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The Antenna Effect in Europium(III) Complexes: Photophysical Principles, Ligand Design, and Device Applications

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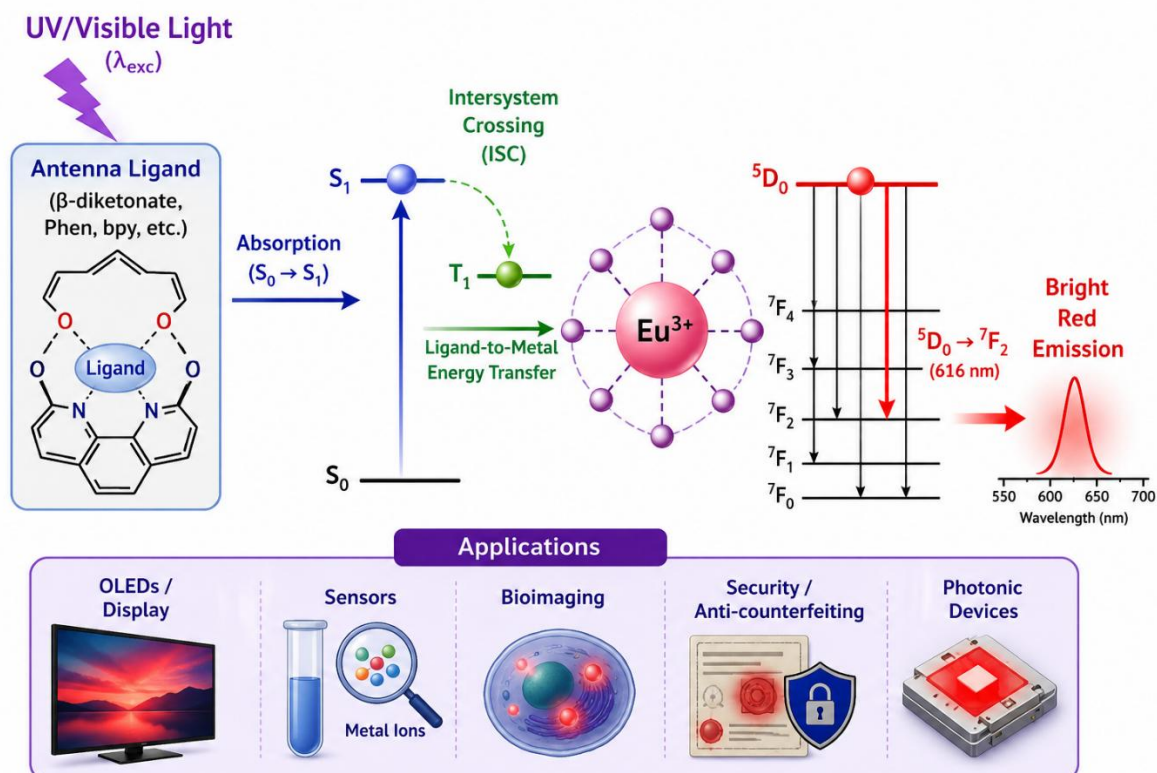
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Graphical abstract:



Abstract

Europium(III) complexes have attracted significant attention owing to their exceptional luminescent properties, including narrow emission bands, long excited-state lifetimes, high color purity, and excellent photostability. However, the intrinsically weak absorption of Eu³⁺ ions, arising from parity-forbidden 4f–4f transitions, limits their direct excitation and practical application. This limitation is effectively overcome by the antenna effect, in which organic ligands act as efficient light-harvesting

chromophores that absorb incident radiation and transfer the excitation energy non-radiatively to the Eu^{3+} ion, thereby markedly enhancing its characteristic red emission. The efficiency of this sensitization process is strongly influenced by ligand structure, triplet-state energy, molecular rigidity, coordination environment, and the suppression of non-radiative decay pathways.

This mini-review highlights the fundamental photophysical principles governing the antenna effect in $\text{Eu}(\text{III})$ complexes, with particular emphasis on ligand-to-metal energy transfer mechanisms and the key factors controlling luminescence efficiency. Recent advances in ligand engineering, including the development of π -conjugated, rigid, and multifunctional antenna ligands, are discussed in relation to improved quantum yields, enhanced thermal and photochemical stability, and superior photophysical performance. Emerging trends involving host–guest architectures, hybrid materials, coordination polymers, and metal–organic frameworks are also briefly examined as promising strategies for next-generation luminescent systems.

