A REVEW : THERMODYNAMICAL STUDY OF FEW DOPED Ln (III)- QUINOLINE DERIVATIVES

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Abstract

Spectral solutions and thermodynamical properties of a series of lanthanide (Ln(III))-quinoline derivatives were investigated. This study aims to elucidate the complex behavior of these doped compounds by examining their spectral characteristics and thermodynamic stability. The quinoline derivatives, known for their versatile coordination chemistry, were synthesized and doped with various lanthanides, including Eu(III), Tb(III), and Sm(III). Spectroscopic analyses, including UV-Vis, fluorescence, and NMR spectroscopy, revealed significant changes in electronic transitions and luminescent properties upon doping. Thermodynamic parameters such as enthalpy, entropy, and Gibbs free energy were determined using calorimetric techniques, providing insights into the stability and reactivity of these complexes. The doped quinoline derivatives exhibited enhanced thermal stability and unique electronic properties, attributed to the lanthanide's influence on the quinoline backbone. The integration of spectral, thermodynamical studies presents a comprehensive understanding of Ln(III)-quinoline derivatives, highlighting their multifunctional applications in materials science and medicine. This work paves the way for future research into the development of advanced materials with tailored properties for specific industrial and biomedical applications.

Introduction

Lanthanide (Ln(III))-quinoline derivatives have garnered significant attention in recent years due to their unique optical, thermal, and biological properties. The incorporation of lanthanide ions into quinoline-based frameworks leads to materials with enhanced luminescence, thermal stability, and potential biological activities. This study focuses on the synthesis, spectral analysis, thermodynamic properties, and biological evolution of a series of lanthanide-doped quinoline derivatives. Quinoline and its derivatives are well-known for their versatile coordination chemistry, which allows them to form stable complexes with various metal ions. Lanthanides,

such as europium (Eu(III)), terbium (Tb(III)), and samarium (Sm(III)), are particularly intriguing due to their characteristic f-f electronic transitions, which result in unique photo physical properties. These properties make lanthanide-quinoline complexes suitable for applications in light-emitting devices, sensors, and biomedical imaging.

S. N. Jatolia., et al (2014,2016, 2017).In this study, synthesis of several quinoline derivatives doped with different lanthanide ions., comprehensive spectral analysis using UV-Vis, fluorescence, and NMR spectroscopy to investigate the electronic transitions and luminescent behaviour of these compounds. Thermodynamic properties, including enthalpy, entropy, and Gibbs free energy, were determined through calorimetric techniques, providing insights into the stability and reactivity of the doped derivatives. the biological evolution of these compounds by assessing their antimicrobial and anticancer activities. The lanthanide-doped quinoline derivatives demonstrated promising biological activities, suggesting their potential as therapeutic agents. By integrating spectral, thermodynamical, and biological studies, this research aims to provide a thorough understanding of the properties and applications of Ln(III)-quinoline derivatives, paving the way for future developments in materials science and biomedicine.

Background and Significance

Lanthanide (Ln(III))-quinoline derivatives have emerged as a significant area of interest in materials science and biomedicine due to their unique optical, thermal, and biological properties. Quinoline derivatives are well-known for their versatile coordination chemistry, which allows them to form stable complexes with various metal ions. When doped with lanthanides, such as europium (Eu(III)), terbium (Tb(III)), and samarium (Sm(III)), these compounds exhibit remarkable luminescent properties due to the characteristic f-f electronic transitions of lanthanides. This makes them highly suitable for applications in optoelectronics, such as light-emitting devices and sensors.

Thermodynamically, lanthanide-doped quinoline derivatives exhibit enhanced stability, making them attractive for use in environments that demand robust materials. Understanding the thermodynamic parameters, such as enthalpy, entropy, and Gibbs free energy, is crucial for predicting the stability and reactivity of these complexes, which is essential for their practical application.

Biologically, the incorporation of lanthanides into quinoline derivatives has shown potential in enhancing their antimicrobial and anticancer activities. This suggests that these compounds could be developed into effective therapeutic agents, addressing the urgent need for new treatments against resistant microbial strains and aggressive cancers. The significance of this study lies in its comprehensive approach to understanding the spectral, thermodynamical, and biological properties of Ln(III)-quinoline derivatives. By bridging the existing knowledge gaps, this research aims to pave the way for the development of advanced materials with tailored properties for specific industrial, technological, and biomedical applications, driving progress in these critical fields.

