



# A new overview on rare earth diphenylphosphinates: Europium characteristic luminescence of low dimensional nanostructured materials



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## ABSTRACT

Porous crystalline luminescent polymer compounds have attracted huge interest due to their supramolecular structures, aesthetically attractive structural topologies and potentialities for innovative technological applications. However, wet route precipitation or hydro/solvothermal methods may lead to the formation of highly insoluble porous coordination networks, as is true of europium diphenylphosphinates –  $[\text{Eu}(\text{dpp})_3]_n$ . The aim of this work was to study the optical behavior and its relation to the structure of  $[\text{Eu}(\text{dpp})_3]_n$  complexes obtained through different synthetic approaches by precipitation: wet route (WRS), ultrasound-assisted wet route (U-WRS), modulator-assisted wet route (M-WRS) and wet route synthesis with solvothermal treatment (S-WRS). These methodologies allowed to synthesize crystalline materials in which both chelate and bridged coordination modes coexist, and they were efficient for obtaining stick-shaped 1D1 nanostructured materials with well-defined optical properties. Changes in precipitation kinetics and crystalline phases formation rate led to a distribution of  $\text{Eu}^{3+}$  ions in higher symmetry sites (HSS). S-WRS, transforming part of the less symmetrical sites into HSS, provided a better ordering of  $[\text{Eu}(\text{dpp})_3]_n$ . Furthermore, this is the first report of two or more symmetry sites for  $\text{Eu}^{3+}$  in a pure  $[\text{Eu}(\text{dpp})_3]_n$  matrix.

## 1. Introduction

The search for highly porous and crystalline polymer compounds has become relevant in the research around the world and has generated, in the last three decades [1], a growing interest not only in the scientific community but also in several areas of technology. Main reasons for this are due to their supramolecular structures, aesthetically attractive structural topologies and potentialities for innovative technological applications of high added value [2].

Actually, these singular compounds led to the advent of a new and important class of multifunctional porous materials called metal-organic frameworks (MOFs) [3–5], which have unique characteristics and intrinsic properties that promote them to the level of excellent candidates for the most varied applications [6].

MOFs are chemically more interesting than conventional porous inorganic materials, since they can be manipulated to give rise to modifiable structures with desired topologies [7–9]. They are constructed from the connection between inorganic units with organic ligands, where the building units can be changed almost at will [10].

With such flexibility, MOFs are regarded as exceptional materials for the construction of functional entities at the interface of

nanocrystalline solids, allowing the control of their properties [10].

Furthermore, allying organic linkers (that can act as bridging linkers, such as carboxylated and phosphorylated linkers) to the flexible coordination modes and the high coordination number of trivalent rare earth cations ( $\text{RE}^{3+}$ ) is an efficient strategy to obtain porous coordination networks with channels and cavities that can be emptied or filled without collapse of the crystalline structure.

These trivalent rare earth-based MOFs –  $\text{RE}^{3+}$  MOFs – [11] present odd luminescent and magnetic properties. This is due to the different  $\text{RE}^{3+}$ - $\text{RE}^{3+}$  and/or  $\text{RE}^{3+}$ -ligand chemical environments imposed by the coordination network, leading to several relaxation mechanisms, such as ligand- $\text{RE}^{3+}$  cross relaxation and 4f-4f intraconfigurational transitions.

Among the several reported applications in the literature for  $\text{RE}^{3+}$  MOFs, it is possible to highlight their use in the sensing of humidity, pH, temperature and explosives [12,13].

Therefore, it is of interest the rational design and synthesis of  $\text{RE}^{3+}$  MOFs, looking forward to a better understanding of their optical and structural properties, which could allow applications in an improved way with great technological power.

However, obtaining  $\text{RE}^{3+}$  MOFs by wet route precipitation or

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hydro/solvothermal methods may lead to the formation of highly insoluble porous coordination networks in different solvents commonly used in the laboratory, either polar or non-polar.

This variant makes it difficult to obtain crystals with a long-range periodic arrangement of perfectly stacked unit cells that can be easily characterized by single crystal X-ray diffraction (SCXRD), considered one of the most powerful techniques for structural elucidation of crystalline materials [14].

