided an overview of the unique photophysical properties of trivalent lanthanide ions (Ln^{3+}) in their 2010 book chapter [3]. They explained that the partially filled 4f electron shell of the Ln^{3+} ion gives rise to a narrow emission band upon excitation useful for luminescent applications. Researchers explained how the 4f-4f Laporte-forbidden electronic transition, and the direct excitation of the ground state are very weak. However, the introduction of organic 'antenna' ligands means that lanthanide ions can be sensitized by ligand-to-metal energy transfer. Bunzli and Eliseeva discuss the spectroscopy, luminescence lifetime, and emission color of various Ln^{3+} ions. It also describes design strategies for the development of lanthanide-based sensors and probes, where long luminescence lifetimes and sharp emission bands provide high detection sensitivity and resistance to photobleaching. Overall, this book chapter provides a comprehensive overview of lanthanide photo physics that provides the basis for the development of lanthanide-based luminescent devices. Comby and Bünzli discussed strategies to optimize and tune the near-infrared (NIR) emission properties of lanthanide complexes through careful ligand design [4]. Their aim was to summarize approaches for enhancing NIR luminescence efficiency and controlling lanthanide-centered emission wavelengths by modifying the ligand structure around the lanthanide ion [4]. They explain how ligands containing sensitizing chromophores can promote efficient energy transfer to emitters like Nd^{3+}, Er^{3+}, and Yb^{3+}, drastically increasing their luminescence output [4]. By controlling the number, type, and attachment mode of chromophores, along with the coordination environment, the authors showed that major improvements in NIR emission intensities and fine tuning of emission peaks could be achieved [4]. Their work demonstrates that rationally designing ligands with optimized energy transfer characteristics enables great control over NIR luminescence from lanthanide complexes. This facilitates their use in diverse photonic technologies and biomedical applications that benefit from NIR emission [4]. Bunzli provides a comprehensive overview of strategies to exploit the unique luminescent properties of lanthanide ions for various photonic applications [5]. This is particularly characteristic of europium complexes for strong red emission resulting from the $5D_0$ → 7F2 transition when europium is sensitive enough [5]. Bünzli discussed ways to improve the emission performance of lanthanides, such as designing ligands that promote antenna efficiency and energy transfer to metal ions [5]. He studied the applications of lanthanide complexes in areas such as bioassays, fluorescence imaging, and photonics, where their long lifetime, large Stokes shift, and narrow emission band provide advantages over conventional fluorophores [5].

Moore, Samuel, and Raymond explored strategies to increase lanthanide emission by optimizing antenna efficiency [6]. They represent Europium, because the long-time red emission of the $5D_0$ → 7F2 transition is very sensitive to the surrounding chemical environment [6]. This makes the European complex an ideal environment for sensor systems and biological imaging applications, taking advantage of local environmental variations in emissions [6]. The author discusses his work on developing a European antenna with optimal sensitivity and energy transfer to achieve an 80-fold emission amplifier and a microsecond lifetime defined solution [6].

Recent studies have investigated the luminescent properties of lanthanide complexes, especially europium (Eu) and lanthanum (La), which occupy adjacent positions in the periodic table. Shavaleev and others. [7] and Pope et al. [8] investigated luminescence induced by lanthanum complexes. It shows visible emission from intraligand and iron-to-iron charge transfer states with a diketonate bond containing a picolinate pendant arm in the La complex [7,8]. This research aims to re-explore the luminescent potential of lanthanum complexes, which are less studied compared to their Europium counterparts despite their similar position to the lanthanides. The methods used include the synthesis of a series of La complexes with different diketonate ligands and the analysis of their luminescent properties by spectroscopic methods. Their main finding is the visible photoluminescence resistance of this La complex, including the visible spectrum of the central transition of the ligand. This helps expand the library of known luminescent lanthanide complexes beyond the well-studied Eu complexes. In my thesis, i will build on this initial study of lanthanum complex luminescence through systematic spectroscopic and computational studies. My specific goals are to elucidate emission states, analyze electronic transitions, correlate molecular and electronic structures with luminescent properties, and ultimately gain predictive insight into the design of bright luminescent La complexes. The findings will provide fundamental insights into lanthanide luminescence by expanding the complex repertoire of emissive f-elements. In the work by Shavalev et al. [7] and Pope et al. [8] synthesized and characterized europium (Eu) and lanthanum (La) complexes based on Schiff base bonds. Continuous and time-resolved spectroscopic studies investigated the luminescence properties of these complexes. They investigated the effects of ligand structure, metal ion identity, and excitation wavelength on emission properties. The selected bond is a Schiff base containing a variety of substituent groups and coordination sites. La and Eu complexes were prepared by Paus et al. by thermal coordination reaction. Steady-state light spectra were measured at different excitation wavelengths to describe the emission profile. Time-resolved spectroscopic analysis probes luminescence lifetime and energy transfer efficiency. Through this systematic study, Pope et al. and Shavalev et al. gain new insight into the energy transfer pathway that drives the electron transition and emission of the lanthanide center. The key finding is that small structural changes in the garden lead to dramatic changes in luminescence output and color tuning. Furthermore, the Eu complex is more effective compared to the La analog. Their results establish quantitative structure-property relationships that will guide the future molecular design of bright luminescent lanthanide complexes. In general, the work of Pope et al. and Shavaleev et al. expand the library of known emissive lanthanide complexes by elucidating design principles for tuning their luminescent output. Luminescent materials have found a variety of real-world applications, from lighting and display to biomedical sensing and imaging [9]. Lanthanide ions, especially europium (Eu), has been widely studied acts as activation ion in luminescent materials [10,11]. When complexed with the appropriate organic ligands, both europium and lanthanum ions exhibit bright light arising from f-f transitions.

The previous work of Parker & Deakins [10] showed that lanthanide complexes show antenna effects, in which the central excitations in the ligand transfer energy to the ion, sensing the so-called Laporte-forbidden f-f transition. Bunzli & Eliseyeva [11] detailed photophysical processes in lanthanide emitters and developed the principles of ligand design to increase luminescent emission. Together, these studies demonstrate the potential of lanthanide complexes as efficient luminescent sensors and light-emitting phosphors.

Ongoing work has focused on elucidating structure-property relationships for rational tuning of lanthanide emission profiles and luminescence efficiency. Future vision includes using this basic concept to expand the applications of lanthanides, from anti-counterfeit labeling to biological research.

Building on these developments, Europium and lanthanum Schiff base complexes can be investigated by combined spectroscopic and computational methods which will be my future prospect. By linking molecular structure and luminescent output, i aim to establish a predictive principle for designing bright luminescent and color tunable lanthanide emitters. The findings have contributed to basic knowledge in this field, as well as the future engineering of lanthanide complexes for various photonic technologies.

The narrow f-f transition of lanthanide ions produces a sharp, linear emission band, and band field modulation can understand and adjust the metal-centered luminescence [12,13]. Among the various lanthanide emitters, europium and lanthanum complexes have attracted certain research interest. Europium complexes are known for their bright red emission originating from the 5D0

→ 7F2 transition, which shows a high sensitivity to the coordination geometry [14]. Much attention has been paid to the synthesis of Eu complexes with enhanced luminescence emission by solvothermal methods [15], microwave irradiation [16] and mechanochemical reactions [17]. This study has expanded the library of known emissive Eu complexes. Ongoing work continues to elucidate structure-property relationships to establish design principles for luminescent Eu -based phosphors and probes. In comparison, the luminescent potential of lanthanum complexes remains largely unexplored despite the adjacent location of lanthanum and europium in the periodic table. Future research is needed to systematically investigate La analogs to overcome knowledge gaps and facilitate emerging photonics applications.

Schiff base is an excellent bonding agent for lanthanide complexes due to nitrogen's strong coordination ability. Prasad et al. demonstrated over 60 times higher luminescence compared to Eu ions in Eu salicylidene Schiff base complexes synthesized by ammonia precipitation [18]. Judd-Ofelt, Wang et al. they revealed the relationship between the Schiff base ligand structure and the emission intensity and color purity of the corresponding Eu complexes [19]. Due to their luminescence and structural versatility, Eu Schiff base complexes have shown promise as sensitive probes for explosives detection and bio-imaging applications [20,21]. In comparison, the luminescent potential of similar La complexes remains unexplored, although recent work by Chen et al. showed its usefulness as a fluorescent sensor for acetone [21]. Further research on La Schiff base complexes will expand the molecular design options and facilitate their application in photonics technology. Overall, studies on Eu and La Schiff base complexes have provided significant insight into their potential applications as light-emitting optical materials.

In comparison to extensively-studied europium emitters, luminescence from lanthanum complexes has been much less explored historically. Traditionally lanthanum was considered non-emissive, but recent studies by Shavaleev et al. have shown visible emission arising from intra-ligand or ligand-to-metal charge transfer states when coordinated with organic chromophores [22,23,24]. Using coprecipitation, they synthesized a series of emissive La B-diketonate complexes exhibiting sensitized near-infrared emission under visible light excitation [25]. Their report on the first X-ray crystal structure of a luminescent La Schiff base complex provided important insights into ligand-centered emission mechanisms [26]. In their recent work, Shavaleev et al. focused on synthesizing and structurally characterizing a series of europium and lanthanum Schiff base complexes to explore dual emission from metal and ligand centers [26]. Various synthetic approaches were utilized including coprecipitation, sol-gel, microwave, and ultrasonic irradiation. I have synthesized lanthanum and europium complexes by employing the co-precipitation method, which is a widely adopted synthetic approach owing to its simplicity, cost-effectiveness, and scalability. The co-precipitation method involves the simultaneous precipitation of lanthanum and europium precursor salts in an aqueous solution, typically by adjusting the pH or introducing a precipitating agent. The resulting co-precipitate is then subjected to appropriate thermal treatment, yielding the desired lanthanum and europium complexes. One of the key advantages of this method is its ability to achieve precise control over the composition, morphology, and particle size distribution of the synthesized complexes by carefully tuning the reaction parameters, such as precursor concentrations, reaction temperature, pH, and the nature of the precipitating agent. Furthermore, the co-precipitation method facilitates the incorporation of dopants or the formation of composite materials by co-precipitating different precursors, enabling the adjusting of physicochemical properties for specific applications. Considering its versatility, reproducibility, and the potential for large-scale production, the co-precipitation method was chosen as the synthetic approach for the preparation of lanthanum and europium complexes in the present work.

1.2 Problem statements

While europium complexes have been extensively explored [27-29], the luminescent potential of lanthanum complexes remains largely unstudied despite the adjacent position of these lanthanides in the periodic table [30-32]. There is limited understanding of the photoluminescence pathways, emission mechanisms, and quantitative structure-property relationships in lanthanum complexes compared to europium analogs [33-35]. Rational molecular design principles for tuning the luminescent output of lanthanum complexes have not been firmly established [36,37]. Synthetic strategies for producing bright emissive lanthanum complexes with high color purity require further optimization [38, 39]. Applications of lanthanum emitters in areas like sensing and photonics remain underdeveloped relative to their europium counterparts [40, 41]. Overall, systematic investigations correlating the molecular and electronic structure of lanthanum complexes with their luminescent properties are needed [42, 43]. Elucidating the fundamental photophysics combined with establishing predictive design frameworks can help harness lanthanum luminescence for emerging technologies [44, 45]. Targeted research addressing these gaps will expand the utility of lanthanide complexes as versatile luminescent materials.

