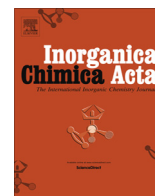




Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: [www.elsevier.com/locate/ica](http://www.elsevier.com/locate/ica)

Research paper

## Microwave Synthesis of a photoluminescent Metal-Organic Framework based on a rigid tetraphosphonate linker

Ana D.G. Firmino<sup>a,b</sup>, Ricardo F. Mendes<sup>a</sup>, Duarte Ananias<sup>a,c</sup>, Sérgio M.F. Vilela<sup>a,b</sup>, Luís D. Carlos<sup>c</sup>, João P.C. Tomé<sup>b,d</sup>, João Rocha<sup>a</sup>, Filipe A. Almeida Paz<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>b</sup> Department of Chemistry, QOPNA, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>c</sup> Department of Physics, CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>d</sup> Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

## ARTICLE INFO

## Article history:

Received 16 March 2016

Received in revised form 10 May 2016

Accepted 13 May 2016

Available online xxxxx

## Keywords:

Metal-Organic Frameworks

Lanthanides

Microwave Synthesis

Phosphonic acids

Photoluminescence

## ABSTRACT

In this manuscript, microwave-assisted synthesis was used to prepare a new organic building block and a Metal-Organic Framework based on this unit. The tetrapodal organic linker [1,1'-biphenyl]-3,3',5,5'-tetrayltetrakis(phosphonic acid) (H<sub>8</sub>btp) was combined with lanthanide cations affording the isotypical 2D lanthanide-organic frameworks [Ln<sub>4</sub>(H<sub>6</sub>btp)<sub>2</sub>(H<sub>4</sub>btp)<sub>2</sub>(H<sub>8</sub>btp)(H<sub>2</sub>O)<sub>16</sub>]·12H<sub>2</sub>O [where Ln<sup>3+</sup> = La<sup>3+</sup> (**1**), (La<sub>0.9</sub>Eu<sub>0.1</sub>)<sup>3+</sup> (**2**) and (La<sub>0.9</sub>Tb<sub>0.1</sub>)<sup>3+</sup> (**3**)]. **1** was isolated as large single-crystals and its crystal structure was solved by single-crystal X-ray diffraction. Phase identification of the Eu<sup>3+</sup>- (**2**) and Tb<sup>3+</sup>-based (**3**) materials was performed by powder X-ray diffraction. Compound **1** consists of two-dimensional double-deck layers, characterized by an unprecedented tetranodal 2,4,4,4-connected layered network, with total point symbol {4-8<sup>5</sup>}<sub>2</sub>{4<sup>2</sup>.8<sup>4</sup>}{4<sup>3</sup>.8<sup>2</sup>.10}<sub>4</sub>{4}<sub>2</sub>. Supramolecular π-π interactions exist both within and between layers. **1-3** were fully characterized in the solid-state by a plethora of techniques [elemental and thermogravimetric analyses, electron microscopy (SEM and EDS), FT-IR spectroscopy and solid-state NMR]. Photoluminescence properties of the optically-active mixed-lanthanide materials **2** and **3** reveal that the employed H<sub>8-x</sub>btp<sup>-x</sup> residues are better suited to sensitize Tb<sup>3+</sup> than Eu<sup>3+</sup>, with the measured lifetimes being of 0.83 ± 0.01 and 0.22 ± 0.01 ms, respectively.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Studies on Metal-Organic Frameworks (MOFs) remain an intensive area of scientific research [1] because of their interesting architectures and properties (i.e., large inner surface areas [2] allied with porosity [3], tunable pore sizes and topologies [4]), making them potential candidates to be applied in a wide range of scientific fields, such as ion exchange [5], gas storage and separation [6], catalysis [7], photoluminescence [8], drug delivery [9], magnetism [10], as sensors [11], in pollutant sequestration [12], protonic conductivity [13], among others.

