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Research Progress in Luminescent Rare Earth Complexes

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ABSTRACT

This paper presents a systematic review and synthesis of the field of luminescent rare earth complexes, highlighting landmark research advances achieved over the past decades and offering perspectives on future research priorities and application scenarios for these materials. Luminescent rare earth complexes are poised to continue playing a pivotal role in driving technological innovation and promoting sustainable development on a global scale. Against this backdrop, and drawing on recently published literature and experimental data, this study systematically organizes and summarizes research progress in luminescent rare earth complexes, with the aim of providing a valuable reference for ongoing investigations in this field.

KEYWORDS

Rare earth luminescent materials; Rare earth complexes; Electroluminescence

1. INTRODUCTION

Under the influence of chemical or light energy, substances absorb energy and transition from a lower-energy ground state to a higher-energy excited state; if no chemical change occurs during this process, the substance will spontaneously return to the ground state. As it returns to the ground state, the substance releases energy in the form of persistent light emission, a process defined as luminescence [1]. For example, when external fields such as electron beams, applied electric fields, or radiation act on a substance, they can induce a specific excited state. The excited substance then releases energy in the form of electromagnetic radiation, with wavelengths covering the ultraviolet, visible, and near-infrared regions. Hence, this energy release process is referred to as luminescence.

From a mechanistic perspective, the luminescence process of luminescent materials can be divided into three core stages: First, the host material absorbs excitation energy from external sources. Second, activators receive the excitation energy transferred from the host material and become excited through electron transitions within their own energy levels. Third, the excited activator ions eventually return to the ground state energy level, accompanied by photon emission, thereby achieving radiative luminescence [2].

The luminescence characteristics of rare-earth ions are primarily determined by the quantum behavior of their 4f shell electrons. As the number of 4f shell electrons varies, rare-earth ions exhibit diverse electron transition forms and abundant energy level transition pathways. This enables rare-earth ions to absorb or emit light of various wavelengths ranging from the ultraviolet to the infrared region, resulting in luminescent materials with distinct performance characteristics. This exceptional luminescence property of rare-earth ions provides a solid physical foundation for the development of highly efficient luminescent materials [3].

China possesses the world's most abundant reserves of rare-earth resources, with the reserves of medium and heavy rare-earth elements in southern regions being particularly prominent. The country's ongoing efforts in regulating rare-earth resource extraction, optimizing industrial chain layout, and providing policy support for related industries have laid an important foundation for both fundamental research and the industrial development of rare-earth materials.

2. RESEARCH STATUS

Rare-earth organic complexes exhibit strong characteristic fluorescence emission from rare-earth ions, owing to the robust ultraviolet absorption capacity of their organic ligands and the highly efficient energy transfer process to the rare-earth ions. These materials are characterized by excellent monochromaticity, high color purity, and good stability, demonstrating broad application potential across various high-tech fields such as laser technology, anti-counterfeiting labels, biomedical imaging, optical amplifiers, organic light-emitting diodes (OLEDs), photovoltaic cells, and agricultural wavelength-converting films.

The history of rare-earth luminescence research can be traced back to 1908 when Becquerel first observed the sharp absorption lines of rare-earth elements. In 1959, researchers discovered that using Yb^{3+} as a sensitizer and Er^{3+}, Ho^{3+}, or Tm^{3+} as activators could achieve the photon addition phenomenon, laying the theoretical foundation for the development of upconversion luminescent materials. In 1964 and 1968, red phosphors for color television, including YVO_4:Eu, Y_2O_3:Eu, and Y_2O_2S:Eu, were successively developed, significantly improving the brightness and color performance of color TVs. During the 1970s, the emergence of infrared-to-visible upconversion materials advanced the development of anti-Stokes luminescence theory. In 1973, rare-earth tri-color phosphors (e.g., $BaMgAl_{10}O_{17}$:Eu^{2+}, $MgAl_{11}O_{19}$:Ce,Tb, Y_2O_3:Eu) were successfully developed, achieving high luminous efficacy and color rendering properties, which substantially enhanced the quality of electric light sources. In 1974, the "photon cutting" phenomenon was observed in Pr^{3+} compounds, where one high-energy photon could be split into two or more lower-energy photons. In the 1990s, rare-earth long-afterglow materials, represented by $SrAl_2O_4$:Eu and $SrAl_2O_4$:Eu,RE, achieved breakthroughs in application. By the early 21st century, the development of rare-earth phosphors for white LED applications entered a phase of rapid progress [4].