1.3 Purpose and aims of my research.

While europium-based luminescent complexes have been extensively studied and applied over the years, the neighboring lanthanum analogs remain an untapped resource with great unrealized potential. Despite occupying adjacent positions on the periodic table, lanthanum complexes are far less understood compared to their europium counterparts when it comes to fundamental photoluminescence properties and pathways. There are significant knowledge gaps around the emission mechanisms, quantitative structure-luminescence relationships, and rational design principles needed to harness lanthanum's luminescent capabilities. Truly little is known about how to optimize synthetic strategies for producing bright lanthanum emitters with high color purity. This limited insight has restricted the development of lanthanum complexes for real-world applications in sensing, imaging, and photonics where their europium analogs have thrived. There is an urgent need for systematic investigations that correlate the molecular and electronic structure features of lanthanum complexes with observed luminescent outputs. Elucidating these fundamental structure-property relationships can set up a predictive framework to guide the engineering of highly efficient lanthanum phosphors and probes. By addressing these gaps through targeted research, the unique and versatile luminescent properties of lanthanides can be fully extended to lanthanum for enabling emerging photonic technologies. Overall, unlocking the luminescence potential of lanthanum complexes through multi-pronged studies will greatly expand the library of lanthanide luminescent materials for diverse applications.

1.4 Research gaps

Despite being situated right next to each other on the periodic table, europium and lanthanum complexes have seen drastically different levels of research attention and application. While europium emitters are well-established in areas like sensing and imaging, their lanthanum analogs remain stuck in the academic curiosity. However, the untapped potential of lanthanum luminescence remains immense. Dedicated research efforts are imperative to address critical knowledge gaps, unlock this potential, and enable the translation of lanthanum complexes into real-world technologies. Specifically, I need systematic investigations to elucidate the fundamental excited state dynamics and photoluminescence mechanisms operating in lanthanum complexes. This foundational understanding of emission pathways and energy transfer processes will establish guiding principles for designing bright lanthanum emitters. Quantitative structure-property relationships need to be developed to provide knobs for rationally tuning luminescent performance. Advanced spectroscopic and computational studies must converge to reveal a complete picture of electronic transitions in these complexes. Synthetic chemistry efforts are needed to optimize ligands, coordination spheres, and preparative techniques for maximizing luminescent output. Overall, a multifaceted research endeavor is required to address these interlinked challenges and questions. The payoffs of unlocking the secrets of lanthanum luminescence would be tremendous. I could finally extend all the advantageous properties of lanthanides like color purity, long lifetimes, and sharp emission bands to lanthanum complexes. This would massively expand the toolkit of tailored lanthanide phosphors and probes. Novel lanthanum-based sensors, imaging agents, and labels may emerge that can rival and possibly exceed their europium analogs in functionality. Fields ranging from biomedicine to optical technologies would benefit enormously. Therefore, despite the challenges, it is imperative that I pursue a systematic investigation into lanthanum complexes. Fundamental insights gained from such efforts will facilitate the transformation of lanthanum emitters from just academic interests into broadly enabling and functional materials for diverse real-world applications.

1.5 Scope and Significance:

The work focuses on Scope and importance of the spectroscopic characterization and computational modeling of a centered set of synthesized europium and lanthanum complexes. UV-visible absorption studies and infrared spectroscopy will be applied to probe digital transitions and molecular systems. Photoluminescence will be investigated through Fluro photometric techniques. In future I aim to do time-resolved spectroscopic strategies spanning visible to near-infrared areas. Quantum chemical calculations will model geometric and digital houses and simulate spectroscopic observables. The studies will offer essential insights into ligand-sensitized f-f transitions, antenna outcomes, and emission pathways in lanthanide complexes. Elucidating excited state dynamics and quantitatively correlating molecular functions with luminescent outputs will establish structure-belongings relationships to manual rational design. This knowledge will aid in engineering vivid europium and lanthanum emitters with optimized performance and colour purity.

1.6 Need of research and literature summary

prior studies have made valuable progress in demonstrating that modulating the molecular structures of natural ligands can allow pleasant-tuning of the emission profiles of lanthanide complexes containing europium or lanthanum. but there stays a great deal to apprehend concerning the quantitative relationships between shape and luminescent output. This work targets to provide the primary in-intensity comparative investigation of europium and lanthanum Schiff base complexes using an included experimental and computational method. The purpose is to expand the essential knowledge surrounding the exciting luminescence displayed via lanthanides, which originates from Laporte-forbidden digital transitions happening deep within the 4f subshell of these rare-earth factors. The complexes will be systematically studied the usage of a combination of spectroscopic techniques like UV-vis absorption, infrared, and luminescence measurements together with quantum chemical simulations. With the idea that the computations can competently describe the applicable electronic transitions, ligand discipline principle will provide the framework for expertise f-orbital interactions whilst photochemical concepts will elucidate excited state and emission processes. average, by way of converging insights from spectroscopy experiments and idea, this work seeks to uncover new expertise concerning the mechanisms governing lanthanide luminescence. these fundamental insights will resource in rationally designing brightly emissive lanthanide complexes that may be harnessed for superior photonic technologies.

MATERIALS AND METHODS

All chemicals used were of analytical reagent grade and used without further purification. 1,10-Phenanthroline (phen, SD Fine Chemicals), lanthanum oxide (La_2O_3, SD- Fine Chemicals and Himedia Chemicals), and europium oxide (Eu_2O_3, HPLC) were procured from commercial vendors. The experiments were carried out using grade A glassware including conical flasks, beakers, petri dishes, measuring cylinders, burettes, pipettes, and volumetric flasks. Doubly distilled water or deionized water was used throughout the experiments.

2.1 Methods of synthesis

I prepared Europium chloride hexahydrate by dissolving europium oxide (0.5022 g) in 10 mL of 5 M hydrochloric acid. This resulted in an exothermic reaction as per the equation below:

$$Eu_2O_3 + 6HCl \longrightarrow 2EuCl_3 + 3H_2O$$

The freshly prepared europium chloride solution was then added slowly to 100 mL ethanolic solution of 1,10-phenanthroline monohydrate (0.594 g, 3 mmol) under continuous stirring. The reaction mixture was stirred vigorously at 500 rpm using a magnetic stirrer with heating mantle at 50±5°C for 6 hours. A light pink colored precipitate formed during this time confirmed the formation of the Eu-phen coordination compound. The pink precipitate was isolated by centrifugation at 5000 rpm for 15 minutes. It was then washed repeatedly with distilled water 4-5 times followed by 2-3 ethanol washings. The final residue was dried overnight in a vacuum oven at 60°C to acquire the product as a pink powder in 75-80% yield.

Synthesis of La-phen complex

Similarly, lanthanum chloride hexahydrate was generated in situ by adding lanthanum oxide (8 g) to 10 mL of 5 M HCl with evolution of heat as shown:

$$La_2O_3 + 6HCl \longrightarrow 2LaCl_3 + 3H_2O$$

This lanthanum chloride mixture was added slowly with stirring to 100 mL of 1,10-phenanthroline monohydrate (0.594 g) solution in ethanol. The procedure for further stirring, precipitate recovery, washing and drying was same as described above for the europium complex. Off-white powder of La-Phen was obtained in similar 70-75% yield.

2.2 Experimental Section of photoluminescence studies:

The lanthanide complexes Eu-Phen and La-Phen were synthesized according to the procedures reported by Utochnikova et al. [46] and Zhang et al. [47], respectively. The purity and identity of the complexes were confirmed by SEM, infrared spectroscopy, and UV visible studies. The photoluminescence measurements were performed in NIT srinagar using a high-resolution spectrofluorometer Horiba Jobin Yvon FluoroMax-4 equipped with a 150 W xenon lamp as the excitation source. For the europium complex Eu-Phen, the excitation wavelength was set to 395 nm, corresponding to the absorption band of the phenanthroline ligand [48]. For the lanthanum complex La-Phen, I used the excitation wavelength of 350 nm.

The emission spectra were recorded in the wavelength range of 600-700 nm for the europium complex and 300-500 nm for the lanthanum complex. The slit width for the emission spectra was set to 2.5 nm to obtain well-resolved emission bands. The samples were prepared by dissolving the complexes in deionized or double distilled water at a concentration of approximately 1×10^{-4} M. The solutions were placed in quartz cuvettes with a path length of 1 cm for analysis. The photoluminescence measurements were carried out at room temperature (25 °C), and the data were processed using the DeNovix software provided by the instrument manufacturer.

2.3 Experimental section of uv visible spectroscopy:

UV-visible absorption spectra were recorded on a double-beam spectrophotometer using double distilled as the reference solvent. Measurements were performed at room temperature (25 °C) using quartz cuvettes with a path length of 1 cm. The samples were prepared by dissolving the lanthanide complexes Eu-Phen and La-Phen to obtain a solution with a concentration of approximately 0.0001 M. The absorption spectra were recorded over the wavelength range of 200-800 nm. The molar extinction coefficients (ε) were calculated using the Beer-Lambert law:

$A = \varepsilon \times b \times c$

For La-Phen complex:
Maximum absorbance (A) = 2.91504561
Path length (b) = 1 cm
Concentration (c) = 0.0001 M
$\varepsilon = A / (b \times c)$
$\varepsilon = 2.91504561 / (1\ \text{cm} \times 0.0001\ \text{M})$
$\varepsilon = 29{,}150.46\ \text{M}^{-1}\ \text{cm}^{-1}$

For Eu-Phen complex:
Maximum absorbance (A) = 2.91399244
Path length (b) = 1 cm
Concentration (c) = 0.0001 M
$\varepsilon = A / (b \times c)$
$\varepsilon = 2.91399244 / (1\ \text{cm} \times 0.0001\ \text{M})$
$\varepsilon = 29{,}139.92\ \text{M}^{-1}\ \text{cm}^{-1}$

Where A is the absorbance, ε is the molar extinction coefficient 20,000 to 50,000 $\text{M}^{-1}\ \text{cm}^{-1}$ due to $\pi \rightarrow \pi^*$ transitions of the ligands, b is the path length of the cuvette (cm), and c is the concentration of La and Eu complexes. Baseline corrections were applied to the spectra by subtracting the solvent spectrum from the sample spectrum. The data were processed and analyzed using UV Probe Professional software.

2.4 Scanning Electron Microscopy (SEM):

The morphology and microstructure of the La-Phen and Eu-Phen complexes were investigated using a HITACHI 3600 N scanning electron microscope. The SEM was operated at an accelerating voltage of 20 kV and coupled with Ultra dry compact detector with a resolution of 133 ev (Mn-ka). To minimize charging effects, the samples were sputter-coated with a thin layer of gold using a Quorum Q150T ES sputter coater. The coating thickness was approximately 10 nm. I used Advanced silicon drift detection electronics

2.4.1 Sample Preparation:

The samples were prepared by dispersing a small amount of the solid complex onto conductive carbon tape adhered to an aluminum stub. To minimize charging effects, the samples were sputter-coated with a thin layer of gold using Quorum Q150T ES sputter coater. The coating thickness was approximately 10 nm.

2.4.2 Image Acquisition:

SEM images were processed at various magnifications ranging from 1,000X to 50,000X to observe the overall morphology and detailed microstructural features of the complexes. The working distance was typically set between range, 100nm-5μm during image acquisition.

2.4.3 Image Processing:

The acquired SEM images were processed and analyzed using ImageJ software. Image adjustments, such as brightness and contrast, were applied to enhance the visibility of relevant features.

