



## Review

Metal–Organic Frameworks assembled from tetraphosphonic ligands and lanthanides <sup>☆</sup>Ana D.G. Firmino <sup>a,b</sup>, Flávio Figueira <sup>a</sup>, João P.C. Tomé <sup>b,c</sup>, Filipe A. Almeida Paz <sup>a,\*</sup>, João Rocha <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> Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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Dedicated to Prof. Pierre Braunstein on the occasion of his 70th birthday.

## ABSTRACT

The number of Metal–Organic Frameworks based on lanthanide (poly)phosphonates reported has been increasing exponentially, mainly because of the many different uses of diphosphonic acid molecules, which are, in general, readily available from commercial sources. Besides their remarkable structural diversity, lanthanide (poly)phosphonate linkers offer advantages over the more widely used carboxylate (or nitrogen-based) molecules for developing new materials, prompted by their remarkable chemical, mechanical and thermal robustness. This work reviews the synthesis routes and the structural types of tetraphosphonic-based Metal–Organic Frameworks bearing lanthanide cations, describing also the plethora of properties and functionalities exhibited by these networks (e.g., photoluminescence, proton conductivity, ion-exchange properties and heterogeneous catalysis). Thermal stability of the reported networks is also addressed in a comparative fashion, assessing the role of additional (ancillary) linkers and the level of hydration.

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**Abbreviations:** C–P, carbon phosphorous bond; dppf, 1,1'-bis(diphenylphosphino)ferrocene;  $H_8L^1$ , 1,2-diaminoethane-*N,N,N',N'*-tetrakis(methylenephosphonic acid);  $H_8L^2$ , 1,4-diaminobutane-*N,N,N',N'*-tetrakis(methylenephosphonic acid);  $H_8L^3$ , 1,6-diaminohexane-*N,N,N',N'*-tetrakis(methylenephosphonic acid);  $H_8L^4$ , 1,2-diaminocyclohexane-*N,N,N',N'*-tetrakis(methylenephosphonic acid);  $H_8L^5$ , 1,4-diaminocyclohexane-*N,N,N',N'*-tetrakis(methylenephosphonic acid);  $H_8L^6$ , 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrakis(methylenephosphonic acid);  $H_8L^7$ , 1,2,4,5-tetrakisphosphonomethylbenzene;  $H_8L^8$ , [1,4-phenylenebis(methanetriyl)]tetraphosphonic acid;  $H_8L^9$ , tetrakis[4-phosphonophenyl]methane;  $H_8L^{10}$ , 1,3,5,7-tetrakis(4-phosphonophenyl)adamantane;  $H_8L^{11}$ , [1,1'-biphenyl]-3,3',5,5'-tetrayltetrakis(phosphonic acid); LnOF, Lanthanide–Organic Framework; MOF, Metal–Organic Framework; MRI, magnetic resonance imaging; NO, nitric oxide; PBU, primary building units; RH, relative humidity; SBU, secondary building units; TPM, tetraphenylmethane; OD, zero dimensional; 1D, unidimensional; 2D, bidimensional; 3D, tridimensional.

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## 1. Introduction

Metal–Organic Frameworks (MOFs) remain the focus of intense research, mostly driven by both, the interest in finding new and intriguing molecular architectures, and the relevance of developing new and more efficient materials for various applications [1–9]. The main goal in MOFs synthesis is to establish the optimal conditions leading to the formation of stable bridges between the inorganic and organic building blocks, while simultaneously controlling the crystallization kinetics allowing the nucleation and growth of a desired pure phase [10]. “Design principles” and “predictability” are, thus, recurrent topics in MOF research. In this context, MOFs based on carboxylate or nitrogen-based ligands are most studied because: (i) molecules are easily synthesized or are readily available from commercial sources at suitable prices; (ii) large-single crystals may be obtained for a wide range of synthetic conditions; (iii) “isoreticular design” of frameworks is possible [11] through the rational design of new ligands based on previously reported ligands. These advantages are shadowed by the well-known poor stability (thermal, mechanical and/or chemical, especially toward hydrolysis) of such MOFs, which ultimately hinders their practical use [12].

