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# Sustainable Synthesis of a Catalytic Active One-Dimensional Lanthanide-Organic Coordination Polymer

Ricardo F. Mendes, Patrícia Silva, Margarida M. Antunes, Anabela A. Valente, Filipe A. Almeida Paz\*

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A rationalization of the synthetic conditions allowed the predictable fast sustainable preparation of  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]\cdot 4.5\text{H}_2\text{O}$  having a 1D coordination polymer. The material exhibits a remarkable chemical stability, can be converted into other layered compounds, and is an excellent catalyst surpassing other related materials.

With 15 years passed since the iconic report of MOF-5 from Yaghi's research group,<sup>1</sup> investigation on Metal-Organic Frameworks (MOFs) and coordination polymers (CPs), is currently being directed towards the use of these compounds as important components in the design of functional devices.<sup>2</sup> The symbiotic presence of metals, or clusters of metals, and organic linkers predictably organized into a well-defined crystalline structure clearly widened up the horizon of researcher working on the creation of novel materials with a wide variety of functionalities and/or applications such as permanent porosity, gas or molecule storage and separation,<sup>3</sup> catalytic activity, proton conductivity,<sup>4</sup> sensors or nanothermometers based on photoluminescence,<sup>5</sup> use as vehicles for drug delivery,<sup>6</sup> among many others.

We have been focused on the development of MOFs based on phosphonate linkers and rare-earth cations.<sup>7</sup> While, on the one hand, the tetrahedral connectivity of the phosphonate groups mimics well what occurs in Nature in, for example, zeolites, on the other hand it also induces the formation of robust, mechanically and thermally stable networks capable of enduring the adverse conditions of many daily applications (*e.g.*, high temperature, the action of oxidants or acids/bases, reutilization). The presence of rare-earth cations, particularly lanthanides, further permits the engineering of optical centers into the materials, leading to the preparation of photoluminescent compounds whose properties cannot only be closely controlled through selection of the centers included in the networks (*e.g.*, light "games" can be designed by dispersing into inert matrices optically-active cations such as  $\text{Tb}^{3+}$  or  $\text{Eu}^{3+}$ ), but also influenced by the organic linkers themselves (*e.g.*, through the so-called antenna effect).

Building on our investigations on lanthanide-polyphosphonate networks, we have recently reported the one-dimensional (1D) polymer  $[\text{Ln}(\text{H}_4\text{bmt})(\text{H}_3\text{bmt})(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$  ( $\text{H}_6\text{bmt}$  = benzene-1,3,5-triyltris(methylene)triphosphonic acid) capable of acting as an excellent heterogeneous catalyst in the methanolysis of styrene oxide, even outperforming commercial MOFs such as the nano-

sized HKUST-1.<sup>7e</sup> Because this 1D MOF exhibited much better catalytic activity than, for example, the 3D zeolitic network  $[\text{La}_2(\text{H}_3\text{bmt})_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$ ,<sup>7f</sup> these results prompted us to revise the organic linker nitrilotris(methylenephosphonic acid) ( $\text{H}_6\text{nmp}$ ) previously used by us to prepare active layered materials,<sup>7g</sup> investigate if low dimensional materials could also be isolated with the main objective to boost catalytic activity.