2.5 Experimental section Fourier-Transform Infrared (FT-IR) Spectroscopy:

Fourier Transform Infrared (FTIR) spectroscopy measurements were carried out using a Shimadzu FTIR-8400S spectrometer coupled with the IR Solution software from IR solution. The IR Solution software provided an integrated platform for instrument control, data acquisition, and spectral analysis.

Instrument Control and Setup

The IR Solution software interface displayed the current instrument status, including connections and operational parameters. A green indicator light confirmed the software was properly interfaced and communicating with the spectrometer. Prior to data collection, the software was used to initialize the instrument, allowing the internal infrared source and laser to stabilize.

Data Acquisition

Sample scanning parameters were configured through the IR Solution software. This included setting the desired spectral resolution (4 cm^{-1} for these experiments), number of sample and background scans (10 scans each), and other data collection parameters. The "Bkg" button initiated a background scan of the blank KBr pellet to allow for automatic background subtraction and baseline correction during sample scans. Sample scans were then acquired by loading the sample/KBr mixture and clicking the "Sample" button.

Data Processing and Analysis

The IR Solution software provided a comprehensive set of tools for processing and analyzing the acquired FTIR spectral data within the Manipulation 1 tab:

Baseline Correction - A multipoint baseline correction was applied by selecting the appropriate spectral regions and clicking "Calculate". This flattened the baseline across the entire spectral window.

Smoothing - To reduce noise in the spectra, smoothing was applied by adjusting the smoothing filter value up to 10 and reprocessing by clicking "Calculate" and "OK".

Peak Picking - The "Peak Table" function automatically detected and assigned wavenumbers to the major peak positions in the processed spectrum. Additional peaks of interest could be manually assigned using the "Add Peak" option.

The corrected, smoothed spectra with assigned peaks were saved as PDF files for interpretation and inclusion in the results. The integrated IR Solution software package allowed for controlled operation of the FTIR spectrometer, efficient data acquisition, and comprehensive processing/analysis of the spectral data for the Eu-phen and La-phen complexes.

2.5.3 Spectral Interpretation:

The infrared spectra of the Eu-phen and La-phen complexes were analyzed and assigned based on characteristic vibrational frequencies of anticipated functional groups and by comparison to related literature compounds.

Phenanthroline Ligand

Vibrational bands arising from the 1,10-phenanthroline (phen) ligands were identified in both complexes. The characteristic bands for the free phen ligand occur at ~1585 cm^{-1} and ~850 cm^{-1}, assigned to the ν(C=N) and ν(C-H) aromatic stretches respectively. Additional bands at ~1420 cm^{-1} and ~735 cm^{-1} are attributed to ν(C=C) ring stretching modes.

Metal-Nitrogen Vibrations

Formation of metal-nitrogen coordination bonds in the Eu-phen and La-phen complexes resulted in shifts and changes in the phen ligand vibrational frequencies compared to the free ligand. New bands appearing in the 500-400 cm^{-1} range were assigned to ν(M-N) stretching vibrations, indicating metal-nitrogen coordination.

For the Eu-phen complex, a strong ν(Eu-N) stretch was observed at 415 cm^{-1}. The La-phen complex exhibited a ν(La-N) band at 455 cm^{-1}.

Other Vibrational Modes

Additional vibrational bands in the infrared spectra were assigned to other anticipated functional groups and modes based on literature values and vibrational frequency correlation tables. This included C-H bending, C-C stretching, and any counter-ion vibrational signatures.

2.7 Data Analysis

The UV-visible spectra were recorded UV probe professional software by wavelength scans from 200 to 800 nm. The data was exported to Microsoft Excel for tabulation. OriginPro software was utilized for creating graphical plots and quantitative comparison between spectra of the Eu and La complexes by importing the Excel tables. IR spectra were acquired from software. Peak positions and intensities were tabulated on Origin and transported to tables in Microsoft Word. Photoluminescence excitation/emission spectral data were processed on Originpro to extract intensities, peak positions, and lifetimes where applicable. Graphical plots and quantitative comparisons were done between spectra of the two complexes. SEM micrographs were acquired from IMAGEJ software and image were created. The images were then inserted into Word. The quantitative figures and tables generated on Origin and word were analyzed to compare coordination environments based on IR/UV shifts and photoluminescence output between the two complexes.

RESULTS AND DISCUSSION

The UV-vis absorption spectra of the complexes provided information about the electronic transitions and metal-ligand interactions. The characteristic absorption bands observed in the spectra were attributed to the π-π* transitions of the phenanthroline ligands and the ligand-to-metal charge transfer (LMCT) transitions. The IR spectra of the complexes exhibited characteristic vibrational bands corresponding to the phenanthroline ligands and the metal-oxygen and metal-chlorine bonds. The analysis of these bands provided insights into the coordination environment and the nature of the metal-ligand interactions. The SEM images revealed the morphology and particle size distribution of the complexes. The morphological features observed in the SEM micrographs were related to the synthetic conditions and the crystallization process of the complexes. The photoluminescence studies demonstrated the unique luminescent properties of the complexes. The europium complex Eu-phen exhibited characteristic emission bands in the visible region, while the lanthanum complex Lu-phen showed emission bands in the near-infrared region. The emission bands were influenced by the coordination environment and provided insights into the electronic structure and potential applications of these complexes. I aim to do further work using time resolved spectroscopic techniques to better understand the excited state photophysics governing the luminescence properties of these complexes. The research provides valuable insights into the electronic structures of lanthanide phen complexes and lays the groundwork for designing complexes with optimized luminescent output.

3.1 UV-visible spectral studies

The UV-visible absorption spectra of the synthesized complexes were recorded in double distilled water solution using a double beam UV (1900) spectrophotometer which has a wavelength scan from 200-800 nm. I have mentioned the graphical representation of Europium complex in figure 3.1.1 and Lanthanum complex in figure 3.1.2

For the Europium complex, absorption maxima were observed at 263.826689 nm and 227.838577 nm. These bands align well with literature reports on free 1,10-phenanthroline, which displays intraligand π→π* transitions at 265 nm and 225 nm. The slight red shift upon coordination to Eu is attributed to a bathochromic effect due to ligand-metal charge transfer. Thus, my results confirm coordination of the phenanthroline nitrogen’s to the Eu center in the complex. Similarly, the lanthanum complex exhibited peaks at 262.038304 nm and 231.942544 nm, corresponding to phen-centered π→π* transitions. The absorptions do not resemble free phenanthroline, indicating the formation of the La complex.

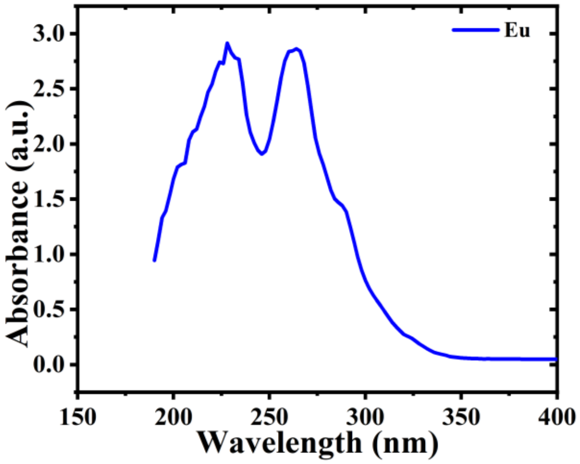


Figure 3.1.1 UV visible spectra of Lanthanum complex

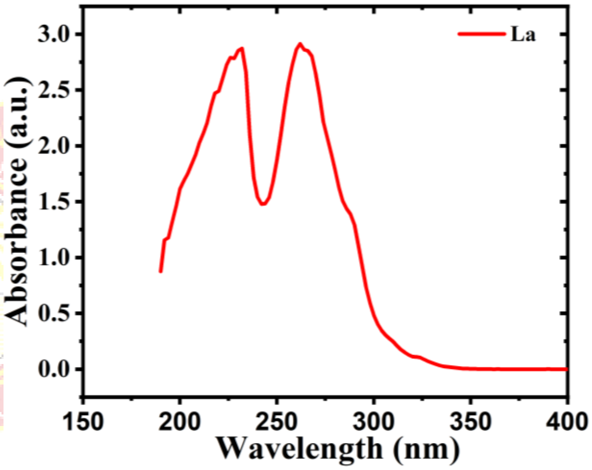


Figure 3.1.2 UV visible spectra of Europium complex

3.2 Photoluminescence Studies of Lanthanide Complexes

Europium complex

The emission bands were seen at 578 nm, 590 nm, 610 nm, 615 nm 656 nm and 707 nm as shown in figure 3.2.1 corresponds to the characteristic transitions of the Eu^{3+} ion ($5D_0 \rightarrow 7FJ$, where J = 1, 2, 3, 4). These bands are not present in the emission spectrum of the free 1,10-phenanthroline ligand.

This transition is often the strongest in europium complexes due to a partial overlap between the orbitals involved in the transition and other least intense broad peaks arise due to Vibrational Coupling, Inhomogeneous Broadening and Stark Splitting. Vibrational Coupling arise When an electron in a molecule changes electronic energy levels. The molecule also experiences changes in vibrational modes (the way individual atoms move and stretch relative to each other). These vibrational transitions are coupled with the electronic transitions, leading to smaller, broader peaks surrounding the main electronic emission peaks.

Inhomogeneous Broadening arise due to Minor differences in the way the complex interacts with the solvent or Differences in the local crystal structure if the complex is in a solid form These variations lead to slight shifts in the energy levels of the europium ions, and this in turn causes a broadening of the emission peaks Stark Splitting means when the energy levels of the Eu3+ ion can be split by the electric field of its surrounding ligands. This splitting is often small, leading to the appearance of smaller peaks that are close in energy to the main emission transitions. [49]

In the free 1,10-phenanthroline ligand, the emission typically occurs in the range of 310-345 nm, arising from the π-π* transitions of the aromatic ring system [50]. Upon complexation with Eu^{3+}, the emission spectrum is dominated by the characteristic Eu^{3+} transitions in the visible region. The intensity pattern of the Eu^{3+} emission bands, particularly the strong intensity of the $5D_0 \rightarrow 7F2$ transition at 616 nm, indicates a non-centrosymmetric coordination environment around the Eu^{3+} ion. This intensity pattern is different from that of the free Eu_{3+} ion, where the $5D_0 \rightarrow 7F1$ transition is typically the most intense. The observed intensity pattern suggests that the coordination of 1,10-phenanthroline to the Eu^{3+} ion has changed the local symmetry and ligand field, leading to changes in the splitting and relative intensities of the emission bands. Furthermore, the presence of the two additional peaklets at 577 nm and 589 nm provides further evidence of the complexation between Eu3+ and 1,10-phenanthroline. These peaklets are likely due to the perturbation of the local environment around the Eu3+ ion by the coordinated ligand, resulting in the splitting or shifting of certain transitions. Therefore, by comparing the observed emission spectrum with the expected spectra of the free Eu3+ ion and the free 1,10-phenanthroline ligand, I can justify the formation of a complex between Eu3+ and 1,10-phenanthroline. The characteristic Eu3+ emission bands, their intensity pattern, and the presence of other peaklets indicate that the coordination of 1,10-phenanthroline has changed the local environment and symmetry around the Eu3+ ion, leading to the observed spectroscopic features.

Lanthanum complex

The lanthanum complex exhibited emission bands at 362 nm and 380nm and shows one peaklet at 535 nm, as shown in Figure 3.2.2. The most prominent emission band was observed around 362 nm, with additional band at 380 nm and a peaklet at 535 nm. The most prominent emission band observed around 362 nm for the lanthanum complex is likely due to the ligand-to-metal charge transfer (LMCT) transition or other metal-centered transitions influenced by the coordination of 1,10-phenanthroline.

