Inorganic Chemistry Communications 93 (2018) 29–32

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

# Syntheses, structures, photoluminescence and magnetic properties of 1D lanthanide chains featuring 2,2′-bipyridine-5-carboxylic ligands

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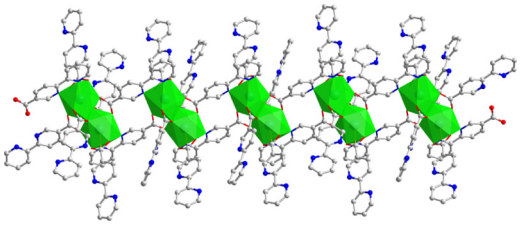
## GRAPHICAL ABSTRACT

Three isostructural lanthanide(III) complexes all have the 1D chain-like structures, which contain di-nuclear lanthanide(III) units. The photoluminescent properties of **1** and **3** show the ligand $L^-$ can effectively transfer energy to lanthanide ions.



## ARTICLE INFO

*Keywords:*
Lanthanide
2,2′-Bipyridine-5-carboxylic acid
Magnetic property
Fluorescence

## ABSTRACT

A series of isostructural coordination polymers based on lanthanide cations and 2,2′-bipyridine-5-carboxylic ligands, i.e. $[Ln_3L_9]_n{\cdot}0.5nH_2O$ (Ln = Eu (**1**), Gd (**2**) and Tb (**3**); HL = 2,2′-bipyridine-5-carboxylic acid), have been synthesized under hydrothermal condition and characterized by single-crystal X-ray diffractions, powder X-ray diffractions (PXRD), thermal analyses (TGA) and elemental analyses (EA). These three complexes all have the 1D chain-like structures containing dinuclear lanthanide units. The solid state luminescent properties of **1** and **3** as well as the magnetic property of **2** are investigated. The results indicate that the 2,2′-bipyridine-5-carboxylic acid ligand is a good sensitizer for the Eu(III) cation.

Owing to diverse structures and excellent photophysical properties, lanthanide metal–organic frameworks (LnMOFs) have aroused wide concerns among scientific research [1]. Lanthanide complexes are widely utilized for biomedical imaging [2], anti-counterfeiting tags [3], optical fiber lasers [4], sensors [5,6] and phosphors [7]. The 4f orbitals of lanthanide ions are shielded by the outer shells of 5 s and 5p orbitals, resulting in characteristic f–f emission transitions. Usually, the light absorption of trivalent lanthanide ions is very weak due to the forbidden f–f transitions [8], making the direct excitation inefficient. Fortunately, this trouble can be effectively solved by organic sensitizers in LnMOFs through energy transfer process, which is called the "antenna effects" [9–15]. The energy of light is absorbed by organic linkers and subsequently transferred to the excited states of lanthanide ions. Afterwards, the lanthanide ions go back to the ground state via radiative transitions, emitting the characteristic fluorescence [10–15]. Consequently, it is important to choose appropriate organic ligands, which possess high light absorption coefficients and suitable energy levels matching with lanthanide ions. In addition, thanks to large magnetic moments, distinct magnetic anisotropy as well as slow magnetic relaxation, lanthanide complexes are applied in the field of magnetic materials [16–20].

In practice, in order to overcome the forbidden f–f transitions, the polypyridine ligands have been exploited as the sensitizers due to their broad and strong absorption bands in the UV region. The energy can be effectively radiated to lanthanide ions through ligand-to-metal charge transfer (LMCT) mechanism [21]. On the basis of above consideration,

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https://doi.org/10.1016/j.inoche.2018.04.031
Received 9 April 2018; Received in revised form 30 April 2018; Accepted 30 April 2018
Available online 01 May 2018
1387-7003/ 

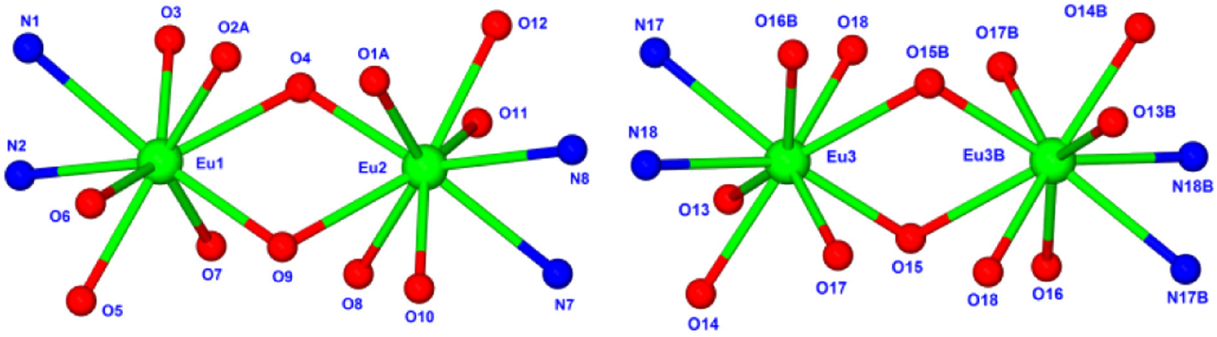


**Fig. 1.** The coordination environments of three crystallographically independent Eu(III) cations in the asymmetric unit. The symmetry codes: A, 1 - x, 2 - y, 1 - z; B, 2 - x, 1 - y, 2 - z.

we have selected 2,2′-bipyridine-5-carboxylic acid as the organic ligand and synthesized a series of lanthanide complexes, i.e. $[Ln_3L_9]_n{\cdot}0.5nH_2O$ (Ln = Eu (**1**), Gd (**2**) and Tb (**3**); HL = 2,2′-bipyridine-5-carboxylic acid) with strong luminescent emissions.