Finally, the review outlines the growing technological importance of $\text{Eu}(\text{III})$ complexes in organic light-emitting diodes (OLEDs), chemical and biological sensing, bioimaging, security printing, and other photonic applications. By correlating ligand design with photophysical behaviour and device performance, this review provides a concise overview of current progress and future perspectives for the rational development of highly efficient europium-based luminescent materials.

Keywords

Europium (III) complexes, Antenna effect, Lanthanide luminescence, Ligand-to-metal energy transfer, Photophysical properties, Organic light-emitting diodes (OLEDs)

1. Introduction

Lanthanide complexes have attracted considerable attention owing to their unique optical and photophysical properties, which arise from the well-shielded 4f electronic orbitals.^{1–3} Among them, europium(III) complexes are particularly distinguished by their intense red emission, long excited-state lifetimes, narrow emission bands, and high color purity.^{2–4} These characteristics have led to their widespread investigation for applications in organic light-emitting diodes (OLEDs), luminescent sensors, bioimaging, security inks, and optical display technologies.^{5–7}

Despite their excellent emission characteristics, $\text{Eu}(\text{III})$ ions exhibit intrinsically weak light absorption because the 4f–4f electronic transitions are parity forbidden.^{1,3} Consequently, direct excitation of Eu^{3+} results in poor luminescence efficiency. This limitation is effectively overcome through the antenna effect, in which an organic ligand with a high absorption coefficient serves as a light-harvesting chromophore.^{6,8} Upon ultraviolet or visible light excitation, the ligand absorbs energy and subsequently transfers it non-radiatively to the excited states of the Eu^{3+} ion, leading to its characteristic red emission.^{3,8}

The efficiency of the antenna effect depends strongly on the nature of the coordinating ligand. Factors such as the ligand's absorption properties, triplet-state energy, molecular rigidity, coordination geometry, and suppression of non-radiative relaxation pathways collectively govern energy-transfer efficiency.^{9–11} Accordingly, rational ligand design has become a central strategy for developing highly luminescent $\text{Eu}(\text{III})$ complexes.^{2,11}

In recent years, considerable progress has been achieved in antenna ligand design to enhance energy-transfer efficiency and stability of europium complexes.^{5,12} These advances have enabled integration into OLEDs, where color purity and stability are critical.^{5,13} Beyond display technologies, $\text{Eu}(\text{III})$ complexes are also used in sensing, imaging, and anti-counterfeiting applications.^{7,14}

This review focuses on the photophysical principles underlying the antenna effect in Eu(III) complexes, emphasizing ligand structure–property relationships and their role in energy-transfer efficiency.^{1,6} Particular attention is given to ligand engineering strategies and device applications.^{5,13}

2. Photophysical Mechanism of the Antenna Effect

The luminescence of Eu(III) complexes originates from intra-4f electronic transitions, which produce sharp emission bands but are Laporte-forbidden, resulting in weak absorption.^{1,3} To overcome this, organic ligands act as antennas that absorb excitation energy and transfer it to Eu³⁺.^{6,8}

Upon irradiation, the ligand is excited from S₀ to S₁, followed by intersystem crossing (ISC) to the triplet state (T₁).¹⁵ The T₁ state transfers energy to the Eu³⁺ ⁵D₀ level, which subsequently relaxes radiatively through ⁵D₀ → ⁷F_J transitions (J = 0–4).^{3,4}

The most intense emission arises from the electric dipole ⁵D₀ → ⁷F₂ transition (~615–620 nm), while the magnetic dipole ⁵D₀ → ⁷F₁ transition is environment-insensitive and often used as a reference.^{3,16} Efficient sensitization requires proper alignment of ligand triplet energy above the Eu³⁺ emitting level.^{9,10} If the energy gap is too small, back-transfer occurs; if too large, transfer becomes inefficient.¹¹

Non-radiative decay via high-energy vibrational oscillators (O–H, N–H, C–H) significantly reduces emission efficiency.¹⁷ Removal of coordinated water molecules greatly improves quantum yield and lifetime.^{17,18}

3. Ligand Design and Factors Affecting Luminescence

Ligand design governs both light absorption and energy transfer efficiency in Eu(III) complexes.^{2,9} Ideal ligands must have strong absorption, suitable triplet energy, and rigid structures.¹¹

Common antenna ligands include β-diketonates, phenanthroline, bipyridine, and aromatic carboxylates.¹⁹ β-diketonates offer high absorption and stable chelation, while nitrogen donors enhance rigidity and reduce solvent quenching.²⁰

