2-6-3. Metal Complexes & Rare Earth Complexes

Overview

Metal complexes provide useful fluorescent and phosphorescent materials and have been applied to photosensitizers, organic light-emitting diodes (OLEDs), sensors, and bioimaging, etc. While noble metal complexes dominate as luminescent materials, recent efforts have focused on developing luminescent materials that are abundant and inexpensive. As a result, complexes using 3d metals have been actively studied based on sophisticated design of ligands and structures, leading to significant diversification of the elements used in luminescent metal complexes. Additionally, in rare earth compounds, alongside ion-doped inorganic phosphors, the construction of molecular rare-earth complexes and coordination polymers has advanced the development of high-performance luminescent materials.

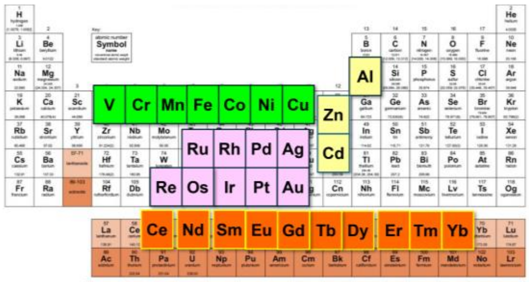

Figure 1. Diversification of elements in luminescent metal complexes.

Current Status and Frontiers

Luminescent metal complexes have been extensively studied as photosensitizers for light energy conversion, with a particular focus on (polypyridine)ruthenium(II) complexes. Metal complexes gained attention as luminescent materials at the end of the 20th century. An organic light emitting device (OLED) was developed using tris(quinolinolato)aluminum(III), and the practical application came into view. The exploration and development of metal complexes as luminescent materials has progressed rapidly. Phosphorescent materials with a theoretical emission quantum yield of 100% were explored, and Ir(III) and Pt(II) complexes bearing cyclometalating ligands were developed, which are currently used as actual emitters for OLEDs. Meanwhile, by controlling the assembled structures, strongly luminescent systems with diverse emission colors have been realized in Pt(II) and Au(I) complexes. Furthermore, aiming for more affordable luminescent materials, research on ubiquitous metal complexes that can replace noble metals has also intensified. Cu(I) complexes in the d^{10} electron system have garnered attention as materials exhibiting strong luminescence because they do not generate dd excited states, which can be a cause in non-radiative deactivation.

Cu(I) complexes with a tetrahedral structure equipped with appropriate π-conjugated systems exhibit small energy differences between singlet and triplet states in metal-ligand charge transfer (MLCT) and halogen-metal-ligand charge transfer (XMLCT) states. This enables effective thermally activated delayed fluorescence (TADF) at room temperature, leading to high-efficiency luminescence. However, many Cu(I) complexes are easily structurally distorted in the excited state, leading to deactivation. To suppress distortion, complexes with rigid structures using bulky and multi-coordinate ligands or those with three-coordinate or two-coordinate structures that do not occur distortion were designed. Additionally, Mn(II) ions with a half-filled shell (d^5) and Cr(III) complexes with a d^3 electronic structure exhibit luminescent states derived from spin-forbidden transitions, making them resistant to deactivation. Research on luminescent complexes utilizing these structures has been actively pursued in recent years. Moreover, researchers have become interested in making non-luminescent 3d complexes luminescent. In 2019, a Fe(III) complex with a luminescence lifetime of 2 ns and a luminescence quantum yield of 0.02 at room temperature was reported. Research on the development of luminescence and photophysical properties and functions in iron, cobalt, and nickel complexes is becoming increasingly active worldwide.

On the other hand, rare earth ions have been widely used as phosphors doped into inorganic compounds since the 1960s. However, with the demand for flexible and highly designable luminescent materials for OLEDs, molecular complexes containing organic ligands responsible for light absorption have attracted attention, and various rare earth complexes have been developed. Applications in lighting, displays, sensors, and bioimaging are also progressing. Furthermore, by expanding into supramolecules and coordination polymers or metal-organic frameworks, functional enhancements such as circularly polarized emission and stimulus-responsive emission have been successfully achieved.

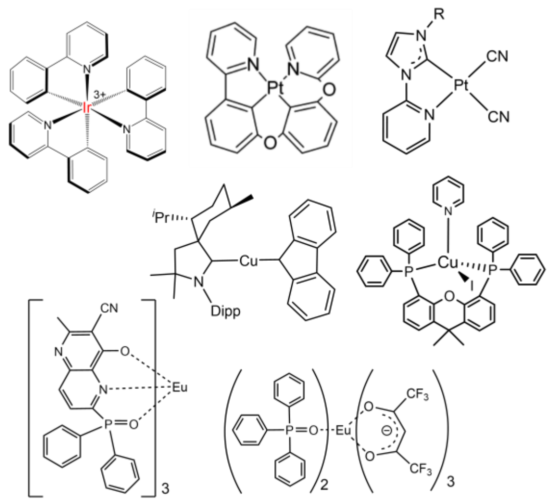

Figure 2. Examples of strongly luminescent metal complexes.

References

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Future Perspectives and Directions

Issues to be resolved and realized within the next 10 years: Development of novel luminescent 3d metal complexes, such as nickel and cobalt complexes, and their scientific elucidatgaion. Development and application of highly efficient and durable luminescent complexes based on comprehensive studies of 3d metal complexes and rare earth complexes.

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