Complexes **1–3** were synthesized under the similar hydrothermal condition. It is generally known that syntheses of lanthanide complexes are impacted by many factors such as the proportion of reactants, solvents, reaction temperature and so forth. Herein, we found that a weak organic base—imidazole plays an important role in the syntheses of **1–3**. By adjusting the pH value of reaction system to 6.0 with a small amount of imidazole, high-quality crystals of **1–3** can be obtained.

Single-crystal X-ray diffraction analyses indicate that complexes **1–3** are isostructural and all crystallize in the triclinic *P*-1 space group. Therefore, the structure of **1** is taken as the example to be discussed in detail. The asymmetric unit of **1** consists of three crystallographically independent Eu(III) cations, nine L ligands and half a water molecule. The coordination environments of these three Eu(III) cations are very similar and all in nine-coordinated geometry (Fig. 1). Every coordination sphere is completed by two nitrogen atoms from one L ligand and seven oxygen atoms from five different L ligands. The Eu—N distances are in the range of 2.62–2.63 Å, and the Eu—O distances are in the range of 2.35–2.68 Å. The Eu1 and Eu2 cations are bridged by O4 and O9 atoms to form a dinuclear unit, with the Eu…Eu separation of 3.97 Å. In addition, Eu3 and Eu3B are linked by O17 and O15B atoms, with the Eu…Eu separations in the range of 3.98 Å. In **1**, the 2,2′-bipyridine-5-carboxylic acid ligands present three types of coordination modes (Fig. S1). Through the coordination of the L ligands with the Eu(III) cations, 1D chains containing dinuclear Eu(III) units are formed (Fig. 2). Every chain interacts with adjacent six chains to form the three-dimensional supramolecular framework (Fig. S2).

To prove that the crystal structures of **1–3** are truly representative of their bulk materials, powder X-ray diffraction (PXRD) experiments were carried out on the as-synthesized samples. The experimental patterns of complexes **1–3** match well with the simulated ones calculated from single-crystal data (Fig. S3), which demonstrating the complexes **1–3** all have good phase purity. Thermogravimetric analysis (TGA) experiments show that complexes **1–3** with excellent thermal stability and no obvious weight losses can be found until 450 °C in $N_2$ atmosphere.

Considering that 2,2′-bipyridine-5-carboxylic acid ligand is a good sensitizer for the lanthanide cations, we have explored the photoluminescence of solid samples of **1** and **3** at room temperature (Fig. 3). The excitation spectra of **1** and **3** were acquired by monitoring the strongest emissions of Eu(III) (613 nm) and Tb(III) (545 nm) upon photo-excitation at room temperature. As shown in Fig. 3, there are prominent ligand bands in the UV range, indicating the existence of the ligand sensitizing process. For **1**, no obvious characteristic photo-excitation of the Eu(III) energy levels have been observed in the excitation spectra. For **3**, however, except for an intense broadband from the L ligand some narrow but weak characteristic photo-excitation of the Tb (III) energy levels have also been observed. These sharp but weak bands are arising from 4f–4f transitions such as the ground $^7F_5$ level to $^5L_{10}$(369 nm) and $^5G_6$ (378 nm) respectively. In comparison, these transitions are much weak than that of the broad band attributed to the ligand level, which shows that the ligand-sensitized luminescence emission is more effective than the direct excitation of the Tb(III) ion absorption levels. On the whole, the above results indicate that the antenna effect is much large because the ligand-to-metal-ion transitions dominate the spectra.

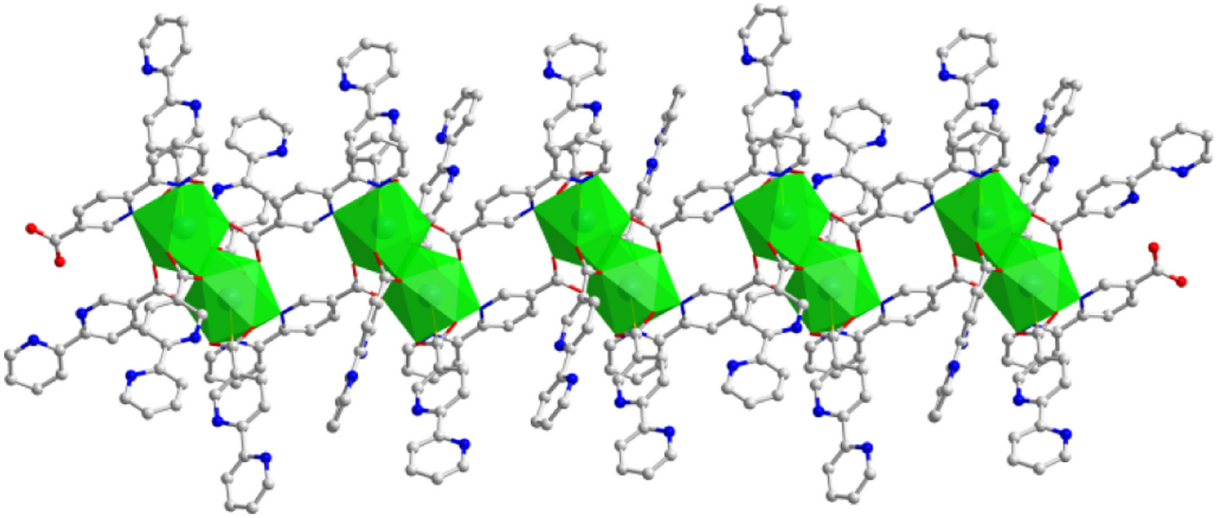

**Fig. 2.** One-dimensional chain containing dinuclear Eu(III) units. All hydrogen atoms are omitted for clarity.