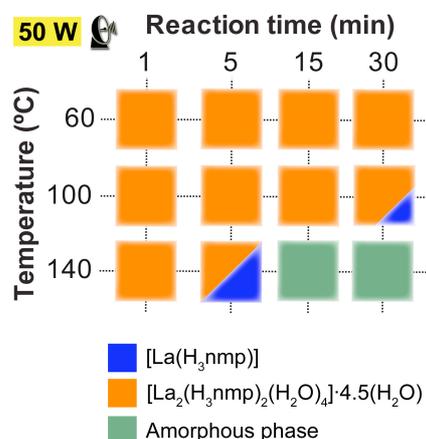
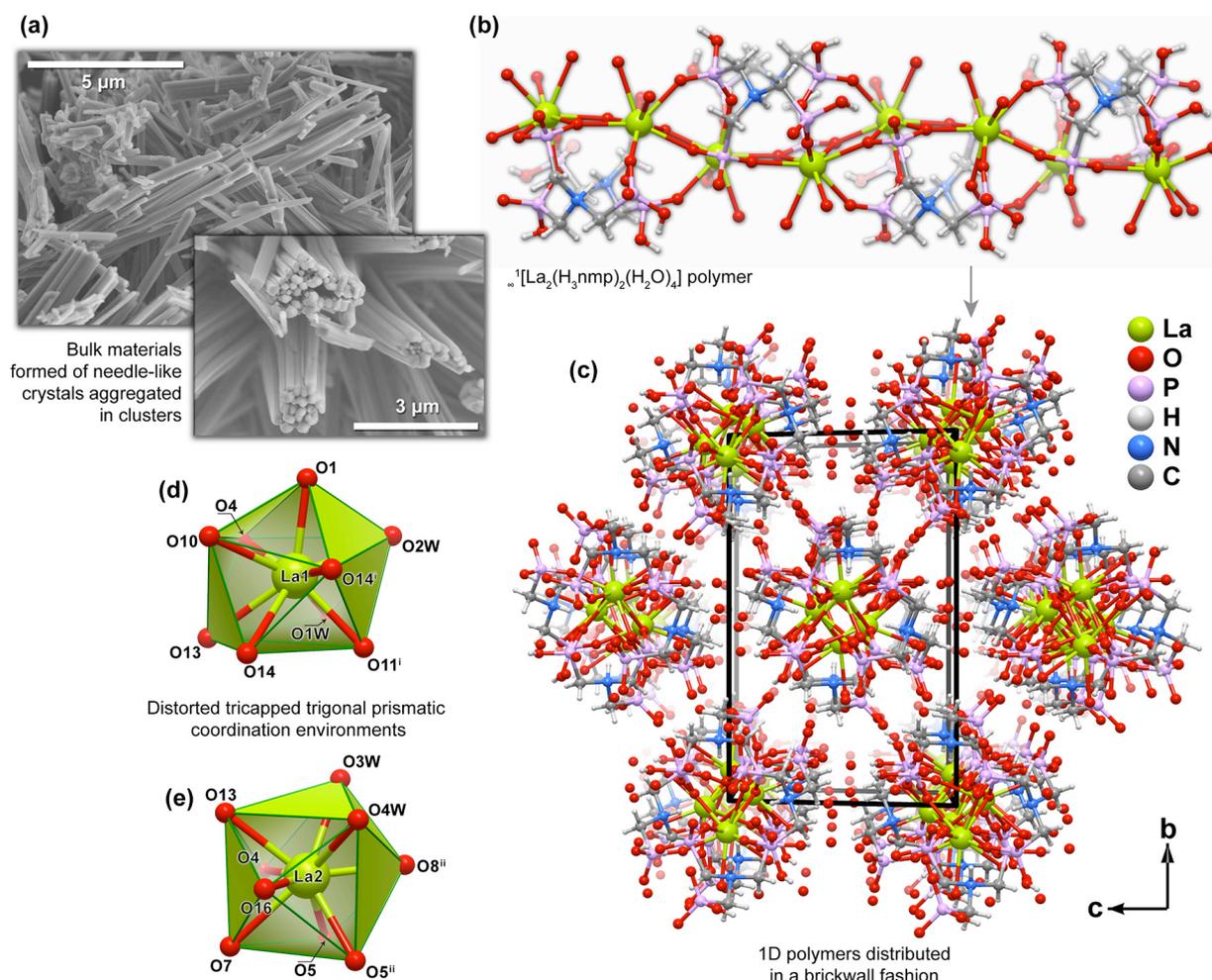


Fig. 1 Optimization diagram for the microwave-assisted synthesis of  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]\cdot 4.5\text{H}_2\text{O}$ .