In 2012, Samuel et al. [5] reported in Organic Electronics on doping $Eu(DBM)_3(phen)$ into a mixed-host system using CBP as the hole-transport material and PBD as the electron-transport material, with an emissive layer thickness of 90 nm. By optimizing the CBP to PBD ratio (optimal at 30:70), balanced carrier transport was achieved. The final device structure was ITO/PEDOT:PSS (40 nm)/PVK (35 nm)/CBP:PBD:Eu (5%, 90 nm)/TPBI (35 nm)/LiF/Al, yielding a maximum current efficiency of 10.0 cd/A, an efficiency of 8.2 cd/A at a practical luminance of 100 cd/m², and an external quantum efficiency (EQE) of 4.3%.

Li et al. [6] utilized transition metal complexes as emissive materials. By designing a double-emissive-layer structure and introducing rare-earth complexes as carrier injection sensitizers, they successfully fabricated blue, green, red, and white OLED devices. The blue device achieved maximum current and power efficiencies of 54.27 cd/A and 56.59 lm/W, respectively; the green device achieved 119.36 cd/A and 121.73 lm/W; the red device achieved 65.53 cd/A and 67.20 lm/W; and the pure white and warm white devices achieved maximum current efficiencies of 54.25 cd/A and 56.27 cd/A, and maximum power efficiencies of 54.95 lm/W and 57.39 lm/W, respectively.

Ivan H. Bechtold et al. [7] investigated the electroluminescence energy transfer mechanism in devices using CBP as the host and $Tb(ACAC)_3TDZP$ as the emitter. By replacing the hole-transport material NPB with MTCD and employing CBP as the host, they obtained a relatively pure Tb(III) characteristic emission spectrum, achieving a maximum luminance of 1673 cd/m² and a maximum efficiency of 0.86 cd/A.

Liu Y et al. [8] used dipyridophenazine (DPPZ) as a neutral ligand to synthesize the complex $Eu(DBM)_3(DPPZ)$ and applied it in polymer light-emitting diodes (PLEDs). They achieved a maximum EQE of 2.5% and a maximum luminance of 1783 cd/m², representing the highest performance for Eu-complex-based PLEDs at the time, providing an important reference for the application of rare-earth complexes in organic optoelectronic devices. In recent years, driven by the growing demand for near-infrared (NIR) light in bioimaging, optical communications, and environmental monitoring, NIR rare-earth complex electroluminescent materials have gained significant research interest due to their narrow bandwidth emission and long fluorescence lifetimes.

Marina A. Katkova et al. [9] designed and synthesized a series of NIR-emitting rare-earth complexes (with central metal ions Pr^{3+}, Nd^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}) using 2-(2-benzothiazolyl)phenol (SON) as the ligand. They systematically characterized the electroluminescence properties using UV-Vis-NIR absorption spectroscopy and electroluminescence spectroscopy. The results indicated that among all tested complex-based devices, those with Nd^{3+} and Yb^{3+} as the central ions exhibited the best radiant efficiencies, reaching 0.82 mW/W and 1.22 mW/W, respectively, providing data support for material selection in NIR electroluminescent devices.

Bian Zuqiang et al. [10] developed a tridentate anionic ligand based on a pyridine-naphthyridine-hydroxy structure. This ligand efficiently sensitized the NIR luminescence of Nd^{3+}, Yb^{3+}, and Er^{3+} through coordination. Subsequently, they fabricated OLED devices based on these complexes using thermal evaporation and tested their optoelectronic properties. The results showed that the maximum NIR radiant intensities for Nd^{3+}-, Er^{3+}-, and Yb^{3+}-based devices were 25 μW/cm², 0.46 μW/cm², and 86 μW/cm², with corresponding maximum EQEs of 0.019%, 0.004%, and 0.14%, respectively, providing experimental basis for optimizing the fabrication process of NIR rare-earth complex devices.

Mikhail N. Bochkarev et al. [11] synthesized a series of rare-earth complexes $Ln(OC_6F_5)_3(L)_x$ (where Ln represents the rare-earth ion, L represents the neutral ligand, and x is the coordination number of the neutral ligand) via a solution method, using pentafluorophenol as the monodentate anionic ligand and ligands like 2,2'-bipyridine as neutral ligands. These complexes were used as the active emitting layer materials to construct electroluminescent devices, systematically exploring the influence of ligand structure on the device's luminescence properties.