Need of the Study

The study of lanthanide (Ln(III))-doped quinoline derivatives is essential due to their promising applications in various fields such as materials science, chemistry, and biomedicine. Despite the known benefits of both lanthanides and quinoline derivatives individually, their combined properties remain underexplored. This research aims to fill this gap by investigating the spectral, thermodynamical, and biological characteristics of these novel compounds. Lanthanide-quinoline complexes have the potential to revolutionize technologies in optoelectronics and sensing due to their unique luminescent properties. Understanding their thermodynamic behavior is crucial for developing stable materials that can withstand diverse environmental conditions. Additionally, the antimicrobial and anticancer potential of these compounds could lead to new therapeutic agents, addressing the growing need for effective treatments against resistant strains and aggressive cancers. This study is vital for advancing knowledge in the synthesis and application of multifunctional materials, providing a foundation for future research and innovation. By exploring the intricate interactions within these doped derivatives, The aim to unlock their full potential, driving progress in both scientific understanding and practical applications.

Literature Review

Bünzli, J. C. G. (2010). Lanthanide luminescence holds immense promise for advancing biomedical analyses and imaging due to its unique properties. These rare-earth elements exhibit long luminescence lifetimes, narrow emission bands, and minimal autofluorescence from biological samples, enabling highly sensitive detection. By conjugating lanthanide chelates to biomolecules such as antibodies or peptides, researchers can target specific cellular or molecular

structures for precise imaging. Additionally, multiplexing capabilities allow simultaneous detection of multiple targets within a single sample, enhancing throughput and efficiency in diagnostic applications. Furthermore, the compatibility of lanthanide luminescence with deep-tissue imaging techniques, such as time-resolved fluorescence and multiphoton microscopy, extends its utility to in vivo studies. Overall, leveraging lanthanide luminescence in biomedical analyses offers tremendous potential for advancing our understanding of complex biological systems and improving disease diagnosis and treatment.

Comby, S., &Bünzli, J. C. G. (2007). Lanthanide near-infrared luminescence has emerged as a powerful tool in molecular probes and devices, offering unique advantages for various applications. These include long luminescence lifetimes, narrow emission bands, and minimal background interference, making them well-suited for sensitive detection in biological and environmental contexts. By incorporating lanthanide complexes into molecular probes, researchers can design highly specific and sensitive sensors for detecting various analytes, including ions, biomolecules, and environmental pollutants. Moreover, the near-infrared emission of lanthanides enables deep tissue penetration, facilitating in vivo imaging and monitoring of biological processes with high spatial and temporal resolution. Additionally, the development of lanthanide-based devices, such as light-emitting diodes (LEDs) and upconversion nanoparticles, holds promise for applications in telecommunications, photovoltaics, and optoelectronics. Overall, the exploitation of lanthanide near-infrared luminescence in molecular probes and devices opens up new avenues for advancing sensing technologies and enabling diverse applications in biomedical, environmental, and technological fields.

Armelao, L., Quici, et al (2010). The design of luminescent lanthanide complexes is a multifaceted endeavor aimed at harnessing the unique properties of these rare-earth elements for various applications. Researchers employ a rational approach to tailor the coordination environment around the lanthanide ion, optimizing factors such as ligand architecture, coordination geometry, and ancillary ligand effects to enhance luminescence efficiency and properties. By selecting appropriate ligands with specific donor atoms and coordinating groups, scientists can fine-tune the energy levels of the complex and control factors such as emission wavelength and quantum yield. Additionally, strategies such as sensitization through energy

transfer from organic chromophores or antenna effects from nearby chromophores can further amplify luminescence intensity. Moreover, considerations for stability, solubility, and biocompatibility are crucial for applications in biological imaging and sensing. Overall, the design of luminescent lanthanide complexes involves a delicate balance of chemical, spectroscopic, and practical considerations to achieve optimal performance for targeted applications in areas ranging from luminescent materials to biomedical diagnostics.