One of the main challenges to prepare low dimensional CPs with polyphosphonic acid molecules is to control, in solution, the coordination step. Because we have already employed microwave irradiation for the  $\text{H}_6\text{nmp}$ , we envisaged that to promote instead the formation of 1D polymers one should first act directly on this step: first, the availability of the lanthanide cation should be diminished by changing the metal source to one much less soluble in water (the "green" solvent selected for the synthesis), second, the deprotonation of the phosphonate groups should also be considerably hindered to reduce the kinetics of crystal growth. Microwave irradiation was again used to promote a fast and uniform reaction between  $\text{La}_2\text{O}_3$  and  $\text{H}_6\text{nmp}$  in the presence of sulphuric acid. A new material, formulated as  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]\cdot 4.5\text{H}_2\text{O}$  (**1mw**), was isolated and, as expected, X-ray diffraction studies show that it is composed by  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$  1D CPs (see below). For a relatively mild microwave irradiation of 50W, **1mw** could be isolated in just 1 min of irradiation at the low temperature of 60 °C. Increasing the reaction time and/or the temperature, the known layered phase



**Fig. 2** (a) SEM pictures of  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4] \cdot 4.5\text{H}_2\text{O}$  (**1mw**). (b) 1D  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$  coordination polymer present in the crystal structure of **1op** and (c) crystal packing viewed in perspective along the [100] direction of the unit cell. (d-e) Polyhedral representation of the two distorted  $\{\text{LaO}_9\}$  tricapped trigonal prismatic coordination environments present in the crystal structure of **1op**. For selected bond lengths and angles see Tables S2 and S3 in the ESI. Symmetry transformations used to generate equivalent atoms: (i)  $1-x, 1-y, 1-z$ ; (ii)  $-x, 1-y, 1-z$ .

$[\text{La}(\text{H}_3\text{nmp})]$  is formed as a minor product,<sup>7b</sup> but at these more extreme synthetic conditions amorphous compounds are, nevertheless, systematically and preferentially obtained (Fig. 1). An alternative synthetic, and still sustainable, approach we have also developed for this material is the use of one-pot synthesis (**1op**): in the absence of acid, the material could be isolated at 120 °C under stirring for 4 hours. Hydrothermal approaches also yield the same material (**1h**) and require a lower temperature (100 °C), but much longer reaction times (3 days<sup>†</sup>) translating into considerable energy consumption.

The structural features of the material could only be unveiled by using a combination of high-resolution synchrotron powder X-ray diffraction with single-crystal X-ray diffraction, closely aided by various advanced bulk techniques such as solid-state NMR, FT-IR spectroscopy, thermoanalytical analyses and electron microscopy (Fig. 2a).<sup>†</sup> Independently of the preparation method, all materials exhibit the same structural features, particularly the  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$  polymer (Fig. S9<sup>†</sup>), with only small variations in average crystallite size being clearly noticeable (Fig. S6).<sup>†</sup>

The  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$  polymer (Fig. 2b) is assembled by

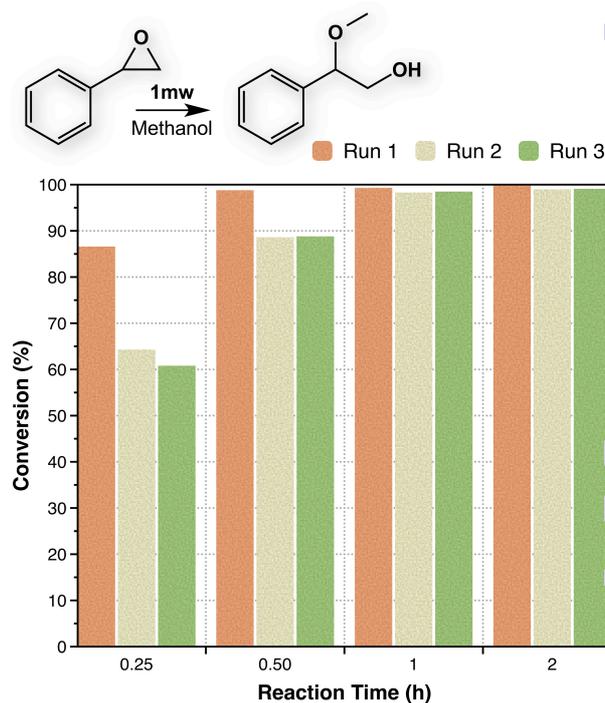
two crystallographically independent organic linkers and two  $\text{La}^{3+}$  metallic centers as depicted in Figs. 2d and 2e. Both metal centers are coordinated to two water molecules and seven oxygen atoms originating from neighbouring phosphonate groups, describing  $\{\text{LaO}_9\}$  coordination environments whose geometries resemble distorted tricapped trigonal prisms. This connectivity between metal centres leads to the formation of a zigzag 1D chain with intermetallic  $\text{La} \cdots \text{La}$  distances ranging between *ca.* 4.25 and 4.26 Å. Polymers grow along the [100] direction of the unit cell, packing in a typical brick-wall like fashion in the *bc* plane of the unit cell (Fig. 2c). Uncoordinated water molecules occupy the interstitial spaces between adjacent polymers. As shown from the thermoanalytical studies, structural integrity of the  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$  polymers is preserved while the coordinated water molecules remain attached to the metal centers. Once these are released (around *ca.* 100 °C), the material loses integrity and the crystal structure collapses (Figs. S4 and S5).<sup>†</sup> Even though  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4] \cdot 4.5\text{H}_2\text{O}$  can easily be obtained under various experimental conditions being composed of a 1D polymer embedded into a matrix of highly disordered water molecules, the compound exhibited an excellent chemical