The energy gap between ligand T₁ and Eu³⁺ ⁵D₀ is critical for efficient sensitization.¹¹ Proper tuning ensures efficient forward transfer while preventing back-transfer.⁹

Coordination of water molecules introduces O–H vibrational quenching, reducing emission efficiency.¹⁷ Replacing water with rigid ligands enhances quantum yield and lifetime.¹⁸

Recent ligand engineering strategies include π-conjugation extension, rigidification, and multifunctional donor design to improve absorption and energy transfer efficiency.^{12,21}

Table 1. Representative antenna ligands employed for Eu(III) sensitization and their photophysical characteristics.

Ligand Class	Representative Ligands	Role in the Antenna Effect	Advantages	Representative Applications
β-Diketonates	Acetylacetone (acac), Thenoyltrifluoroacetone (tta), Dibenzoylmethane (DBM)	Strong UV absorption and efficient ligand-to-metal energy transfer	High absorptivity; chelation	molar OLEDs, stable luminescent probes
	1,10-Phenanthroline (Phen), 2,2'-Bipyridine (bpy)	Enhance structural rigidity suppress	Improved quantum yield and lifetime	OLEDs, sensing

Ligand Class	Representative Ligands	Role in the Antenna Effect	Advantages	Representative Applications
Aromatic Carboxylates	Benzoate, Salicylate, Sulfosalicylate (SSA)	solvent quenching Efficient sensitization through conjugated systems	Good thermal stability; π -photophysical properties	Luminescent materials, bioimaging
Schiff Bases	Salicylidene-based ligands	Tunable triplet-state energies strong coordination	Structural and versatility and high luminescence	Chemical sensors
Macrocyclic/Hybrid Ligands	Crown ethers, MOF linkers	Improved coordination stability reduced radiative decay	High stability and non-multifunctionality	MOFs, optical devices

4. Device Applications of Eu(III) Complexes

The exceptional luminescent properties of Eu(III) complexes, including narrow emission bands, long excited-state lifetimes, large Stokes shifts, and excellent photochemical stability, have made them promising materials for a broad range of photonic and optoelectronic applications.^{5,7} Their high color purity and resistance to photobleaching distinguish them from conventional organic fluorophores, enabling their use in advanced display technologies, sensing platforms, biomedical imaging, and optical security systems. Continuous progress in ligand engineering and coordination chemistry has further expanded the scope of Eu(III)-based materials for next-generation functional devices.^{12,21}

*OLEDs

Eu(III) complexes are highly efficient red emitters in organic light-emitting diodes (OLEDs) owing to the intense and spectrally pure $^5D_0 \rightarrow ^7F_2$ emission centered around 615–620 nm.^{5,13} Their narrow emission bandwidth provides excellent color purity, which is essential for high-resolution display technologies and solid-state lighting applications. Rational ligand design enhances electroluminescence by improving light absorption, facilitating efficient ligand-to-metal energy transfer, and suppressing non-radiative decay pathways.^{13,22} Furthermore, the incorporation of Eu(III) complexes into suitable host-guest architectures has improved charge transport, thermal stability, and device lifetime, making these materials attractive candidates for high-performance OLEDs.²²

*Sensing and Bioimaging

The long emission lifetimes and large Stokes shifts of Eu(III) complexes enable highly sensitive detection of metal ions, biomolecules, environmental pollutants, and changes in pH or temperature.^{7,14} Time-resolved luminescence measurements effectively suppress background fluorescence, resulting in enhanced detection sensitivity and analytical accuracy. Their bright red emission, relatively low cytotoxicity, and excellent photostability have also promoted their

application as fluorescent probes in cellular imaging, immunoassays, and biomedical diagnostics.^{14,23} In addition, the tunable coordination chemistry of Eu(III) complexes allows the development of selective luminescent sensors for a wide variety of biological and environmental targets.