Microwave-assisted synthesis (MWAS) is often considered to be an excellent new “green” synthetic tool in current organic chemistry. The uniform and efficient irradiation dispersion in the reaction medium accelerates the synthetic processes leading to the synthesis of the targeted molecules in shorter times and in a much cleaner way (when compared with conventional heating methods)

[14]. This simple and convenient synthetic approach is also an excellent choice for the preparation of large amounts of phase-pure MOFs with high reaction yields. Compared with other methods (e.g., slow diffusion, ultrasound-assisted, one-pot and conventional hydro(solvo)thermal synthesis) MWAS is an energy efficient synthetic methodology towards the preparation of MOF materials: i) with control of morphology; ii) phase selectivity; iii) homogeneous particle distribution; and iv) close control of several reaction parameters (i.e., temperature, pressure, irradiation power and stirring) [15]. Additionally, MWAS has also been used to scale-up reactions because the heating process is relatively independent of the reaction volume [16].

Contrasting with MOFs based on carboxylate-containing organic ligands, phosphonate-based networks still remain an underexplored research area [17], though clearly the number of reported structures bearing this type of ligands has been steadily increasing in recent years [18]. Phosphonic acid functional groups, possessing a tetrahedral geometry, allow nevertheless the formation of strong interactions with metal centers while the C-PO<sub>3</sub> bond is very stable at high temperatures. These features confer to the isolated MOF

\* Corresponding author.

E-mail address: [filipe.paz@ua.pt](mailto:filipe.paz@ua.pt) (F.A. Almeida Paz).

architectures great thermal and mechanical stabilities, crucial parameters for certain applications. In this context, tetrapodal phosphonate-based organic linkers are very scarcely used in the synthesis of MOFs, particularly when the selected metal centers are rare-earth cations. Based on an extensive literature search, only a few of lanthanide-organic frameworks (LnOFs) containing aromatic ( $H_8L^1$ ,  $H_8L^2$  and  $H_8L^3$ ; Scheme 1) and aliphatic ( $H_8L^4$ ,  $H_8L^5$ ,  $H_8L^6$ ,  $H_8L^7$  and  $H_8L^8$ ; Scheme 1) tetrapodal phosphonate organic molecules were reported to date [19]. In this work, and following our previous incursions in the design of LnOFs, we wish to report the novel [1,1'-biphenyl]-3,3',5,5'-tetrayltetrakis(phosphonic acid) ( $H_8btp$ ) organic linker bearing four phosphonic acid groups attached to a semi-rigid organic core based on two aromatic rings. This molecule was used in the preparation of a new family of isotypical LnOF materials formulated as  $[Ln_4(H_6btp)_2(H_4btp)_2(H_8btp)(H_2O)_{16}] \cdot 12H_2O$  [where  $Ln^{3+} = La^{3+}$  (**1**),  $(La_{0.9}Eu_{0.1})^{3+}$  (**2**) and  $(La_{0.9}Tb_{0.1})^{3+}$  (**3**)], under microwave irradiation (100 °C for 60 min; 50 W). The crystal structure of **1** was unveiled by single-crystal X-ray diffraction showing that this compound crystallizes in the tetragonal space group  $P-4b2$ . The photoluminescence properties of compounds **2** and **3** were investigated both at ambient and at low temperature, clearly evidencing that  $H_{8-x}btp^{-x}$  residues are good sensitizers for the  $Tb^{3+}$  cations.

## 2. Experimental section

### 2.1. General instrumentation

SEM (Scanning Electron Microscopy) images were acquired using a high-resolution Hitachi SU-70 working at 4 kV. Samples