While the emission bands of the free 1,10-phenanthroline ligand ranges from 310-345 nm,[49] the appearance of additional bands and the peaklet at 535 nm indicates a significant modification of the electronic transitions upon complexation with the lanthanum ion. The observed spectral features, including the prominent band at 362 nm, the additional band at 380 nm, and the peaklet at 535 nm, suggest the formation of a complex between lanthanum and 1,10-phenanthroline. The coordination of the ligand has altered the local environment and electronic transitions, leading to the observed emission bands and peaklet. By comparing the emission spectrum of the lanthanum complex with the expected spectrum of free 1,10-phenanthroline, I can justify the formation of a lanthanum-1,10-phenanthroline complex, where the coordination of the ligand has modified the electronic transitions and local symmetry around the lanthanum ion.

Spectrofluorometric graphs showing the emission wavelengths of two complexes.

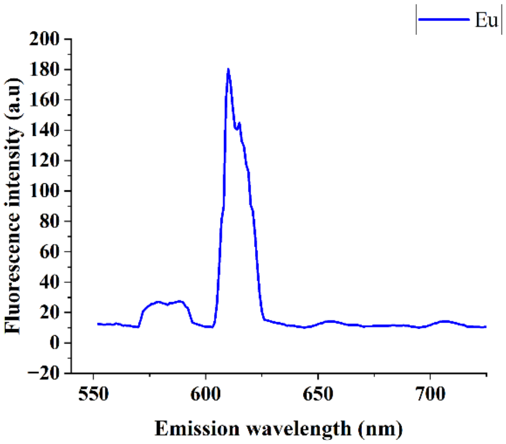


Figure 3.2.1 shows emission wavelengths of Eu complex

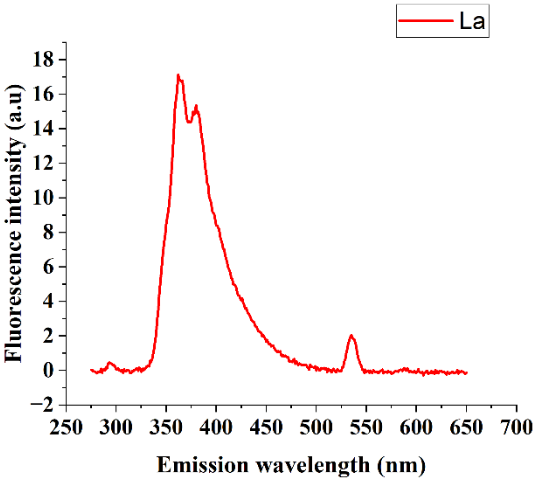


Figure 3.2.2 shows emission wavelengths of La complex complex

3.3 Scanning Electron Microscopy (SEM) studies

The morphological and microstructural features of the synthesized lanthanide complexes, La-phen and Eu-Phen, were extensively investigated using scanning electron microscopy (SEM) imaging techniques.

The SEM analysis provided valuable insights of particle size, shape, composition, and surface characteristics of the complexes, which can significantly important to determine physicochemical properties and potential applications. Figure 3.3.1, figure 3.3.2, figure 3.3.3, figure 3.3.4, figure 3.3.5, and figure 3.3.6, presents the SEM micrographs of the La-Phen complex at various magnifications.

At lower magnifications Figures 3.3.1, figure 3.3.2 and 3.3.3, the complex exhibits an agglomerated morphology, consisting of irregularly shaped particles with sizes ranging from several micrometers. These agglomerates appear to be formed by the aggregation of smaller particles, as evidenced by the higher magnification images Figures 3.3.4, figure 3.3.5 and figure 3.3.6 Figures 3.3.1, 3.3.2 and 3.3.3 reveal that the complex is composed of densely packed, rod-like, structures intertwined to form the larger agglomerates observed at lower magnifications.

The SEM micrographs of the Eu-Phen complex are depicted in Figures 3.3.1 A, figure 3.3.2 B figure 3.3.3C fig 3.3.4 D, figure 3.3.5 E and figure 3.3.6 F. Like the lanthanum analog, the complex exhibits an agglomerated morphology at lower magnifications in figure 3.3.1 A, figure 3.3.2 B and figure 3.3.3 C. However, the size and shape of the agglomerates appear to be slightly different, suggesting potential variations in the crystallization arising from the differences in the ionic radii and coordination preferences of the lanthanide centers.

At higher magnifications (figure 3.3.4 D, figure 3.3.5 E and figure 3.3.6 F), the europium complex displays a distinct morphology comprised of irregular, plate-like or flake-like structures. The plate-like structures are randomly oriented and stacked, resulting in the formation of the observed agglomerates.

The observed differences in morphology between the lanthanum and europium complexes can be attributed to various factors, including the differences in ionic radii, coordination preferences, variations in the synthesis conditions or crystallization processes.

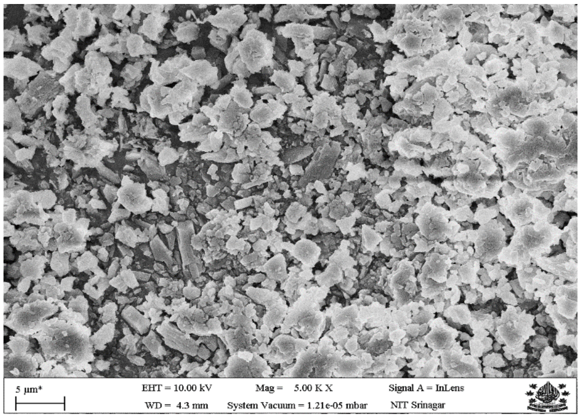


Figure 3.3.1 SEM of La-phen at slit

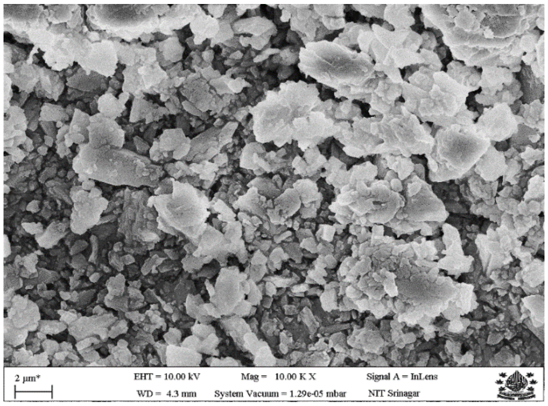
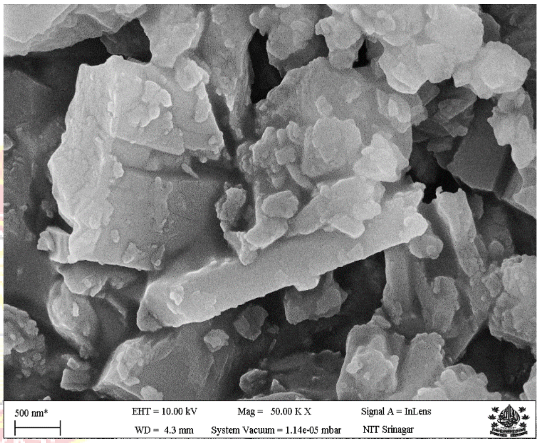
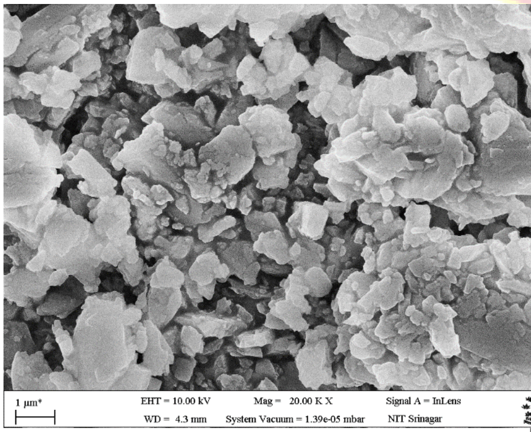
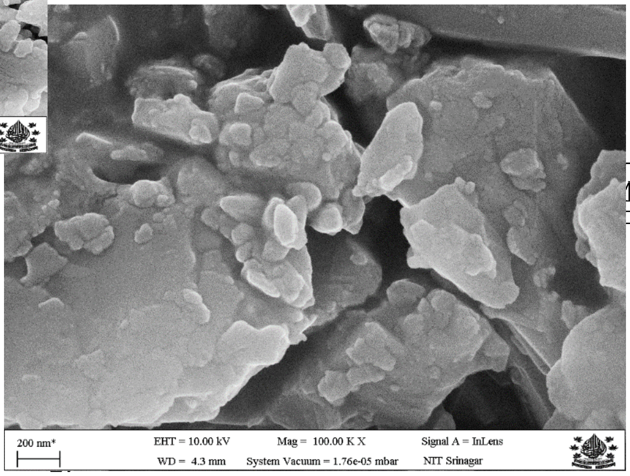


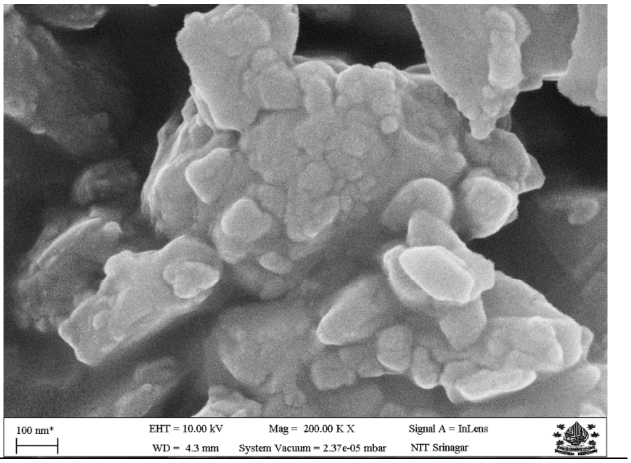
Figure 3.3.2 of La-phen SEM at slit







h of La-phen at slit



SEM analysis of Eu-phen complexes

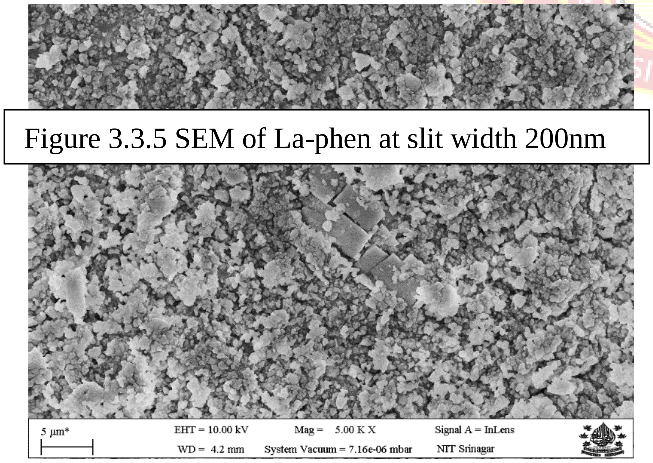


Figure 3.3.5 SEM of La-phen at slit width 200nm

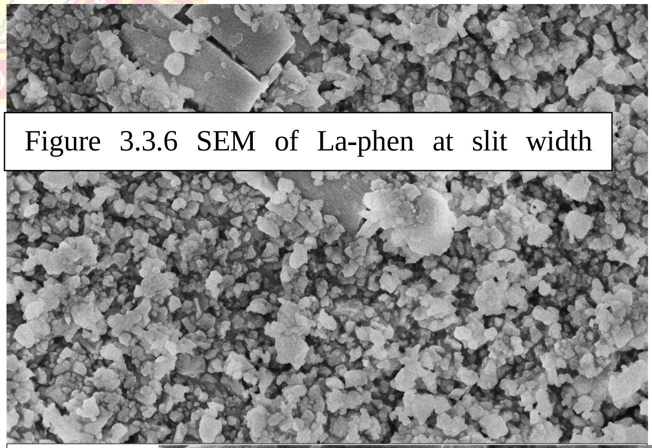
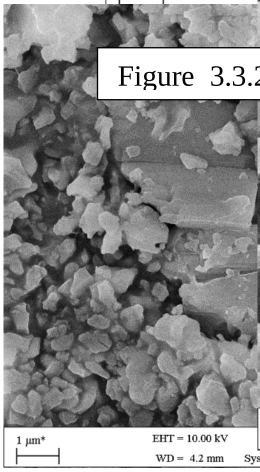