resilience. The material was submitted to both acidic and basic conditions (see ESI for details<sup>†</sup>) and it was able to tolerate the addition of HCl 6M without the destruction of the network. The use of 50  $\mu\text{L}$  of either 1 M  $\text{H}_2\text{SO}_4$  or NaOH did not affect the compound; higher amounts led to the dissolution of the material. At neutral pH, the material retained crystallinity and structural integrity when immersed in boiling water for long periods of time.

**1mw** was tested as a heterogeneous catalyst in the alcoholysis of styrene oxide (PhEtO) with methanol or ethanol, and in the acetalization of benzaldehyde (BA) with methanol (see ESI for more details on the studies – Tables S5 and S6). The alcoholysis of PhEtO was faster with methanol than with ethanol, in line with that reported in the literature,<sup>7g, 8</sup> giving the corresponding  $\beta$ -alkoxy alcohol products with 100% selectivity and 99% yield at 30 min (2-methoxy-2-phenylethanol, MeOPhEtOH) and 3 h (2-ethoxy-2-phenylethanol, EtOPhEtOH). All reactions were always 100% selective and in the absence of **1mw** no reaction occurred. Catalytic tests were also performed in the polymer precursors ( $\text{La}_2\text{O}_3$  and  $\text{H}_6\text{nmp}$ ) and the heterogeneous nature of the reactions was investigated through leaching tests (see the ESI for experimental details and results and also a proposed mechanism for the heterogeneous catalytic reaction). A six-fold decrease in the amount of **1mw** from 20 to 3.3  $\text{g}_1 \text{L}^{-1}$  also led to similar outstanding catalytic results (Table S5).<sup>†</sup> The catalyst was reused in consecutive batch runs of the methanolysis of PhEtO (Fig. 3), using simple centrifugation and filtration operations: a slight decrease of the initial reaction rate from the first to the second run was observed, but then it remained fairly similar. Conversion was, at least, 99% in consecutive 2 h batch runs, with MeOPhEtOH selectivity being always 100%. While the structural integrity of **1mw** was always preserved, the average crystallite size decreased very slightly after the 1<sup>st</sup> run remaining relatively unchanged in subsequent runs (Figs. S11 and S12).<sup>†</sup> Comparing the catalytic performance of **1mw** with that of the precursors one can infer that it resembles more closely that of the ligand precursor, being thus associated with the Brønsted acid sites. The important role of Brønsted acidity of the catalyst for the target reaction has also been found for the 1D hybrid polymer  $[\text{La}(\text{H}_4\text{bmt})(\text{H}_3\text{bmt})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$  that exhibited outstanding catalytic performance in the same reaction,<sup>7c</sup> even outperforming the nano-sized commercial  $[\text{Cu}_3(\text{BTC})_2]$  MOF (well known as HKUST-1).<sup>9</sup> As shown in Table S5,<sup>†</sup> **1mw** is more efficient than  $[\text{La}(\text{H}_4\text{bmt})(\text{H}_3\text{bmt})(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ , with a total conversion of 97% reached at just 2 h of reaction, in opposition of 6 h for our previously reported material.