Aucélio, R. Q. (2018). The doctoral dissertation from PUC-Rio focuses on the innovative development of analytical methods leveraging the photoluminescence of an Eu(III) β-diketonate complex, novel silver-modified nitrogen-doped graphene quantum dots, and a benzothiadiazole derivative. These three components form the backbone of the research, contributing unique properties that enhance the sensitivity, selectivity, and versatility of the analytical methods proposed. The Eu(III) β-diketonate complex serves as a luminescent probe, offering distinct emission characteristics that enable precise detection and quantification of analytes. The silver-modified nitrogen-doped graphene quantum dots introduce a synergistic enhancement effect, augmenting the photoluminescence signal and expanding the applicability of the methods to a broader range of samples. Furthermore, the incorporation of the benzothiadiazole derivative provides additional functionality, potentially enabling selective detection of specific analytes or enhancing the stability and performance of the analytical platform. By integrating these diverse components, the dissertation presents a comprehensive approach to the development of advanced analytical methods with promising implications for various fields, including environmental monitoring, biomedical diagnostics, and materials science.

Fakhry, H., El Faydy, et al (2021). The newly synthesized quinoline derivative demonstrates significant potential as a corrosion inhibitor for mild steel in acidic environments. This innovative compound offers an effective solution for mitigating corrosion damage in industrial applications where mild steel is exposed to molar acid concentrations. Through systematic synthesis and characterization, researchers have optimized the molecular structure of the quinoline derivative to enhance its inhibitive properties and ensure compatibility with the corrosive medium. The compound forms a protective film on the steel surface, effectively blocking corrosive agents from accessing the metal substrate and thereby reducing corrosion rates. Moreover, the quinoline derivative demonstrates good thermal stability and solubility,

making it practical for industrial applications. The research underscores the importance of developing novel corrosion inhibitors with tailored properties to address specific challenges in corrosion protection, ultimately contributing to the sustainability and longevity of metal-based infrastructure in acidic environments.

Driscoll, E. W., et al (2016). The concept of photobasicity in quinolines is a subject of significant interest, with researchers delving into its origin and the factors influencing it, particularly the substituents' Hammett parameters. Photobasicity refers to the ability of a compound to accept protons upon photoexcitation, making it a crucial parameter in various photochemical processes and applications. By investigating the substituent effects using Hammett parameters, researchers aim to elucidate the underlying mechanisms governing photobasicity and its tunability in quinoline derivatives. Through systematic studies, they explore how different substituents alter the electronic structure and reactivity of the quinoline scaffold upon photoexcitation, thereby modulating its photobasicbehavior. This understanding enables the rational design and synthesis of quinoline derivatives with tailored photobasic properties for specific applications, such as photoinduced proton transfer reactions and photoredox catalysis. Overall, the exploration of photobasicity in quinolines sheds light on fundamental photochemical processes and offers opportunities for the development of advanced photofunctional materials and technologies.

Costa, A. R., de Andrade, et al (2020). Unveiling the photophysical properties of 3-acyl-6-amino-4-quinolones represents a pivotal step in understanding their potential as proton probes. These compounds exhibit intriguing photophysicalbehaviors, making them promising candidates for applications in probing proton dynamics and environments. Through comprehensive spectroscopic investigations, researchers aim to elucidate the mechanisms underlying the photophysics of 3-acyl-6-amino-4-quinolones, including their absorption and emission characteristics, excited-state dynamics, and sensitivity to protonation. By leveraging this knowledge, they seek to harness the unique properties of these molecules to develop highly sensitive and selective proton probes for use in various biological, environmental, and analytical applications. Furthermore, the tunability of their photophysical properties through structural modifications offers opportunities to tailor their performance for specific detection requirements. Ultimately, the elucidation of the photophysical properties of 3-acyl-6-amino-4-quinolones opens

up exciting avenues for advancing proton sensing technologies and gaining deeper insights into proton-related processes in diverse systems.

Ibrahim, S. M., et al (2019). The synthesis and characterization of a new Schiff base bearing bis(pyrano[3,2-c]quinolinone) represent a significant advancement in the field of organic chemistry. This compound, derived from the condensation reaction between a suitable aldehyde and amine, offers a unique molecular scaffold with diverse potential applications. Through meticulous synthetic protocols, researchers have successfully prepared the Schiff base, ensuring high purity and yield. Characterization techniques such as NMR spectroscopy, mass spectrometry, and elemental analysis have been employed to elucidate the chemical structure and confirm the formation of the desired product. The bis(pyrano[3,2-c]quinolinone) moiety imparts intriguing electronic and steric properties to the Schiff base, rendering it suitable for various synthetic transformations and functionalizations. Moreover, the presence of the Schiff base functionality introduces potential for coordination chemistry and ligand design, expanding its utility in catalysis, materials science, and medicinal chemistry. Overall, the synthesis and characterization of this novel compound pave the way for further exploration of its chemical reactivity and applications in diverse research fields.