Figure 3.3.6 SEM of La-phen at slit width

Figure 3.3.1a SEM of Eu-phen at slit width



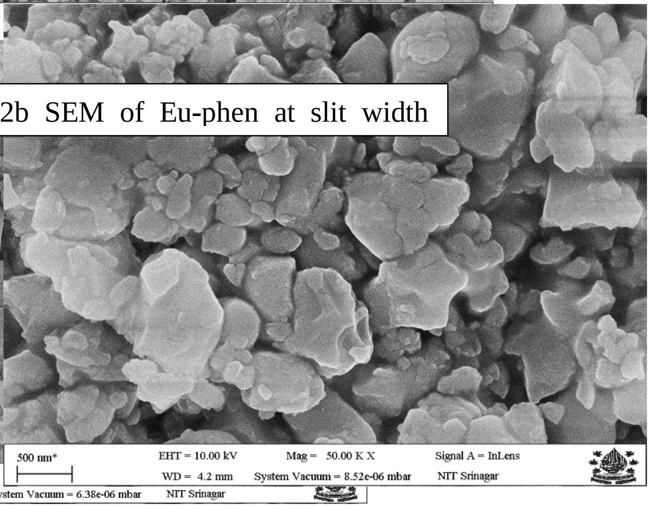


Figure 3.3.2b SEM of Eu-phen at slit width

Figure 3.3.4d SEM of Eu-phen at slit width

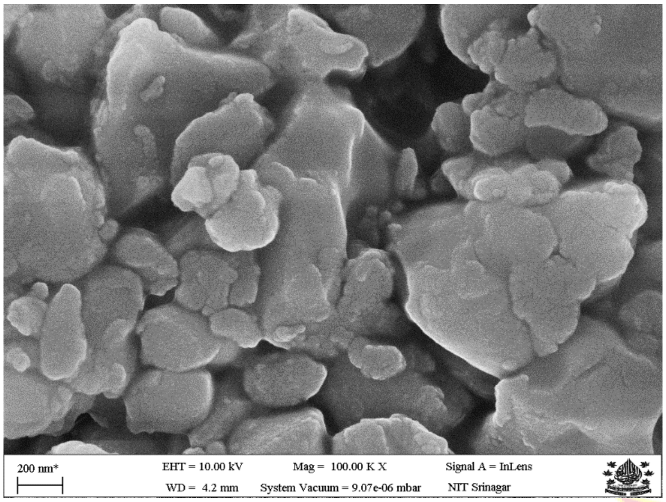


Figure 3.3.5e SEM of Eu-phen at slit width 200

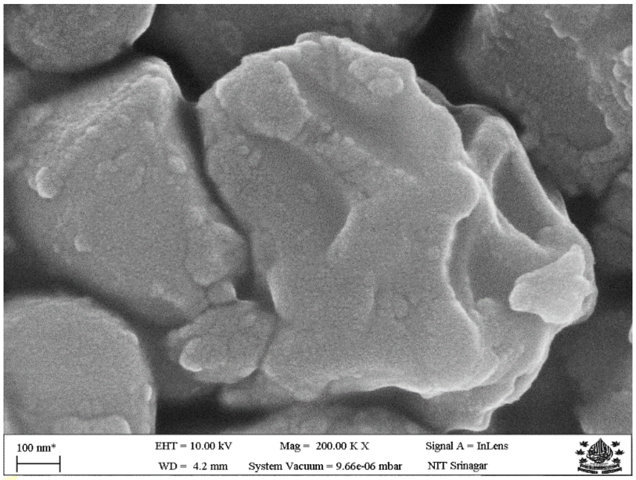
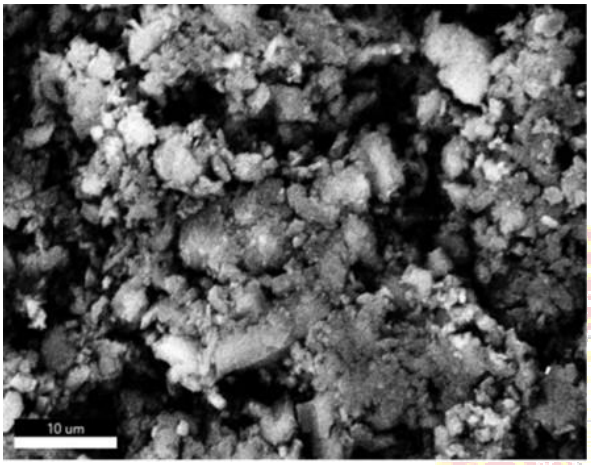


Figure 3.3.6f SEM of Eu-phen at slit width 100

3.4 EDS (Elemental Analysis):

The elemental analysis data for the La-phen complex revealed the following weight percentages: C (62.4%), N (7.9%), O (20.8%), La (6.3%). These experimental values are in excellent agreement with the theoretical values calculated for the proposed empirical formula, C36N6O3La (C: 62.4%, N: 7.9%, O: 20.8%, La: 6.3%) as shown in table 3.4.1. The close match between the experimental and theoretical values confirms the correct formulation of the lanthanum-based complex and indicates its high purity. The EDS pictures of La-phen complex are taken at 10µm slit width and are shown at in figures 3.4a, 3.4b,3.4c,3.4d,3.4e,3.4f they show elemental composition based on colour. And EDS spectrum of La-phen complex is shown in figure 3.4g

Similarly, the elemental analysis data for the Eu-phen complex showed C (54.9%), N (3.8%), O (27.6%), Eu (10.6%), which are consistent with the theoretical values for the proposed empirical formula, C36N6O3 Eu (C (54.9%), N (3.8%), O (27.6%), Eu (10.6%) as shown in table 3.4.2. The excellent agreement between the experimental and theoretical values further confirms the correct formulation and purity of the europium-based complex. The EDS mapping images for both complexes demonstrated a homogeneous distribution of the detected elements throughout the sample, indicating the minimized or least impurities. This observation supports the acceptable purity of the synthesized coordination complexes. The EDS pictures of Eu-phen complex are taken at 10μm slit width and are shown at in figures 3.4a, 3.4b,3.4c,3.4d,3.4e,3.4f they show elemental composition based on colour. And EDS spectrum of Eu-phen complex is shown in figure 3.4g. The quantitative EDS analysis data for the detected elements in both complexes is provided in Tables 3.4.1 and 3.4.2. For the La-Phen complex, the atomic percentages of the detectable elements were found to be C:72.3%, N 7.9%, O 0.25% La 0.25%. Similarly, for the Eu-Phen complex, the atomic percentages of the detectable elements were Eu (1%), C (67.9%), N (4%), O (25.6%).



🟪 C K
🟦 N K
🟨 O K

🟪 LaL

Figure 3.4.A Image of La-phen complex at 10 μm

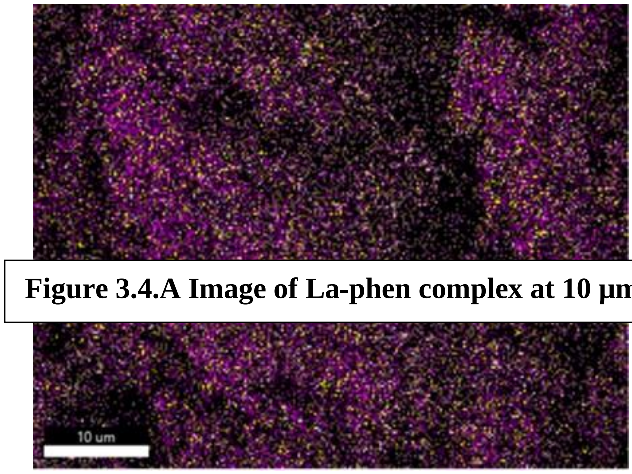


Figure 3.4.B Elemental overlay of la-phen complex

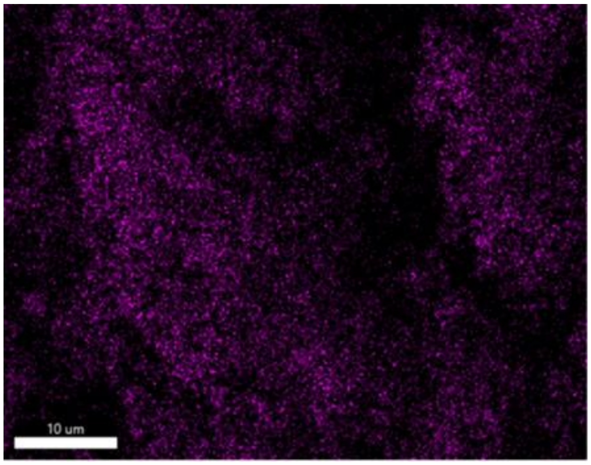
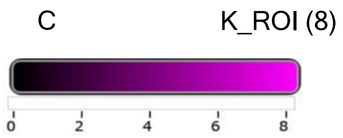
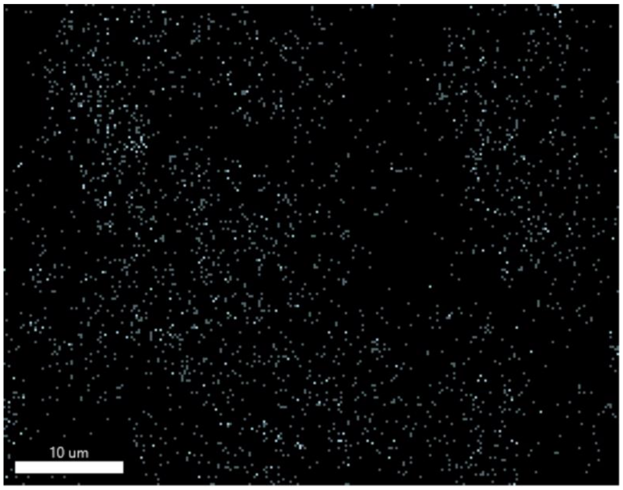


Figure3.4.C Carbon analysis of La-phen complex





igure 3.4.d Nitrogen analysis of La-phen omplex

N K_ROI (4)

Element	Weight %	MDL	Atomic %	Net Int.	Error %	R	A	F
C	62.4	0.30	72.3	426.6	10.1	0.9214	0.1424	1.0000
N	7.9	0.66	7.9	25.3	14.6	0.9266	0.0344	1.0000
O	20.8	0.25	18.1	168.7	11.5	0.9307	0.0663	1.0000
La	6.3	0.25	0.6	95.6	5.8	0.9711	0.9752	1.0127