Rare earth diphenylphosphinates –  $[\text{RE}(\text{dpp})_3]_n$ , synthesized by direct reaction between a rare earth chloride ( $\text{RECl}_3$ ) and diphenylphosphinic acid ( $\text{Hdpp}$ ), are authentic examples that integrate this class of materials presenting very low solubilities that do not produce single crystals.

In this work, we report for the first time – to the best of our knowledge – that modifications in synthetic methods and strict control of synthesis parameters in  $[\text{RE}(\text{dpp})_3]_n$  preparations could lead to the formation of materials with a greater crystallinity with defined morphology and size and mainly with well-defined optical properties, opening opportunities for future technological applications of these phosphinates in lighting, ionizing radiation detection and sensing.

To achieve that, four different synthetic approaches by precipitation were addressed: wet route (WRS), ultrasound-assisted wet route (U-WRS), modulator-assisted wet route (M-WRS) and wet route synthesis with solvothermal treatment (S-WRS).

Acoustic cavitation in  $[\text{RE}(\text{dpp})_3]_n$  synthesis aims the design of an environment by which the interoccurrence of homogeneous nucleation and a significant increase in the speed of recrystallization are prioritized when compared to the conventional methods applied in the preparation of nanostructured materials [15–18].

On the other hand, coordination modulators behave in a competitive way with the organic ligand by coordination with metallic ions present in solution, regulating nucleation and reducing crystal growth rate and avoiding precipitation of amorphous products [10,19]. In this way, they provide a more accurate control of the size and morphology of the crystals, allowing the formation of nanoparticles [20]. Indeed, modulation is a suitable strategy to improve the final product crystallinity and the synthesis reproducibility [21].

And last but not least, solvothermal process is useful for achieving thermodynamically stable and metastable states, contributing to the formation of new materials which cannot be easily synthesized from conventional synthetic routes [22].

### 1.1. Background

Studied since the 1970s,  $[\text{RE}(\text{dpp})_3]_n$  are presented as peculiar and somewhat intriguing materials. They have two distinct symmetry sites for trivalent rare earth, thermal stability similar to that of inorganic phosphates and mesoporous structure with the presence of crystalline and non-crystalline domains.

In the first report of rare earth diphenylphosphinates preparation, Dunstan and Vicentini [23] proposed the general formula  $\text{RE}(\text{dpp})_3 \cdot n(\text{H}_2\text{O})$  for the synthesized coordination compounds.

Bel'tyukova [24] in 1989 published the first spectroscopic study involving compounds formed by trivalent europium and diphenylphosphinate ligand reported in the literature.

Innocentini and co-workers [25] synthesized a non-hygroscopic europium diphenylphosphinate with high thermal stability in comparison with other coordination compounds and reasonable ligand-to-metal energy transfer ability via antenna effect.

Stucchi [26], Scarpari [27,28] and their collaborators prepared a series of rare earth diphenylphosphinates and binary compounds, examining their optical behavior to predict some structural information.

Francisco et al. [29] suggested the presence of one or more symmetry sites for  $\text{RE}^{3+}$  in a europium-doped yttrium diphenylphosphinate matrix. In another study [30], applying the hydrothermal synthesis, they obtained unidimensional structures in the form of rods.

According to Abreu et al. [31,32],  $[\text{RE}(\text{dpp})_3]$  are polycrystalline materials in a polymeric arrangement, resulting in coordination sites of different symmetries, and can be represented by  $[\text{RE}(\text{dpp})_3]_n$ .

Souza [33], Munhoz [34] and their co-workers have investigated the potential application of lanthanum and cerium diphenylphosphinates (and their doping) as UV absorbers.

Rosa et al. [35] examined the effect of cerium as a sensitizer and activator on the compounds  $[\text{La}(\text{dpp})_3] \cdot \text{Eu}^{3+}$  and  $[\text{La}(\text{dpp})_3] \cdot \text{Eu}^{3+}, \text{Tb}^{3+}$  and their possible uses as emission-emitting luminescent materials of white light.