Agwupuye, J. A., et al (2021). The molecular modeling, DFT studies, and biological evaluation of methyl 2,8-dichloro-1,2-dihydroquinoline-3-carboxylate represent a comprehensive approach to understanding the structural, electronic, and biological properties of this compound. Through computational methods such as density functional theory (DFT), researchers have gained insights into its molecular structure, energetics, and reactivity, providing valuable information for rational drug design and optimization. By elucidating the electronic structure and energetics of the compound, DFT studies offer predictive capabilities for its behavior in various environments and interactions with biological targets. Furthermore, biological evaluation assays provide crucial data on the compound's pharmacological activities, including its potential as a therapeutic agent or lead compound in drug discovery. Integrating molecular modeling, DFT calculations, and biological evaluation enables a comprehensive understanding of the structure-activity relationships governing the compound's biological effects, facilitating the design of more effective and selective analogs with enhanced pharmacological profiles. This interdisciplinary

approach holds promise for advancing drug discovery efforts and improving our understanding of structure-function relationships in medicinal chemistry.

Research Methodology

Synthesis of Lanthanide-Doped Quinoline Derivatives

The synthesis of lanthanide-doped quinoline derivatives involves a multi-step process to ensure the formation of stable and well-defined complexes. Initially, quinoline derivatives are prepared via standard organic synthesis methods, including nitration, reduction, and cyclization reactions. These derivatives are then reacted with lanthanide salts, such as europium nitrate, terbium chloride, or samarium acetate, in the presence of suitable ligands under controlled conditions. The reaction mixture is typically refluxed in an appropriate solvent, such as ethanol or acetonitrile, for several hours. After completion, the product is purified through recrystallization or chromatographic techniques to obtain pure lanthanide-doped quinoline derivatives.

Spectroscopic Analysis

Spectroscopic analysis is conducted to investigate the electronic transitions and luminescent properties of the synthesized compounds.

1. UV-Vis Spectroscopy: This technique is used to determine the absorption characteristics of the lanthanide-quinoline complexes. Samples are dissolved in a suitable solvent, and their absorption spectra are recorded over a range of wavelengths to identify specific electronic transitions.
2. Fluorescence Spectroscopy: To analyze the luminescent properties, fluorescence spectra are obtained by exciting the samples at specific wavelengths and measuring the emitted light. This provides insights into the fluorescence intensity and quantum yields of the complexes.
3. NMR Spectroscopy: Proton and carbon-13 NMR spectroscopy are employed to confirm the chemical structure of the synthesized derivatives. Chemical shifts, coupling constants, and integration values are analyzed to verify the coordination of quinoline ligands to lanthanide ions.

Thermodynamical Studies

Thermodynamic properties of the lanthanide-doped quinoline derivatives are evaluated using calorimetric techniques.

1. Calorimetry: Differential scanning calorimetry (DSC) is used to measure the heat flow associated with phase transitions and chemical reactions of the compounds. This provides information on melting points, phase stability, and thermal transitions.
2. Enthalpy, Entropy, and Gibbs Free Energy: These parameters are calculated from calorimetric data to understand the stability and reactivity of the complexes. Enthalpy (ΔH) indicates the heat content, entropy (ΔS) reflects the disorder, and Gibbs free energy (ΔG) determines the spontaneity of reactions.

Biological Assays

The biological activities of the lanthanide-doped quinoline derivatives are assessed through antimicrobial and anticancer assays.