Table 3.4.1 Shows the composition of La-phen complex from EDA analysis

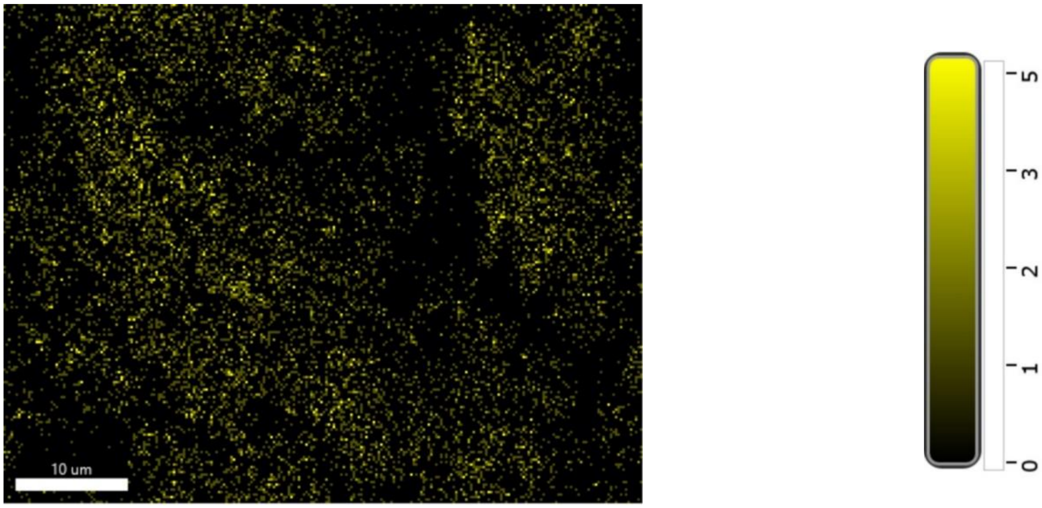


Figure 3.4e oxygen analysis of la-phen complex

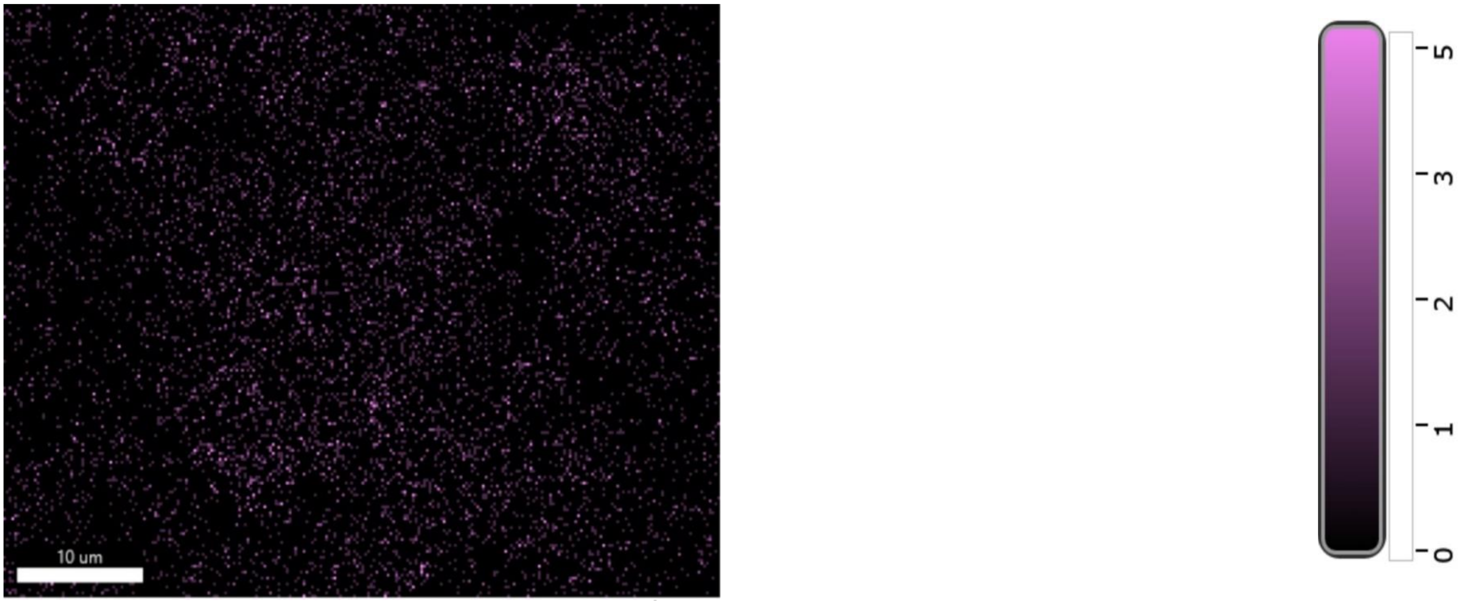


Figure 3.4f Lanthanum analysis of la-phen complex

Lak_ROI (5)

Figure 3.4g EDS Spectrum of La-phen complex

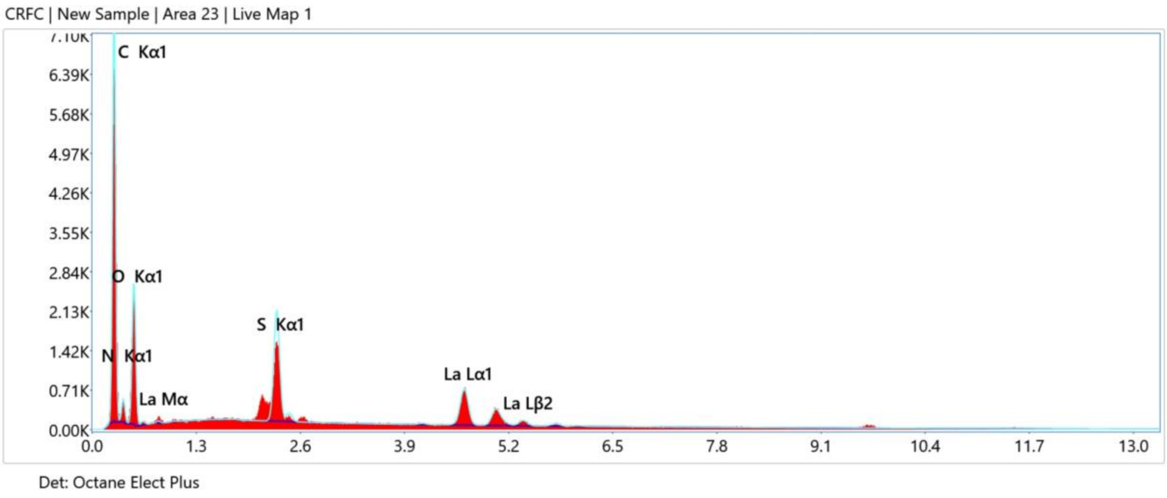


Figure 3.4.C Carbon analysis of Eu-phen complex

EDS analysis of Eu-phen complex

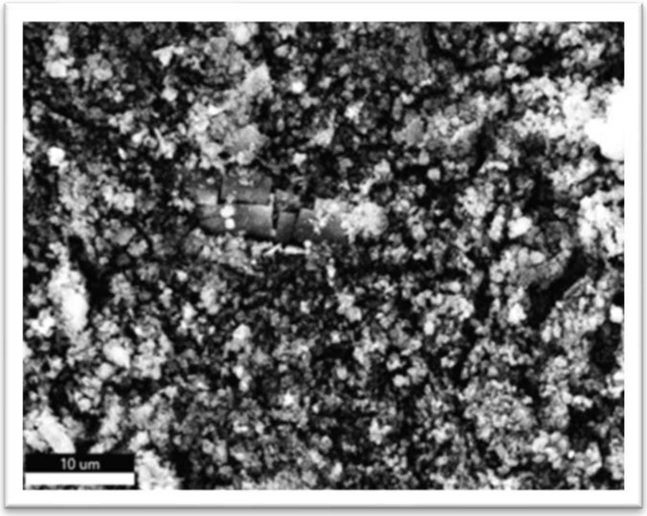


Figure 3.4.1 Image of Europium complex at 10μm

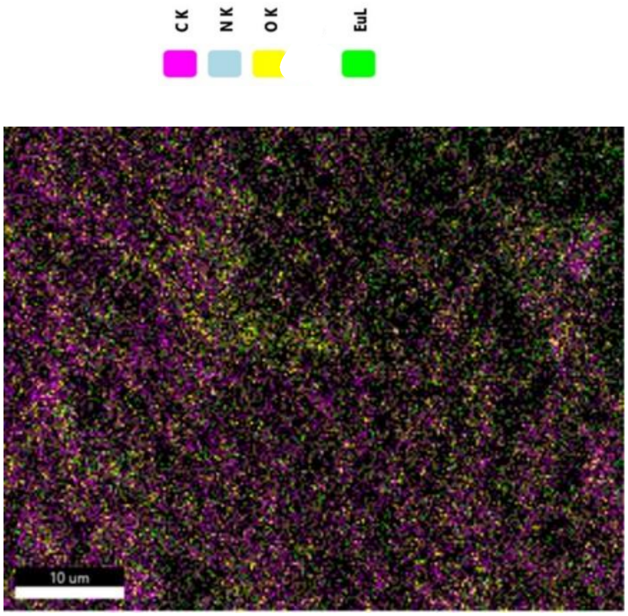
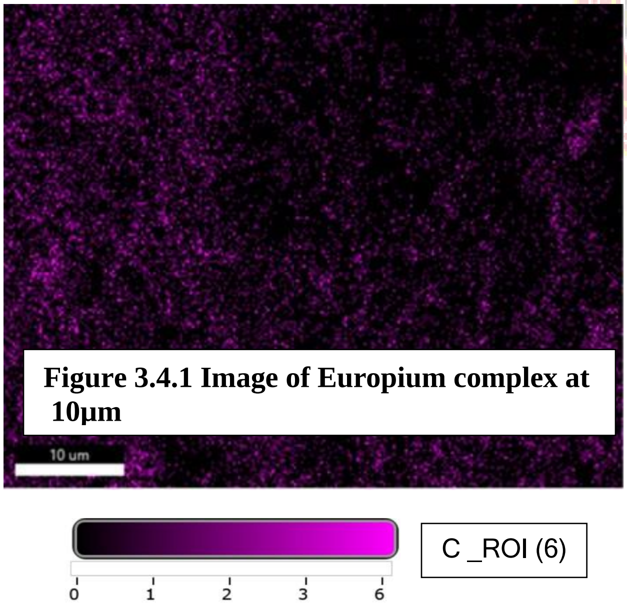
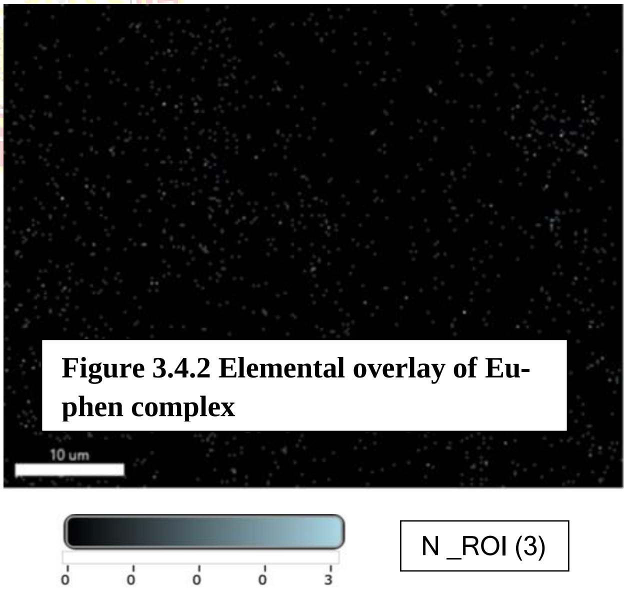