Gillin et al. [12] proposed doping the perfluoro-substituted erbium complex $Er(F\text{-}TPIP)_3$ into a $Zn(F\text{-}BTZ)_2$ host matrix to form the emissive layer of an optical amplifier. The introduction of perfluorinated ligands effectively suppressed non-radiative transitions induced by C–H bond vibrations, significantly reducing the quenching of NIR luminescence. Test results indicated a high quantum efficiency of 7% for this system, far superior to non-fluorinated systems (typically below 1%). This study not only confirmed the effectiveness of the fluorination strategy for enhancing the luminescence performance of rare-earth NIR materials but also highlighted their application potential in optical communication fields, such as optical fiber amplifiers. Furthermore, based on this material system, the research team successfully constructed an electroluminescent NIR OLED, laying the groundwork for the integrated development of NIR optoelectronic devices.

The rare earth luminescent materials industry in China started relatively late but has developed rapidly. In the early stages, the domestic technological level in this field was relatively low, relying primarily on imports. With increasing national emphasis on the rare earth industry and growing investment in scientific research, domestic enterprises and research institutions gradually mastered the core technologies of rare earth luminescent materials and began achieving import substitution. Particularly after 2010, the state strengthened the management and protection of rare earth resources, promoting the industry's shift towards higher value-added development.

Initially, rare earth luminescent materials were predominantly used in lighting applications. In 2011, white-light LEDs rapidly entered the lighting market, encroaching upon the market share of rare-earth energy-saving lamps. As the lighting industry underwent product upgrades, the application focus of rare earth luminescent materials gradually shifted towards higher value-added industries such as electronic products. These materials possess numerous advantages, including strong light absorption capacity, high conversion efficiency, a wide range of emission wavelengths, broad fluorescence lifetimes spanning six orders of magnitude from nanoseconds to milliseconds, and stable physical and chemical properties that confer resistance to high temperatures and tolerance to high-power electron beams, high-energy radiation, and intense light exposure. These characteristics endow them with superior performance that is unmatched by other luminescent materials [13]. One crucial pathway for achieving white light emission involves utilizing the fluorescence conversion technology of rare earth luminescent materials [14].

Currently, rare earth luminescent materials have established a mature application system covering multiple fields, with industrial production and consumer market scale continuing to expand.

In the lighting field, they are core components of high-efficiency, energy-saving light sources such as white LEDs, rare-earth energy-saving lamps, and ceramic metal halide lamps. Among these, lamp-use rare earth tri-color phosphors enable high color rendering indices and low lumen depreciation, supporting the lighting industry's transition from traditional incandescent bulbs to energy-saving light sources.

In the display field, although the demand for CRT TV phosphors and CCFL backlight tri-color phosphors has adjusted with technological iteration, novel materials like rare-earth quantum dots and upconversion luminescent materials are providing key support for cutting-edge technologies such as 8K ultra-high-definition displays and AR/VR near-eye displays.

In medical radiography, rare earth phosphor intensifying screens, characterized by high photosensitivity and excellent image resolution, can significantly reduce radiation doses in medical examinations, ensuring the safety and accuracy of clinical diagnostics.

In radiation field detection and recording, these materials can rapidly respond to signals like ionizing radiation and ultraviolet light, finding widespread use in nuclear facility monitoring, environmental radiation detection, and industrial non-destructive testing, thereby providing technical assurance for safety protection and quality control.

Recent years have witnessed a continuous emergence of cutting-edge scientific and technological achievements in the field of rare earth luminescent materials in China.

In 2024, a breakthrough addressed the long-standing international "blue light bottleneck" in OLED development – the lack of blue light materials combining high efficiency and high stability – which had persisted for nearly three decades. This also resolved a critical "chokepoint" challenge for China's OLED industry: the absence of proprietary red, green, and blue primary color luminescent materials [15].

On July 24, 2024, Huazhong University of Science and Technology reported in Nature Communications the successful fabrication of a rare-earth-based light-emitting diode by optimizing the energy transfer process in Ce(III)-based metal halide Cs_3CeI_6, avoiding the shielding effect of outer electron orbitals during direct carrier injection [16]. The device achieved a maximum luminance of 1075 cd m^{-2} and an external quantum efficiency (EQE) of 7.9%, representing the highest efficiency reported for deep-blue metal halide LEDs at the time and offering a new pathway for electroluminescent blue light development.

