

## Novel lanthanide complexes as platform for ligand-to-metal charge transfer of low energies

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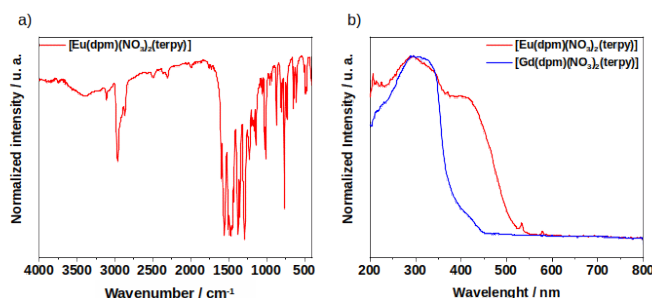
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### Highlights

Synthesis, characterization and investigation of the luminescence quenching processes via ligand-to-metal charge transfer in lanthanide ion coordination compounds.

### Abstract

Coordination compounds of trivalent lanthanide ions ( $\text{Ln}^{3+}$ ) are an important field of research due to their unique spectroscopic properties. Generally, these compounds exhibit high emission intensities with characteristic colors, reflecting the energy structure of the lanthanide ion when it is coordinated by luminescence-sensitizing ligands. However, the presence of non-radiative channels such as multiphonon relaxation and low-energy ligand-to-metal charge transfer (LMCT) states can contribute to the luminescence quenching processes. Despite advances in the investigation of the nature of LMCT states, the main structural factors that contribute to these deactivating processes are not well understood in the literature yet. In this context, the present work reports the synthesis, characterization and studies of the luminescent properties of new trivalent lanthanide ion compounds ( $\text{Ln}^{3+}$ :  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$ ) containing 2,2',6',2''-terpyridine (terpy) and  $\beta$ -diketonate ligands, where  $\beta$ -dic: acetylacetonate (acac), dibenzoylmethanate (dpm) and benzoylacetonate (bzac), presenting the  $[\text{Ln}(\beta\text{-dic})(\text{NO}_3)_2(\text{terpy})]$  general formula. Particularly, this study is focused on a class of compounds that present LMCT states of low energies. The synthesized complexes were characterized using infrared absorption spectroscopy (FT-IR), thermogravimetric analysis (TGA), diffuse reflectance and luminescence spectroscopy techniques. The characterization data for  $[\text{Ln}(\text{dpm})(\text{NO}_3)_2(\text{terpy})]$  are presented as representative ones (Figures 1a and 1b). The FT-IR spectrum of this complex suggests that ligands are coordinated to the metal ion via oxygen atoms. Interestingly, the diffuse reflectance spectrum for the  $[\text{Eu}(\text{dpm})(\text{NO}_3)_2(\text{terpy})]$  complex (Figure 1b) shows a broad band in the longer wavelength spectral region that may be assigned to a ligand-LMCT state. Similar behavior has been observed for analogous complexes with different diketonate ligands. This finding suggests that the luminescence quenching via LMCT state is quite efficient in these compounds. Consequently, all investigated complexes exhibited very low luminescence intensities, which make them good candidates for further understanding the role of the LMCT state in lanthanide ion compounds.



**Figure 1.** (a) Absorption spectra in the infrared region (b) Reflectance spectra of the complexes in the solid state.

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