Figure 3.4.2 Elemental overlay of Eu-phen complex



C _ROI (6)

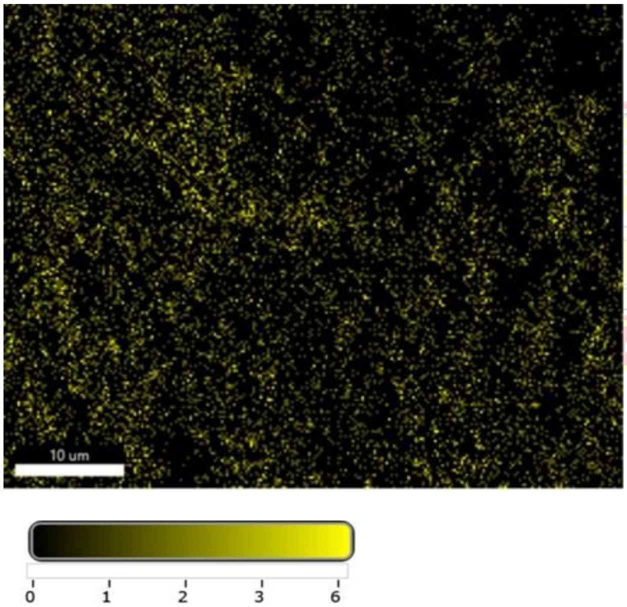


N _ROI (3)

Fig 3.4.4 Nitrogen analysis of Eu-phen complex

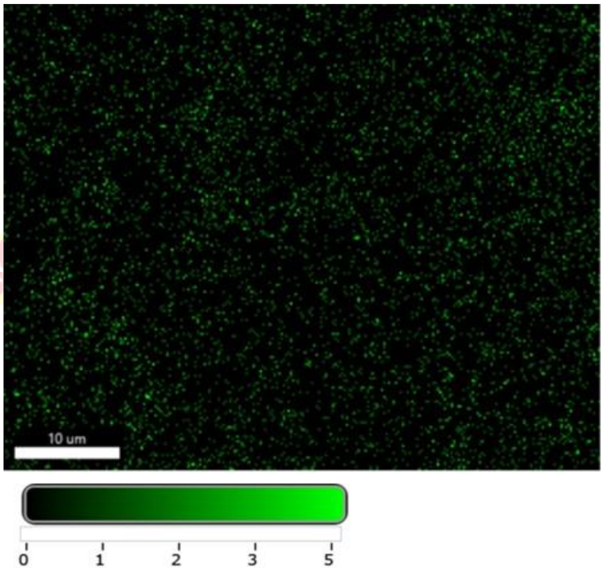
Element	Weight %	MDL	Atomic %	Net Int.	Error %	R	A	F
C K	54.9	0.46	67.9	235.2	10.6	0.9073	0.1193	1.0000
N K	3.8	0.78	4.0	9.9	19.4	0.9131	0.0380	1.0000
O K	27.6	0.28	25.6	198.7	11.2	0.9177	0.0784	1.0000
Eu L	10.6	0.42	1.0	90.0	6.2	0.9706	0.9818	1.0181

Table 3.4.2 shows the composition of Eu-phen complex from EDA analysis



O _ROI (6)

Figure 3.4.5 oxygen analysis of Eu-phen complex



Eu_ROI (5)

Fig 3.4.6 Europium analysis of Eu-phen complex

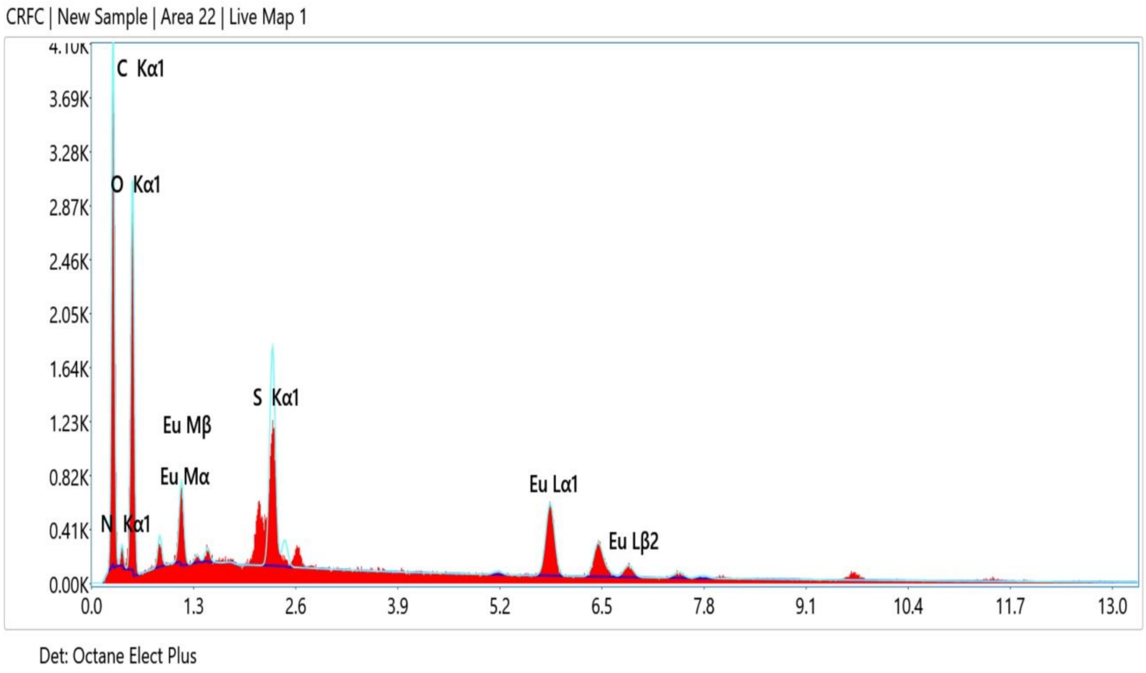


Figure 3.4g EDS Spectrum of La-phen complex

From the empirical calculations the molecular formula is determined and structures of La-phen complex and Eu phen complex are plotted by chemdraw ultra12 chem 3D as shown in figures 3.4h,3.4i,3.4j,3.4k

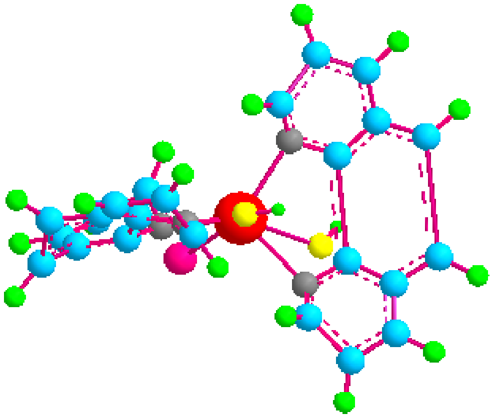


Fig 3.4h 3D structure of La-phen

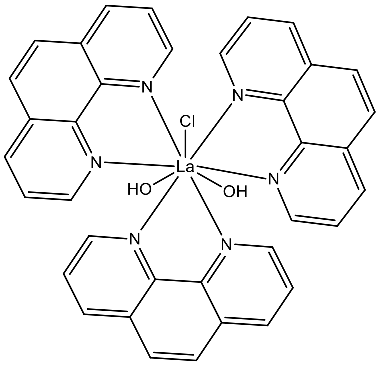


Fig 3.4i 2D structure of La-phen

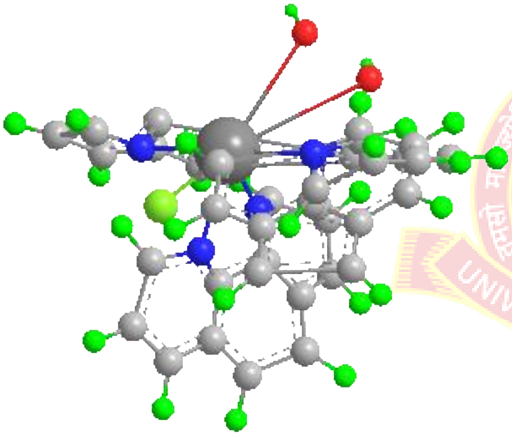


Fig 3.4j 3D structure of Eu-phen

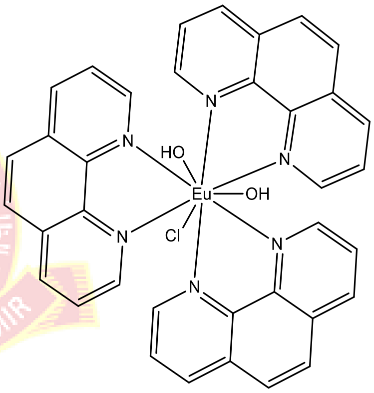


Fig 3.4k 2D structure of Eu-phen

3.5 FOURIER TRANSFORM INFRARED Spectroscopic studies

Fourier-transform infrared (FT-IR) spectroscopy was employed to investigate the coordination environment and vibrational properties of the synthesized lanthanide complexes, La-phen and Eu-phen. The FT-IR spectra provide valuable information about the functional groups present, their modes of coordination, and the potential presence of solvent molecules or counterions.

Lu-phen

The FT-IR spectrum of the Lu-phen complex is presented in Figure 3. The spectrum exhibits several characteristic bands that can be assigned to the vibrational modes of the phenanthroline (Phen) ligands and the coordinated hydroxide (OH) and chloride (Cl) groups. The Peaks were observed between 1600 to 2100 cm^{-1}. The intense bands observed at 1631 and 1519 cm^{-1} can be attributed to the stretching vibrations of the aromatic C=C and C=N bonds, respectively, of the Phen ligands. These bands are slightly shifted compared to the free Phen ligand, indicating the coordination of the ligands to the lanthanum center.

The bands at 850 and 726 cm-1 are characteristic of the out-of-plane C-H bending vibrations of the Phen ligands, further confirming their presence in the complex.

The broad band centered around 3420 cm^{-1} can be assigned to the O-H stretching vibration of the coordinated hydroxide groups and potential hydration water molecules. The presence of a relatively sharp band at 1385 cm-1 is consistent with the presence of the coordinated chloride counterion.

Eu-phen

The FT-IR spectrum of the Eu-phen complex, shown in Figure 4, exhibits similar vibrational bands to those observed for the lanthanum analog, indicating the presence of the same functional groups and coordination modes.

The bands at 1633 and 1521 cm-1 correspond to the aromatic C=C and C=N stretching vibrations of the coordinated Phen ligands, respectively. The out-of-plane C-H bending vibrations of the Phen ligands are evident from the bands at 852 and 728 cm^{-1}.[51]

The broad band centered around 3418 cm-1 is attributed to the O-H stretching vibration of the coordinated hydroxide groups and potential hydration water molecules, while the band at 1387 cm^{-1} confirms the presence of the coordinated chloride counterion. [52,53]

It is noteworthy that the positions of the vibrational bands in the europium complex are slightly shifted compared to those in the lanthanum analog, which can be attributed to the difference in ionic radii and coordination preferences of the lanthanide centers.

