



Luminescent lanthanide coordination compounds with pyridine-2,6-dicarboxylic acid

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ABSTRACT

The rapidly growing number of luminescent compounds based on lanthanide ions illustrates high interest due to the numerous applications on lighting, optical communications, sensors, photonics and biomedical devices. In this review, we choose luminescent compounds based on pyridine-2,6-dicarboxylic acid to discuss the synthetic strategy of functional luminescent compounds, various types of emitting, tunable emission colors, and the mechanism of enhancing and quenching fluorescence. The unique luminescence features them as promising materials. We focus on recent significant advances of this field and provide a comprehensive review on multifunctional lanthanide compounds.

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Contents

1. Introduction	273
2. Nature of the luminescence	274
2.1. Ligand-based luminescence	274
2.2. Charge-transfer (CT) luminescence	275
2.2.1. Metal-to-ligand charge transfer (MLCT) luminescence	275
2.2.2. Ligand-to-metal charge transfer (LMCT) luminescence	275
2.3. Lanthanide-based luminescence	275
2.3.1. Near-infrared (NIR) emitting	276
2.3.2. Visible emitting	277
3. Applications	278
3.1. Tunable luminescence	278
3.2. Chemical sensors	279
3.3. Other applications	280
4. Conclusion and outlook	280
Acknowledgment	281
References	281

1. Introduction

Lanthanide(Ln)-based coordination compounds, as an emerging type of multifunctional luminescent materials, have attracted

extensive attraction in the last two decades because of their unique optical properties such as large Stokes shifts, long lifetimes, and characteristic narrow line-like emission bands [1–13]. The luminescent nature of lanthanide coordination compounds is associated with the organic ligand moieties and lanthanide centers. Furthermore, luminescent properties are not only related to the composition of the materials, but also heavily dependent on the structure and intermolecular packing for their energy transfer [14].

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Therefore, luminescence can arise from direct organic ligands excitation (particularly the highly conjugated ligands), metal-centered emission (observed in lanthanide complexes through the so-called “antenna” effect), and charge-transfer such as ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT).

Pyridine-2,6-dicarboxylic acid (H_2pydc), as a high conjugated ligand, is commonly used as the linker to construct coordination compounds for the valuable characters: (a) heterocyclic H_2pydc contains a rigid 120° angle between the central pyridine ring and two symmetrical carboxyl groups, and can adopt varied coordination modes such as monodentate, chelating bidentate, bridging bidentate and multidentate. This could potentially provide various coordination motifs to form discrete or infinite structures with different metal centers; (b) the carboxylic O atoms are beneficial to form hydrogen bonds, while the rigid pyridyl ring is general origin of π - π stacking interactions; (c) the diverse coordination patterns of N or O atoms can result in novel topological structures. Owing to the rigidity and high symmetry of H_2pydc , H_2pydc is a good polycarboxylic acid for constructing coordination compounds.

A systematic study of lanthanide compounds with H_2pydc has been carried out in our previous work, including $4f$, $4f-2p$, $4f-3d$ and $4f-4d$ systems [15–20]. This work makes a huge contribution

to the development of coordination polymers, which not only provides a rational synthetic strategy but also reveals the relationship between the structures and luminescent properties. Besides the theoretical research, the potential applications of these luminescent compounds are also mentioned, which ranges from fluorescent materials to sensors. The aim of this review is to give a comprehensive overview of the lanthanide compounds based on H_2pydc , particularly those with intriguing luminescent applications. We separated this review to two sections: nature and applications of the luminescence.

2. Nature of the luminescence

2.1. Ligand-based luminescence

When an organic molecule absorbs a photon of appropriate energy, a chain of photophysical events occur, including internal conversion or vibrational relaxation, fluorescence, intersystem crossing, and phosphorescence (Fig. 1). Ligand-centered (LC) luminescence plays an important role in the luminescence of lanthanide compounds and has been thoroughly described in the past two decades [21–23]. Ligand-centered emissions are based on the organic ligands, especially the highly conjugated molecules. Generally, it does not exhibit significant difference from the luminescence of the free ligands.

From the literatures, it is obvious that a fluorescent or a phosphorescent ligand should be chosen to generate ligand-based luminescence. Moreover, metal ions usually are those with closed shell electron configurations such as alkaline and alkaline earth ions, transition metal ions with d^0 or d^{10} configurations as well as the La(III) ($4f^0$) and Lu(III) ($4f^{14}$).