In September 2024, a team led by Professor Lu Canzhong at the Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, also made a breakthrough by proposing a novel sensitization strategy for blue OLEDs: doublet-sensitized fluorescence (DSF). Their DSF-OLED utilized a doublet-emitting rare-earth complex (Ce-2) as the sensitizer and an MR-TADF material (ν-DABNA) as the terminal emitter. This strategy leveraged the unique hole-trapping and electron-transport capabilities of the Ce(III) complex, ensuring the predominant formation of doublet excitons in the emissive layer and achieving highly efficient (93.5%) Förster energy transfer. The DSF-OLED demonstrated a maximum EQE of 30.0% (more than double that before sensitization), significantly increased maximum luminance, excellent CIE coordinates at 1000 cd m^{-2}, a low efficiency roll-off of 14.7%, and substantially extended operational lifetime, injecting new impetus into the development of ultra-high-definition OLED displays.

In March 2025, a collaborative study led by Professor Guo Hai from Zhejiang Normal University and Professor Qian Guodong from Zhejiang University was published in Advanced Materials titled "Thermal-Adaptive Photonic MOFs for High-Performance X-ray Scintillator". The research involved constructing the ZJNU-1000 material from inorganic Ln^{3+} ions and the organic ligand H_2BDC. By adjusting the ratio of Tb^{3+} to Eu^{3+}, the material's luminescence could be tuned from the green to red spectral regions. Upon temperature increase, contraction of the metal-ligand chains enhanced energy transfer from the ligand to the rare earth ions and improved carrier migration efficiency, endowing the material with a thermally adaptive "thermal-induced radioluminescence enhancement" property [17]. ZJNU-1000 exhibited a high relative light yield (max ~ 49700 photons MeV^{-1}), a low detection limit (118.7 nGy air s^{-1}), and low cost. Polymer composites based on it achieved extremely high imaging resolution (max ~ 24 lp mm^{-1}), showing promising application prospects in high-temperature in-situ radiation imaging and customized pattern printing [18].

3. PROSPECTS

In recent years, rare earth luminescent materials have achieved phased breakthroughs in enhancing luminous efficiency, optimizing thermal stability, and improving high-temperature resistance, laying a crucial foundation for their applications across various fields. However, from the perspective of practical application requirements, these materials still exhibit critical performance shortcomings that need urgent resolution:

Firstly, the service life of the materials often falls short of industrial demands, as performance degradation tends to occur under long-term exposure to light, temperature fluctuations, and other operational conditions.

Secondly, precise control over the consistency of luminescent brightness and color during batch preparation remains challenging, hindering their large-scale application in fields like displays and lighting, which demand high uniformity.

Thirdly, insufficient long-term stability can lead to structural degradation and functional failure in complex environments involving humidity or chemical corrosion.

These performance bottlenecks directly determine the application reliability and industrialization potential of rare earth luminescent materials. Addressing them through targeted research is a core prerequisite for facilitating their transition from laboratory research to large-scale civilian applications and achieving the goal of serving societal production and daily life.

Owing to their unique energy level transition characteristics, broad spectral response range, and excellent environmental tolerance, rare earth luminescent materials demonstrate irreplaceable research value and broad application prospects in various high-technology fields such as lighting and displays, new energy, biomedicine, and information storage. Looking ahead, with continued efforts by Chinese research teams in key technologies and engineering applications—including material molecular design, optimization of preparation processes, and device integration—it is anticipated that the current performance bottlenecks and industrialization challenges facing rare earth luminescent materials and devices will be gradually resolved. This will promote their role as core materials in a wider range of industrial sectors, providing solid material support for the innovative development of China's high-tech industries.

Notably, as technological research and development deepen, the application boundaries of rare earth luminescent materials are rapidly expanding into emerging technological fields:

In the new energy sector, their application in spectral conversion layers for solar cells can effectively enhance the utilization of ultraviolet and near-infrared light by modulating the solar spectrum, thereby aiding in breaking efficiency limits of photovoltaic devices.

In biomedicine, near-infrared rare earth luminescent materials, leveraging advantages such as deep tissue penetration and minimal absorption by biological tissues, enable precise deep-tissue imaging. Simultaneously, they serve as fluorescent probes for targeted drug carriers, providing key tools for the development of precision medicine.

In information storage, rare-earth-doped long-afterglow luminescent materials and photochromic materials can utilize light-controlled energy level transitions for data writing and reading, potentially overcoming the density limitations of traditional storage technologies and enabling high-density, non-volatile information storage systems.

In intelligent sensing, the high sensitivity of these materials to external stimuli such as temperature, pressure, magnetic fields, and ion concentration provides a fundamental material basis for developing multi-parameter integrated sensor devices and constructing intelligent sensor networks.

This cross-domain application expansion not only further enlarges the industrial scale and market space for rare earth luminescent materials but also positions them as a key material support bridging multiple high-tech fields and fostering interdisciplinary innovation, holding significant importance for promoting technological upgrades in related industries.

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