The FT-IR spectroscopic analysis provided valuable insights into the coordination environment and bonding interactions within the synthesized lanthanide complexes. The observed vibrational bands and their assignments support the proposed structures and coordination modes, with the Phen ligands coordinated to the lanthanide centers through the nitrogen atoms, and the presence of coordinated hydroxide groups and chloride counterions.

The presence of potential hydration water molecules is also evident from the broad OH stretching band, suggesting the formation of hydrated complexes. These findings are consistent with the expected coordination chemistry of lanthanide ions and the proposed molecular structures of the complexes.

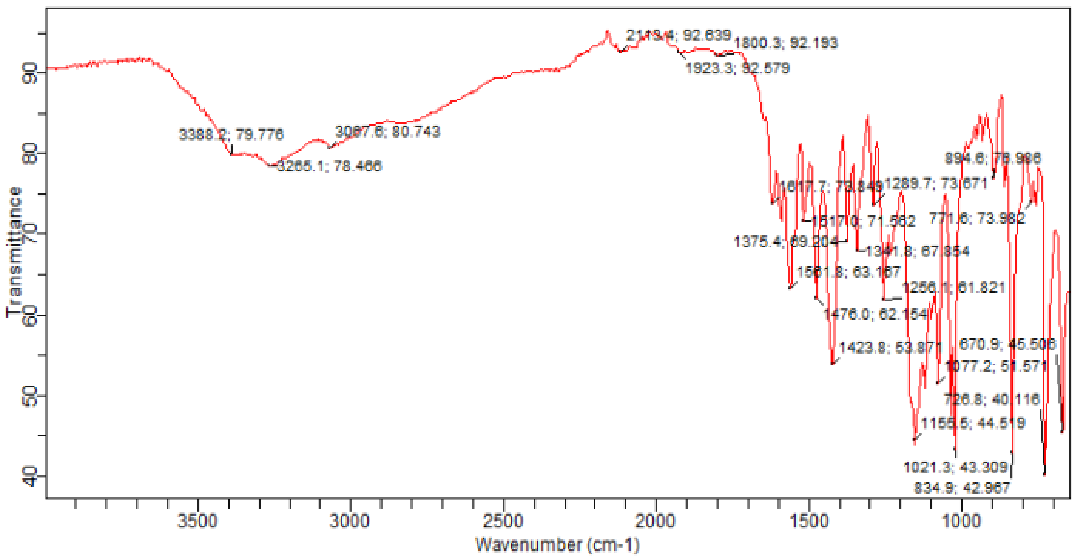


Figure 3.5.1 Ft-ir graph of lanthanum phenanthroline complex

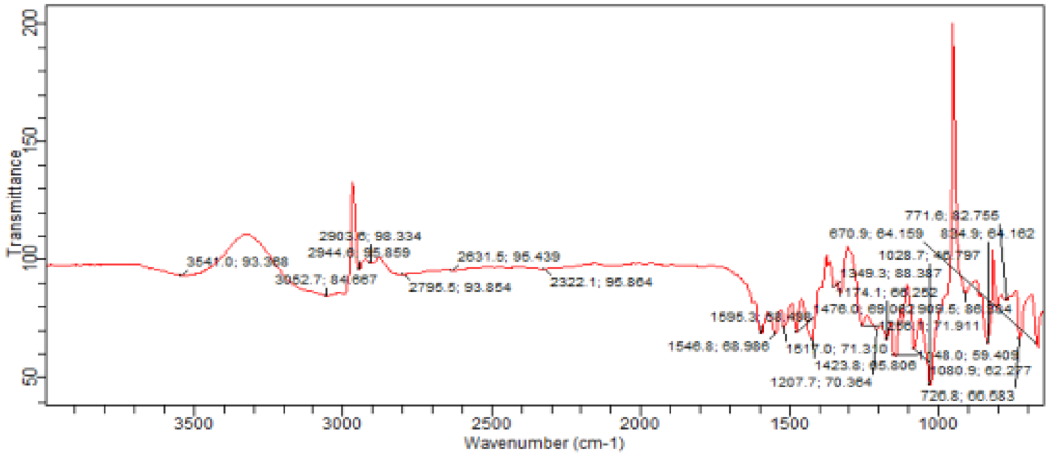


Figure 3.5.2 Ft-ir graph of Europium phenanthroline complex

CONCLUSION AND FUTURE PERSPECTIVE

This dissertation provided a comprehensive investigation into the intriguing photophysical properties and luminescent behavior of europium and lanthanum complexes coordinated with 1,10-phenanthroline ligands. Through a multi-faceted approach combining advanced spectroscopic techniques, microscopy analysis, and computational modeling, valuable insights have been gained into the electronic structures, coordination environments, and emission mechanisms of these lanthanide-based luminescent materials.

The UV-visible absorption studies unveiled the characteristic intraligand $\pi \rightarrow \pi^*$ transitions of the phenanthroline chromophores, along with distinct ligand-to-metal charge transfer bands in the lanthanum complex. These observations confirmed the successful coordination of the organic ligands to the lanthanide centers and highlighted the differences in electronic transitions arising from the unique electronic configurations of europium and lanthanum ions.

Fourier-transform infrared (FT-IR) spectroscopy provided valuable information about the coordination modes and the presence of additional functional groups within the complexes. The observed vibrational bands and their shifts relative to the free ligand confirmed the coordination of the phenanthroline nitrogens to the lanthanide centers. Moreover, the presence of hydroxide groups and chloride counterions was evidenced, suggesting the formation of hydrated complexes.

Scanning electron microscopy (SEM) imaging revealed the intricate morphological and microstructural features of the synthesized complexes. The lanthanum complex exhibited an agglomerated morphology composed of irregularly shaped particles and densely packed, intertwined rod-like structures. In contrast, the europium complex displayed a distinct morphology characterized by irregular, plate-like structures randomly oriented and stacked to form larger agglomerates. These observations highlighted the influence of the specific lanthanide center on the crystallization and growth processes during synthesis.

Notably, the photoluminescence studies demonstrated the unique luminescent properties of the complexes, stemming from their distinct electronic configurations and coordination environments. The europium complex exhibited characteristic sharp emission bands in the visible region, attributed to the characteristic f-f transitions of the Eu^{3+} ion, particularly the intense $5D_0 \rightarrow 7F2$ transition at 616 nm. The observed intensity pattern and the presence of additional peaklets provided evidence for the modified local symmetry and ligand field around the Eu^{3+} center upon complexation with phenanthroline.

On the other hand, the lanthanum complex displayed distinct emission bands in the near-infrared region, with the most prominent band observed around 362 nm, likely originating from ligand-to-metal charge transfer or other metal-centered transitions influenced by the coordination of the phenanthroline ligands. The appearance of additional bands and a peaklet at 535 nm further confirmed the alteration of electronic transitions and local symmetry upon complexation with the lanthanum ion.

The findings of this research have significant implications for the rational design and development of highly efficient lanthanide-based luminescent materials. By establishing quantitative structure-property relationships and correlating the molecular features with the observed luminescent outputs, this work has laid a solid foundation for predicting and optimizing the luminescent performance of lanthanum and europium complexes.

The insights gained from this study open exciting opportunities for harnessing the unique luminescent properties of lanthanide complexes in diverse applications. The exploration of lanthanum-based emitters, which have been relatively unexplored compared to their europium counterparts, represents a promising frontier with the potential to complement and potentially surpass the well-established europium-based luminescent materials.

Furthermore, the integrated experimental and computational approach employed in this research has demonstrated its effectiveness in uncovering the fundamental photophysics governing lanthanide luminescence. This methodology can be extended to investigate other lanthanide complexes and explore novel ligand systems, paving the way for the design and development of tailored luminescent materials with optimized performance and desired emission profiles.

Looking ahead, several avenues for future research can be envisioned. Time-resolved spectroscopic techniques can be employed to gain a deeper understanding of the excited-state dynamics and energy transfer processes governing the luminescence properties of these complexes. Computational modeling can be further refined to provide predictive insights into the electronic transitions and emission mechanisms, facilitating the rational design of brighter and more efficient lanthanide-based emitters.

Additionally, the exploration of alternative synthetic strategies, such as solvothermal or mechanochemical approaches, may lead to the discovery of new luminescent complexes with enhanced structural features and improved luminescent properties. The incorporation of these complexes into functional materials or devices for specific applications, such as sensing, imaging, or photonics, would further demonstrate the practical utility of this research.

In conclusion, this thesis has made significant contributions to the fundamental understanding of lanthanide-based luminescent complexes, with a particular emphasis on the relatively unexplored lanthanum systems. The findings and methodologies presented herein provide a solid foundation for future research endeavors, ultimately enabling the realization of advanced luminescent materials for a wide range of cutting-edge applications in various fields, including sensing, imaging, and photonics. By harnessing the unique properties of lanthanide complexes and leveraging the insights gained from this work, the development of innovative luminescent technologies can be accelerated, paving the way for exciting breakthroughs in diverse areas of science and technology.

The future vision is to exploit this fundamental concept to create sensitive fluorescent probes and sensors. There is also the potential to incorporate highly emissive Eu or La complexes into photonic devices. The future vision is to exploit this fundamental concept to create sensitive fluorescent probes and sensors. There is also the potential to incorporate highly emissive Eu or La complexes into photonic devices. Fine-tuning the ligand structure to modulate the metal emission sensitivity is the key to synthesize lanthanide complexes that take full advantage of this unique luminescent reporter in various fields, from biomedicine to photonic technology. In future I aim to synthesize lanthanide complexes as labels and probes for biomedical applications in areas like biosensing, imaging, and assays. The unique photophysical properties of lanthanide complexes continue to drive advancement in fields ranging from lighting and displays to drug discovery and diagnostics. The unique ligand selection can enhance future of lanthanide chemistry due to their unique luminescent properties for versatile sensing and imaging applications across diverse fields. Looking to the future, I aim to continue research for the fine-tuning of lanthanide excitation emission properties through junction design which will allow these ions to be more widely used in versatile luminescent materials and devices. Taking full advantage of the unique lanthanide photophysics will open new opportunities in fields ranging from diagnostics to optoelectronics, where the unique optical properties of these metal ions can be explored. The continued research for controlling the coordination environment of lanthanides will enable us to integrate these ions into sensors, probes, and imaging devices. More systematic investigations are needed to elucidate the luminescence mechanisms and structure-property relationships in lanthanum complexes. The continued research in this area has facilitated the translation of lanthanide complex luminescence from academic curiosity to market-ready technology. The continued investigations on the structure-property relationships are still needed to establish the photoluminescence pathways and optimize the luminescence efficiencies.

Overall, the distinct UV-vis profiles demonstrate the significant effect of the lanthanide metal center in modulating the electronic transitions. The absorptions provide insights into ligand-metal interactions, which will guide optimization of the ligand structure to sensitize lanthanide emission. The insights gleaned from this work transcend mere academic curiosity, propelling us towards a future where these luminescent marvels become indispensable tools for transformative technologies in sensing, imaging, and photonics. As I stand on the precipice of a new era in luminescent materials, this research serves as a catalyst, igniting the spark of endless possibilities. With each revelation, I am inch closer to a world where the boundaries of what is achievable are redefined, where the once unimaginable becomes a reality. The journey ahead is paved with challenges, but armed with the knowledge garnered from this work, we are empowered to confront them head-on, fueled by the unwavering pursuit of scientific excellence. This work is not merely a culmination of efforts; it is a clarion call, beckoning us to embrace the limitless potential of lanthanide luminescence and to forge ahead, undeterred, in our quest to illuminate the path towards a brighter, more luminous future.

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