*Security Applications

The characteristic narrow emission bands, long-lived luminescence, and unique spectral fingerprints of Eu(III) complexes make them highly suitable for security printing and anti-counterfeiting technologies.^{7,24} These materials have been incorporated into security inks, authentication labels, optical barcodes, and encrypted information storage systems, where their luminescent signatures are difficult to duplicate. Their excellent photostability and resistance to environmental degradation ensure long-term reliability, making europium-based luminescent materials valuable for protecting currency, official documents, pharmaceuticals, and high-value commercial products.²⁴

Emerging Trends and Design Strategies in Eu(III) Photophysics

Recent developments in Eu(III) coordination chemistry have shifted the focus from simple luminescent complexes toward **functionally engineered photonic systems** where ligand design is used not only to sensitize emission but also to control directionality, stability, and device compatibility.^{1,2} In particular, the concept of **multifunctional antenna ligands** has gained prominence, where a single ligand framework simultaneously acts as a light harvester, structural stabilizer, and electronic modulator of the Eu³⁺ center.³

A major advancement in this direction is the use of **extended π -conjugated systems**, which significantly enhance molar absorption coefficients in the UV–visible region.⁴ Such ligands improve the probability of photon capture and thereby increase the overall efficiency of ligand-to-metal energy transfer. However, excessive conjugation can sometimes lower triplet-state energies below the optimal range, leading to back energy transfer.⁵ This highlights the delicate balance required between optical absorption strength and energetic alignment in antenna ligand design.

Another important strategy involves **rigidification of ligand frameworks**, which suppresses vibrational and conformational relaxation pathways.⁶ Increased rigidity reduces non-radiative decay rates and stabilizes the excited triplet state, resulting in longer Eu³⁺ emission lifetimes and higher quantum yields. In many modern systems, rigidity is achieved through fused aromatic scaffolds, chelating polydentate architectures, or incorporation into macrocyclic frameworks.⁷

Recent studies also emphasize the role of **secondary coordination sphere effects**, particularly hydrogen bonding and π – π stacking interactions in the solid state.⁸ These weak interactions can significantly influence emission intensity by modifying local symmetry around Eu³⁺ and restricting vibrational freedom. In crystalline and polymeric Eu(III) systems, such supramolecular interactions often lead to enhanced solid-state luminescence compared to solution-phase behavior.⁹

From a device perspective, a key emerging direction is the development of **host–guest architectures for OLEDs**, where Eu(III) complexes are embedded in wide-bandgap organic matrices.¹⁰ This strategy improves charge balance, prevents aggregation-induced quenching, and enhances operational stability under electrical excitation. However, challenges such as poor charge mobility and energy leakage from host to ligand still limit external quantum efficiency.

Another rapidly growing area is **hybrid Eu(III) systems**, including metal–organic frameworks (MOFs), coordination polymers, and nanoparticle-supported complexes.¹¹ These systems provide structural tunability and high surface area, allowing fine control over energy transfer pathways. In particular, Eu-based MOFs have demonstrated promising applications in sensing due to their porous structures and accessible coordination sites.¹²

Despite these advances, several fundamental challenges remain. One of the most critical is the **limited absorption window of Eu(III) antenna systems**, which are still largely restricted to UV excitation.¹³ Developing ligands that harvest visible or near-infrared light remains a major research goal. Additionally, improving **photochemical stability under prolonged device operation** is essential for commercial OLED applications.

Overall, the future of Eu(III) photophysics lies in the integration of **molecular design, supramolecular chemistry, and device engineering**, enabling systems that combine high brightness, tunable emission, and long-term stability. Continued progress in these directions is expected to establish Eu(III) complexes as core components of next-generation luminescent technologies.^{1–3}

5. Conclusions and Future Perspectives

The antenna effect remains the cornerstone of the exceptional luminescent performance of Eu(III) complexes, effectively overcoming the intrinsically weak parity-forbidden 4f–4f absorption by enabling efficient ligand-to-metal energy transfer.^{1,6} Advances in ligand engineering have significantly enhanced quantum yields, photostability, and overall device performance through the development of rigid antenna ligands, optimized coordination environments, and improved suppression of non-radiative decay pathways.¹² These improvements have reinforced the importance of Eu(III) complexes as highly efficient luminescent materials for organic light-emitting diodes (OLEDs), chemical and biological sensing, bioimaging, and anti-counterfeiting technologies owing to their outstanding photophysical properties, including narrow emission bands, long excited-state lifetimes, and excellent color purity.^{5,22} Looking ahead, future research is expected to focus on the design of multifunctional antenna ligands, visible-light-harvesting systems, sustainable synthetic approaches, and hybrid luminescent materials to further enhance energy-transfer efficiency and device stability.²⁵ The integration of computational molecular design, supramolecular engineering, and advanced photonic platforms is anticipated to accelerate the development of next-generation Eu(III)-based luminescent materials, ensuring that the antenna effect continues to play a pivotal role in the advancement of optoelectronic devices, sensing technologies, bioimaging, and optical security applications.

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