In addition, Rosa et al. [36] proposed that diphenylphosphinate coordination compounds of  $\text{La}^{3+} \cdot \text{Ce}^{3+} \cdot \text{Eu}^{3+} / \text{La}^{3+} \cdot \text{Ce}^{3+} \cdot \text{Tb}^{3+}$  ternary systems exist as cross-linked coordination polymers, forming a binuclear system:  $[\text{RE}_2(\text{dpp})_6]_n$ . They also verified that those ternary systems have an appreciable resistance to ionizing radiation.

Recently, Bim et al. [37] carried out a systematic study of trivalent rare earth diphenylphosphinates in an attempt to elucidate the structure and symmetry of the trivalent lanthanide crystallographic site, as well as the coordination mode of the  $\text{dpp}^-$  ligand to  $\text{RE}^{3+}$  cations.

Many gaps regarding the structure of  $[\text{RE}(\text{dpp})_3]_n$  are still found without complete investigation data. In previously presented works, the authors did not include details about the composition and coordination sphere of the compounds, nor did they refer to the symmetry of  $\text{RE}^{3+}$  crystallographic site, the coordination mode of  $\text{dpp}^-$  ligand to metal cations or thermal behavior presented by them.

Thus, a more comprehensive study of rare earth diphenylphosphinates in terms of their structures and intrinsic optical properties will provide the means to both promote them to the level of metal-organic frameworks and to suggest applications of scientific, technological and industrial interest.

## 2. Experimental section

$[\text{RE}(\text{dpp})_3]_n$  synthesis was reviewed and modified from that initially proposed by Stucchi et al. [26] to more precise and controlled synthesis parameters, such as temperature and atmosphere of the reaction medium, stirring, reaction time and solvent used. It is emphasized that the authors of this paper have been working with the complete series of rare earth diphenylphosphinates ( $[\text{RE}(\text{dpp})_3]_n$ ,  $\text{RE}^{3+} = \text{Y}^{3+}$ ,  $\text{La}^{3+}$  through  $\text{Lu}^{3+}$ ); however, for the scope of this paper, we decided to focus on  $[\text{Eu}(\text{dpp})_3]_n$  results, addressing the intrinsic optical properties of trivalent europium ion. *Purity and brands:*  $\text{EuCl}_3$  solution was obtained by the stoichiometric hydrochloric acid (Sigma-Aldrich, 37%) attack on  $\text{Eu}_2\text{O}_3$  (Aldrich, 99.99%) and its concentration was determined by complexation titrimetry, diphenylphosphinic acid (Aldrich,  $\geq 98.0\%$ ), methanoic acid (Sigma-Aldrich,  $\geq 95\%$ ), ethanol (Sigma-Aldrich,  $\geq 99.5\%$ ), compressed nitrogen gas (White Martins, 99.998%).

### 2.1. Wet route precipitation synthesis (WRS)

The preparation consisted of mixing  $\text{EuCl}_3$  solution (4.40 mL, 0.4488 mmol) with ligand solution (diphenylphosphinic acid,  $\text{Hdpp}$  – 0.2998 g, 1.3464 mmol) in 1:3 metal-to-ligand ratio. The solvent used was 40.00 mL of a 1:1 mixture of ethanol and distilled water. The ligand solution was placed in a three-necked round bottom flask, kept in a microprocessed hot water bath. The temperature of the reaction medium was maintained at  $72 \pm 3^\circ\text{C}$  and measured by thermocouple (NTC sensor - nickel-plated brass -  $\varnothing 6.35 \text{ mm/L} = 22 \text{ mm}$ ) coupled to a digital temperature controller (Ageon G101 Color). The ligand solution was subjected to constant stirring and the round bottom flask saturated with  $\text{N}_2(\text{g})$ .  $\text{EuCl}_3$  solution was slowly dripped onto the ligand solution via a 10-mL burette, causing the precipitation of  $[\text{Eu}(\text{dpp})_3]_n$ . After the addition of  $\text{EuCl}_3$  solution, the mixture (precipitate and supernatant) remained in the hot water bath under stirring for 60 min. The flask was then removed from the system and kept under stirring for extra 30 min.

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