When used as a heterogeneous acid catalyst in the acetalization of BA with methanol at 35  $^\circ\text{C}$ , **1mw** exhibited excellent selectivity towards benzaldehyde dimethyl acetal (BADMA), which was in the end formed as the sole product with 94% yield at 20 h reaction. A search in the literature shows that many MOF-type materials have been tested in the same reaction (Table S6<sup>†</sup>), and to the best of our knowledge only UIO-66- $\text{NO}_2$  could surpass **1mw** (at 4 h of reaction it converts 100 % of the substrate).<sup>10</sup> We note, however, that UIO-66- $\text{NO}_2$  is significantly more difficult to prepare than **1mw** (solvothermal synthesis in a mixture of DMF /  $\text{H}_2\text{O}$  / HCl, for 2 days at 180  $^\circ\text{C}$ ) and it has to be activated at 200  $^\circ\text{C}$  after each catalytic cycle. In short, we believe that based on

purely practical and environmental reasons, **1mw** arises as the most efficient MOF material reported to date for the acetalization of BA with methanol.



**Fig. 3** Conversion of styrene oxide with methanol in the presence of  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4] \cdot 4.5\text{H}_2\text{O}$  (**1mw**) at 35  $^\circ\text{C}$  (catalyst load = 20  $\text{g}_1 \text{L}^{-1}$ ) for three consecutive batch runs.

Motivated by the isolation of layered  $[\text{La}(\text{H}_3\text{nmp})]^{7g}$  at more drastic synthetic conditions (Fig. 1), and the observed structural robustness of the  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$  polymer, we have investigated the possibility of transforming the phase herein reported into other functional materials. From the conducted experiments, **1mw** can be transformed (at 100  $^\circ\text{C}$ ) into layered  $[\text{La}(\text{H}_3\text{nmp})] \cdot 1.5\text{H}_2\text{O}^{7h}$  and  $[\text{La}(\text{H}_3\text{nmp})]^{7g}$  (Fig. S16).<sup>†</sup> Using one-pot conditions, the former material is isolated as a pure phase after 24 h. The same occurs when a hydrothermal approach is employed in conjunction with slow cooling of the reaction vessels. Quenching the vessels in cold water leads to mixtures with  $[\text{La}(\text{H}_3\text{nmp})]$  being the predominant phase. As described in the ESI,<sup>†</sup> these transformations can be rationalized based on relationships between the topological features of the layered materials and  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$ . The performed tests do not seem to indicate, or disprove, the existence of single-crystal-to-single-crystal transformations associated with these phase modifications. The nature of these processes is still under scrutiny.

In summary, to avoid the systematic isolation of layered materials using the highly flexible nitrilotris(methylenephosphonic acid) ( $\text{H}_6\text{nmp}$ ) organic linker, and in order to promote the formation of 1D polymers, we have used  $\text{La}_2\text{O}_3$  and the metal source which was self-assembled with  $\text{H}_6\text{nmp}$  under acidic conditions *via* microwave irradiation. A novel 1D polymer  $[\text{La}_2(\text{H}_3\text{nmp})_2(\text{H}_2\text{O})_4]$ , was isolated in just under 1 min and, as expected, exhibited a remarkable catalytic activity in both the alcoholysis of styrene oxide with methanol or ethanol and in the

acetalization of benzaldehyde with methanol. Results clearly show that this new material surpasses all known compounds reported to date, including another 1D polymer previously reported by us, and that the reduction of the dimensionality boosted significantly the catalytic activity. The material exhibited a remarkable structural resilience enduring both extreme acidic and moderate basic conditions, as well as boiling water for long periods of time. In addition, we have also demonstrated that the previously layered materials reported by our group could be obtained by chemical transformation of this low-dimensional MOF under appropriate conditions. We are currently exploring new ways to retain the low dimensionality of the MOFs while also reducing to the nano-range the crystallite size. We thus envisage that these materials can be processed into functional devices while the properties herein described could further be improved toward meeting greater accessibility to the catalytic sites.

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### Notes and references

CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal. Fax: +351 234 401470;

Tel: +351 234 401418; E-mail: filipe.paz@ua.pt

† Electronic Supplementary Information (ESI) available: detailed synthesis and structural characterization details for **1mw**, **1op** and **1h** materials, including X-ray diffraction (synchrotron and single-crystal), solid-state NMR, Electron Microscopy (EDS and SEM), thermoanalytical studies and vibrational spectroscopy. Detailed data on the performed heterogeneous catalytic and transformation studies. For ESI and crystallographic data in CIF or other electronic format see DOI: XXXXX/XXXXX.

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