



## Research paper

# Synthesis, structural characterization and photoluminescence properties of mononuclear $\text{Eu}^{3+}$ , $\text{Gd}^{3+}$ and $\text{Tb}^{3+}$ complexes derived from *cis*-( $\pm$ )-2,4,5-tris(pyridin-2-yl)-imidazoline as ligand

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## ABSTRACT

Three mononuclear lanthanide complexes of compositions  $[\text{Eu}(\text{L})(\text{NO}_3)_3(\text{MeOH})] \cdot 0.5\text{MeOH} \cdot \text{Et}_2\text{O}$  (**1**),  $[\text{Gd}(\text{L})(\text{NO}_3)_3(\text{MeOH})] \cdot 0.5\text{MeOH} \cdot \text{Et}_2\text{O}$  (**2**) and  $[\text{Tb}(\text{L})(\text{NO}_3)_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O} \cdot 0.5\text{MeOH} \cdot \text{Et}_2\text{O}$  (**3**) with  $\text{L} = \textit{cis}$ -( $\pm$ )-2,4,5-tris(pyridin-2-yl)-imidazoline were successfully synthesized and characterized by elemental and TG-DSC analysis, single-crystal X-ray crystallography and FT-IR, UV-Vis and fluorescence spectroscopy. Complexes **1–3** are isostructural with ten-coordinate  $\text{Ln}^{3+}$  ions embedded in distorted bicapped square-antiprismatic polyhedra formed by three nitrogen atoms of ligand  $\text{L}$ , a solvent molecule ( $\text{MeOH}$  or  $\text{H}_2\text{O}$ ) and three nitrate anions bound in the bidentate mode. In the solid state, complexes **1–3** are linked via  $\text{O} \cdots \text{H} \cdots \text{O}$ ,  $\text{N} \cdots \text{H} \cdots \text{O}$ ,  $\text{C} \cdots \text{H} \cdots \text{O}$  and  $\pi \cdots \pi$  interactions. Complex **3** exhibits bright green luminescence (CIE 0.28, 0.56) with a quantum yield of 58% due to the favorable energy difference between the ligand triplet state ( ${}^3\pi - \pi^*$ ) and the excited state of  $\text{Tb}^{3+}$  [ $\Delta E$  ( ${}^3\pi\pi^* - {}^5\text{D}_4$ ) =  $3129 \text{ cm}^{-1}$ ], rendering this compound a promising candidate for the fabrication of luminescent materials. On the contrary, for the  $\text{Eu}^{3+}$ -polypyridyl complex **1**, red emission (CIE 0.41, 0.23) and a relatively low luminescence efficiency are noted (quantum yield 21%), which is attributed to poor matching of the ligand triplet state and the excited emissive states of the metal ion [ $\Delta E$  ( ${}^3\pi\pi^* - {}^5\text{D}_0$ ) =  $6269 \text{ cm}^{-1}$ ]. For **1** and **3**, the lifetimes of the excited states are 960 and 1700  $\mu\text{s}$ , respectively.

## 1. Introduction

In recent years, lanthanide complexes have attracted great interest because of applications as light-converting optical materials, light-emitting layers in electroluminescent devices, and contrast agents for magnetic resonance imaging and luminescent probes in biology [2–4]. The chemistry and spectroscopy of lanthanide ions and d-shell transition metal ions differ considerably, and the shielding of the 4f orbitals by the filled  $5p^6 6s^2$  subshells results in special optical features (characteristic sharp emission, excited-state luminescence lifetime up to milliseconds, Stokes-shift larger than 200 nm). Lanthanide ions have characteristic narrow line-like emissions of optically pure colors that are nearly unaffected by the ligand field [6]. However, the spin and

parity forbidden nature of the f-f transitions in lanthanide ions renders direct photoexcitation disfavored, which causes small UV-vis absorption coefficients (usually less than  $10 \text{ M}^{-1} \text{ cm}^{-1}$ ). Advantageous is that the emission color can be easily tuned over the visible spectrum simply by interchanging lanthanide ions, which is facilitated by the common coordination chemistry, for example,  $\text{Eu}^{3+}$  (red),  $\text{Tb}^{3+}$  (green),  $\text{Sm}^{3+}$  (pink/orange), and  $\text{Dy}^{3+}$  (yellow/white) [7].

To overcome the forbidden nature and low energy absorption of the 4f-4f transitions, organic ligands, which function as chromophores for the absorption of light and assist the energy transfer to the lanthanide ions, can be introduced in the metal coordination sphere. This phenomenon is known as “antenna effect” and plays a notable role in the improvement of the emission efficiency of lanthanide ions [8]. In this

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