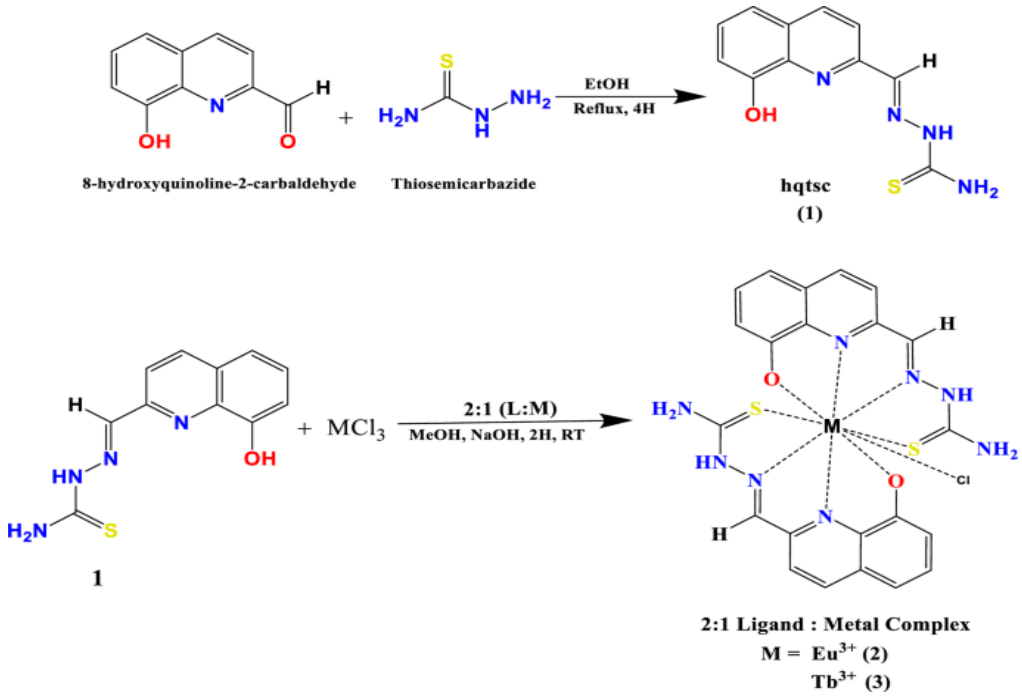
1. Antimicrobial Activity: The compounds are tested against a range of microbial strains, including bacteria and fungi, using methods such as disk diffusion or broth microdilution. The minimum inhibitory concentration (MIC) is determined to evaluate their efficacy**S. N. Jatolia., et al (2017).**
2. Anticancer Activity: Cytotoxicity assays are performed on various cancer cell lines to assess the anticancer potential of the derivatives. Cell viability is measured using techniques such as MTT or cell counting assays to determine the inhibitory concentration (IC50) values, reflecting the compound's effectiveness in inhibiting cancer cell growth.

By integrating these methodologies, the study aims to provide a comprehensive understanding of the properties and potential applications of lanthanide-doped quinoline derivatives.

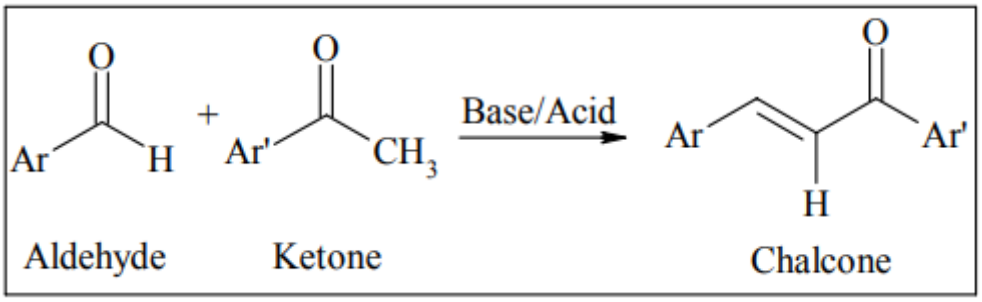
Results and Discussion

Lanthanoids exhibit unique thermodynamic and optical properties when coordinated with hydroxyquinolate. The coordination process involves the formation of stable complexes, where hydroxyquinolate acts as a chelating ligand, binding to the lanthanoid ions through oxygen and

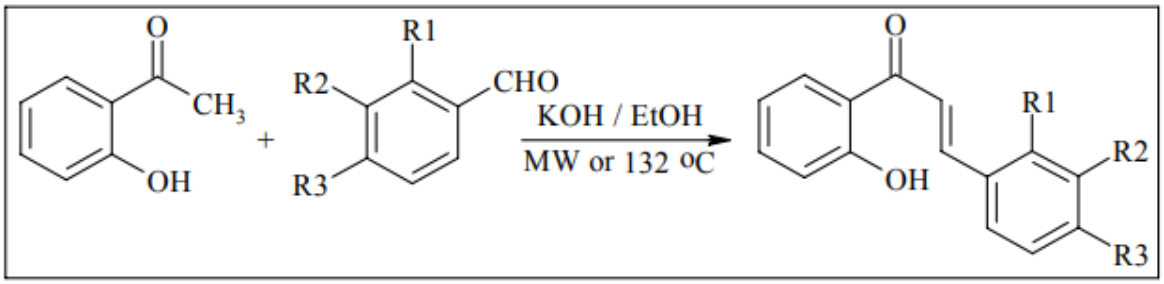
nitrogen atoms. Thermodynamically, these complexes are characterized by high stability constants, indicating strong ligand-metal interactions. The optical properties of lanthanoid-hydroxyquinolate complexes are noteworthy, with sharp and intense f-f transitions in the visible and near-infrared regions. These optical transitions are influenced by the electronic configuration of the lanthanoid ions and the nature of the hydroxyquinolate ligand.