Over the years, a number of research groups working on metal phosphonates chemistry have pioneered the discovery of many interesting framework architectures, including layered and microporous structures based on bi-, tri- or multitopic anionic organic units, such as multipodal phosphonates [13–16], aminophosphonates [17] and phosphonocarboxylates [18]. Advantages of the phosphonate groups include: (i) C–PO<sub>3</sub> bond is stable at high temperatures and under a wide range of chemical conditions; (ii) three oxygens connected to the phosphorus atom form tetrahedral building units reminiscent of zeolite building blocks [19]. The latter feature ensures bonds to metal centers stronger than the bonds formed by the carboxylate (or nitrogen-based) groups, endowing stability and robustness to the ensuing MOFs. However, this feature makes phosphonate coordination less predictable: the richness and variety of coordination modes of these tetrahedral groups to metal centers are vast, increasing when lanthanides are used (due to their large coordination numbers), ultimately leading to the statistical possibility of a wide variety of secondary building units (SBUs) in solution during the crystallization process [20]. This accounts, to a large extent, for the poor solubility of metal phosphonates and their typical isolation as microcrystalline powders. It is, therefore, not surprising that most research in this field has been focused on diphosphonates, often leading to densely stacked layered structures displaying excellent thermal and mechanical robustness [21–23]. Recently, researchers have focused their attention on tripodal nonlinear phosphonoaromatic ligands, which afford the interesting architectures already reviewed by Taddei and co-workers [24]. The present review goes further and focuses on more complex and larger organic molecules, particularly tetraphosphonic acids, self-assembled with lanthanide cations. We note that these molecules are not common and usually not readily available from commercial suppliers [25]. They have to be

individually prepared in good yields and using straightforward reaction procedures. A brief compilation of the various organic chemistry reactions most commonly used is also provided here.

## 2. Tetrapodal phosphonic acids and LnOFs: general overview

A search in the literature and in the Cambridge Structural Database showed that the most significant and structurally relevant tetrapodal phosphonate-based organic molecules used to date in the preparation of LnOFs are those depicted in Scheme 1. For a better comparative purpose, these ligands can immediately be divided into two main families: phosphonoaliphatic and phosphonoaromatic organic linkers,  $\text{HgL}^1$ – $\text{HgL}^6$  and  $\text{HgL}^7$ – $\text{HgL}^{11}$ , respectively. Noteworthy, in the former family the ligands are rich in nitrogen atoms, mostly originating from the synthetic routes used to prepare the molecules and briefly reviewed in this manuscript. Table 1 summarizes the various LnOFs prepared and reported using these tetraphosphonic acid linkers.

In the broad field of MOFs, there are two main architectural factors upon which these networks are typically based: secondary building units and organic linkers [26]. Due to the unpredictability of phosphonate groups toward the rational design or reticular synthesis of LnOFs, *i.e.*, their usual inability to maintain topological features or to form the same secondary building unit, either by extension of the organic ligand or modification of the lanthanide cations, researchers have focused their efforts on the preparation of new (pre-determined) ligands with specific shapes and sizes of the organic motif. Thus, the location of the C–P bond in the overall organic backbone of the MOF represents an important challenge and in the following section we summarize the principal routes for the synthesis of these molecules, particularly those depicted in Scheme 1.

Mono- or di-organophosphonates have a strong propensity to form layered structures. Efforts have been made to create porosity using this type of ligands [27]. Some of the strategies used to attempt to disrupt this “too efficient” crystal packing mode are: (i) use of polyphosphonate ligands; (ii) selection of phosphonate-based molecules with strong non-linear geometry motifs (mainly because flexible carbon chains tend to align and form pillared structures); (iii) increase the networks dimensionality using ancillary linkers. Systematization of all these factors to obtain a pre-designed porous phosphonate-MOF has not yet been accomplished. Phosphonates, as networks’ primary building units, do not follow the same “architectural” behavior observed in some families of isoreticular MOFs based on carboxylate or nitrogen-bearing ligands [11].

Phosphonate group may be bonded to metal cations in various ways. Combination of lanthanides and phosphonates constitutes a small group of compounds showing interesting architectures and properties [28]. It has been established that the wide range of coordination numbers shown by lanthanides is an advantage when they are coordinated to tetrahedral phosphonate-based compounds and their high level of protonation, *i.e.* protons that will

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