Although lanthanide compounds with H_2pydc usually exhibit narrow and characteristic $4f \rightarrow 4f$ transitions, some of them, especially La(III)- and Lu(III)-based compounds can show the ligand-based emission as above-mentioned. The luminescence of $\{[La(H_2O)_4(pydc)]_4[SiMo_{12}O_{40}] \cdot 2H_2O\}$ (**1**), similar to the free ligand, is observed at about 392 nm upon excitation at 245 nm (Fig. 2), implying the ligand-based emission [24]. The luminescence of $\{[La_8(SeO_3)_4(pydc)_8(H_2O)_{10}] \cdot 2H_2O\}$ (**2**) is observed at 416 nm, while the free ligand molecule shows a weak luminescence at 410 nm at room temperature (Fig. 3) [25]. The fluorescent enhancement and red-shift are attributed to the formation of the crystal lattice, which increases the rigidity and the extended π -conjugacy of the ligand, and decreases the intraligand HOMO-LUMO energy gap.

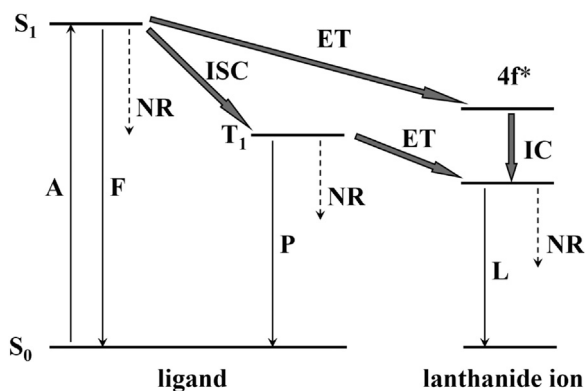


Fig. 1. Schematic representation of energy absorption, migration, emission, and processes in complexes. Abbreviations: A=absorption; F=fluorescence; P=phosphorescence; L=lanthanide-centered luminescence; ISC=intersystem crossing; ET=energy transfer; IC=internal conversion; S=singlet; T=triplet. Plain arrows indicate radiative transitions; dotted arrows indicate nonradiative transitions. Reproduced with permission from Ref. [14] Copyright (2012) American Chemical Society.

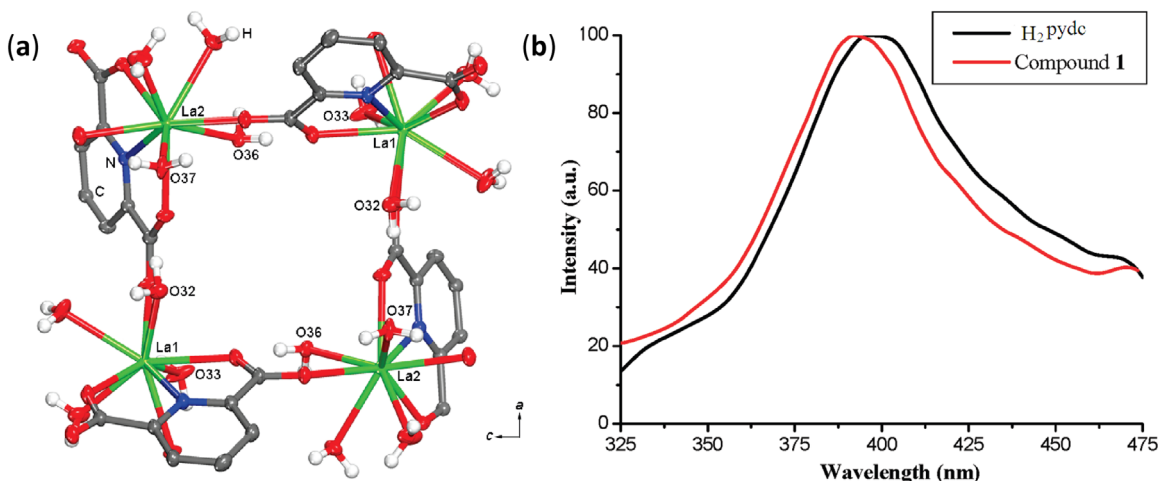


Fig. 2. (a) Structure of the tetranuclear cyclic unit in compound **1**; (b) emission spectra of ligand H_2pydc and compound **1** in the solid state at room temperature. Reproduced with permission from Ref. [24]. Copyright (2009) American Chemical Society.

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