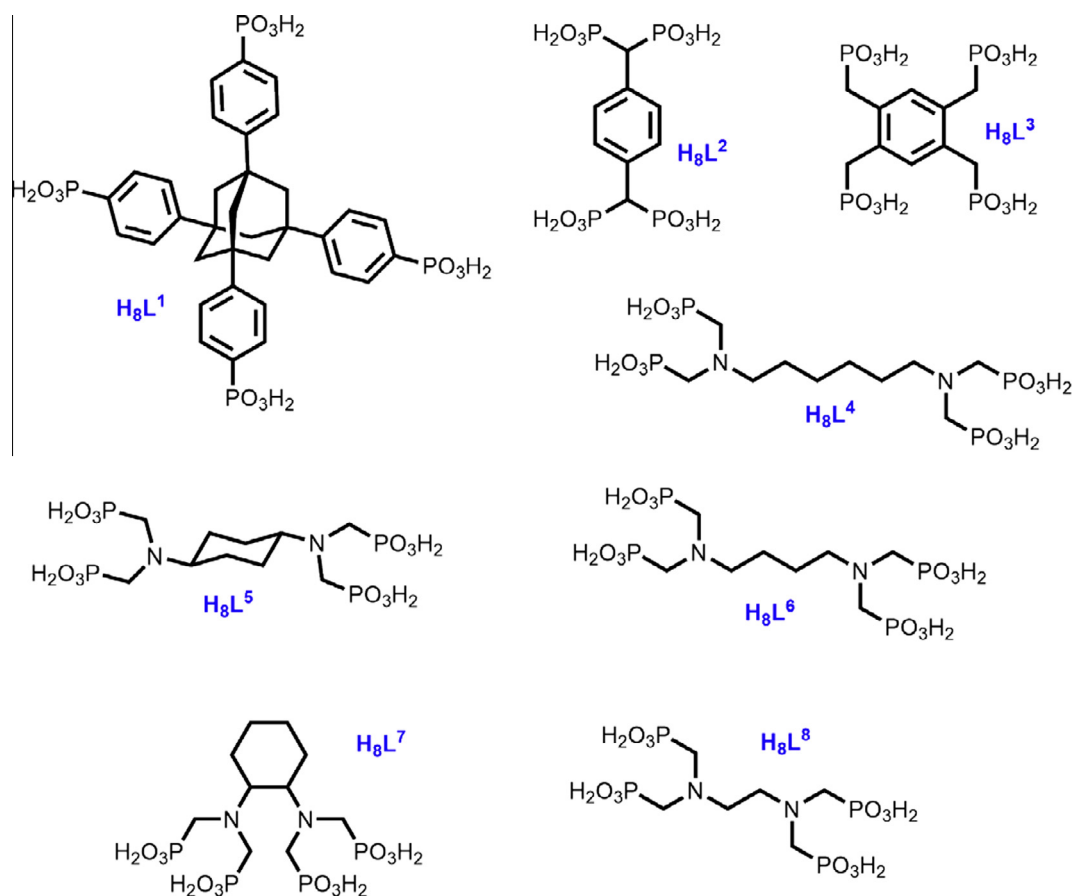
were prepared by deposition on aluminium sample holders followed by carbon coating using an Emitech K950X carbon evaporator. EDS (Energy Dispersive X-ray Spectroscopy) data and SEM mapping images were recorded using the same microscope working at 15 kV while employing either a Bruker Quantax 400 or a Sprit 1.9 EDS microanalysis system.

Thermogravimetric analyses (TGA) were carried out using a Shimadzu TGA 50, from ambient temperature to ca. 800 °C (heating rate of 5 °C/min) under a continuous stream of air at a flow rate of 20 mL min<sup>-1</sup>.

Fourier Transform Infrared (FT-IR) spectra (in the spectral range of 4000–350 cm<sup>-1</sup>) were recorded as KBr pellets (2 mg of sample were mixed in a mortar with 200 mg of KBr) using a Bruker Tensor 27 spectrometer by averaging 256 scans at a maximum resolution of 2 cm<sup>-1</sup>.

Elemental analyses for C and H were performed with a Truspec Micro CHNS 630-200-200 elemental analyzer at the Department of Chemistry, University of Aveiro. Analysis parameters: sample amount between 1 and 2 mg; combustion furnace temperature = 1075 °C; after burner temperature = 850 °C. Detection method: carbon – infrared absorption; hydrogen – infrared absorption. Analysis time = 4 min. Gasses required: carrier – helium; combustion – oxygen; pneumatic – compressed air.

Routine Powder X-ray Diffraction (PXRD) data for all prepared materials were collected at ambient temperature on a Empyrean PANalytical diffractometer (Cu K<sub>α1,2</sub> X-radiation,  $\lambda_1 = 1.540598$  Å;  $\lambda_2 = 1.544426$  Å), equipped with an PIXcel 1D detector and a flat-plate sample holder in a Bragg-Brentano para-focusing optics configuration (45 kV, 40 mA). Intensity data were collected by the



**Scheme 1.** Chemical structure of tetrapodal phosphonate-based organic ligands reported in the literature and used in the preparation of lanthanide-organic frameworks (LnOFs).

Download English Version:

<https://daneshyari.com/en/article/5151948>

Download Persian Version:

<https://daneshyari.com/article/5151948>

[Daneshyari.com](https://daneshyari.com)