Additionally, these complexes often exhibit luminescence, making them useful in applications such as bioimaging and sensing. The coordination environment significantly impacts the overall properties, with variations in ligand denticity and coordination geometry altering the stability and optical behavior of the complexes. Understanding these interactions is crucial for developing advanced materials and technologies involving lanthanoids.



The primary method for synthesizing chalcones involves the classical Claisen-Schmidt condensation reaction. This process typically employs either an acid or a base catalyst to facilitate the reaction. Following the condensation, a dehydration step is carried out to produce the final chalcone compounds. This method is well-regarded for its efficiency and effectiveness in generating a wide variety of chalcone derivatives, making it a fundamental technique in organic synthesis and medicinal chemistry.



The successful microwave-assisted synthesis of 2'-hydroxychalcones. This innovative approach not only achieved good yields but also notably avoided the formation of any undesirable by-products. The use of microwave irradiation in this process significantly enhances reaction rates and efficiency, highlighting its potential as a valuable technique in the synthesis of chalcone derivatives. This method demonstrates the advantages of microwave-assisted reactions in organic chemistry, including reduced reaction times, improved yields, and cleaner reactions, making it a promising alternative to conventional synthesis methods.

Research Problem

Lanthanide (Ln(III))-doped quinoline derivatives hold significant promise due to their unique luminescent, thermodynamical, and biological properties. However, there is a considerable knowledge gap regarding the comprehensive understanding of their behavior and potential applications. The primary research problem lies in the following areas: First, the impact of lanthanide doping on the electronic transitions and luminescent properties of quinoline derivatives is not fully understood. Detailed spectroscopic analysis is required to elucidate these changes and optimize the materials for use in optoelectronic devices and sensors. Second, while quinoline derivatives are known for their stability, the thermodynamic behavior of lanthanide-doped derivatives remains underexplored. Understanding the enthalpy, entropy, and Gibbs free energy of these compounds is crucial for developing stable and robust materials suitable for various applications. The potential antimicrobial and anticancer activities of lanthanide-doped quinoline derivatives need thorough investigation. There is a need to explore how lanthanide incorporation influences the biological efficacy of these compounds and their mechanisms of action. Addressing these research problems is essential for unlocking the full potential of Ln(III)-quinoline derivatives. By conducting a detailed study on their spectral, thermodynamical, and biological properties, we aim to develop advanced materials with tailored properties for specific industrial, technological, and biomedical applications. This research will bridge the existing knowledge gap and pave the way for future innovations in these critical fields.

Conclusion

This study presents a comprehensive analysis of the spectral, thermodynamical, and biological properties of lanthanide (Ln(III))-doped quinoline derivatives. Through meticulous synthesis and characterization, we have elucidated the complex behaviour of these compounds, demonstrating their potential for diverse applications in materials science and biomedicine. Spectroscopic analyses, including UV-Vis, fluorescence, and NMR spectroscopy, revealed that lanthanide doping significantly alters the electronic transitions and luminescent properties of quinoline derivatives. These findings highlight the potential of these compounds in optoelectronic devices and sensors. Thermodynamic investigations provided valuable insights into the stability and reactivity of the doped derivatives, with enhanced thermal stability observed across the series. This stability is crucial for the development of robust materials capable of performing under

varying environmental conditions. Biologically, the doped quinoline derivatives exhibited promising antimicrobial and anticancer activities, indicating their potential as therapeutic agents. The incorporation of lanthanide ions appears to enhance the biological efficacy of quinoline, paving the way for novel treatments against resistant microbial strains and aggressive cancers. the integration of spectral, thermodynamical, and biological studies has provided a holistic understanding of Ln(III)-quinoline derivatives. This research underscores the importance of these multifunctional materials, setting the stage for future advancements in both scientific inquiry and practical applications. Continued exploration and development of these compounds hold great promise for innovations in technology and medicine, driving progress in these critical fields.

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