

# Synthesis and characterization of a new Cd-based metal-organic framework isostructural with MOF-74/CPO-27 materials



Manuel Díaz-García, Manuel Sánchez-Sánchez\*

Instituto de Catálisis y Petroleoquímica, ICP-CSIC, C/Marie Curie 2, 28049 Madrid, Spain

## ARTICLE INFO

### Article history:

Received 20 November 2013  
Received in revised form 6 February 2014  
Accepted 9 February 2014  
Available online 19 February 2014

### Keywords:

MOF-74  
CPO-27-Cd  
Unit cell dimensions  
etb topology  
<sup>113</sup>Cd NMR

## ABSTRACT

A new M-MOF-74 material, with M being cadmium, is described. The so-called Cd-MOF-74 material was prepared under solvothermal conditions using cadmium acetate as metal source. It was characterized by a variety of physico-chemical techniques including PXRD, TGA, N<sub>2</sub> adsorption-desorption isotherms, SEM, IR and multinuclear solid-state NMR. Although the quality and/or the size of the afforded crystals did not allow us solving the structure by single-crystal X-ray diffraction, the information given by different characterization techniques is enough to confirm that the sample is indeed a Cd-based MOF-74-like material. Fingerprint-based PXRD and FTIR techniques showed a good matching between the Cd-MOF-74 and the well-known Zn-MOF-74 samples. Likewise, TGA and N<sub>2</sub> adsorption-desorption at 196 °C gave expected values of Cd/linker ratio and textural properties, respectively. SEM certified the homogeneity of crystals and the absence of impurities. Among the divalent metal ions capable to produce MOF-74 materials, Cd<sup>2+</sup> presents some singularities: (i) it is the first metal of the second transition metal row able to lead to a M-MOF-74 material; (ii) due to reasonably good magnetic properties of the diamagnetic non-quadrupolar <sup>113</sup>Cd and <sup>111</sup>Cd nuclei, metal-adsorbate interactions can be studied from a metal point of view by means of NMR techniques.

© 2014 Elsevier Inc. All rights reserved.

## 1. Introduction

Among the families of porous materials, that of the metal-organic frameworks (MOFs) is certainly the most emerging one for so many applications [1,2]. Apart from the exceptional textural properties reached by some MOFs, widely overcome these of conventional microporous materials such as zeolites, the MOF materials family has some properties unprecedented or at least uncommonly found in any other known porous materials, such as network catenation [3], flexibility [4], structural chirality [5], or exposed and unsaturated metal centers [6]. Some of the most deeply studied MOF materials having open metal sites are these of the CPO-27-M family, also known as MOF-74 or simply M<sub>2</sub>(dhtp) or M<sub>2</sub>(dohbdc), where dhtp or dohbc represent the organic linker 2,5-dihydroxybenzylidene dicarboxylate. Several reasons are behind the interest in this particular isostructural MOF materials: (i) the already-mentioned presence of open metal sites; (ii) their versatility of being prepared with different divalent ions (Mg [7,8], Mn [9], Fe [10], Co [11], Ni [12] and Zn [13,14]) or with a mixture of them at any extension [15]; (iii) their thermal and chemical stability under

ambient conditions and in presence of water [16]; (iv) the possibility of being prepared at room temperature [17]; (v) their high adsorption heat for highly-demanded gases such as H<sub>2</sub> [18] and CO<sub>2</sub> [19]; and (vi) their high efficiency in the separation of molecules of similar size [20]. A proof of the attention paid to these MOFs can be deduced from three papers published in the last few months, which expand both the compositional diversity and the potential applications of MOF-74-like materials: (i) a new Cu-based MOF-74 [21], (ii) a Mn-based MOF-74-like MOF using a 2,5-dithiolbenzenedicarboxylate as linker (that is, -SH groups instead of the -OH groups found in the dhtp linker) with potential applications in conductivity [22]; and (iii) the series of isorecticular IRMOF-74 materials prepared with organic linkers similar to dhtp but having different length and/or functionalization, leading to the IRMOF-74-XI material [23] having the largest pore (near 10 nm of diameter) ever reported in MOFs.

MOF-74 materials were firstly described with Zn as metal [13]. In spite of the undoubted interest for some other members of the M-MOF-74 family, Zn seems to have a particular propensity to lead these materials, what has been made clear by its choice to develop the IRMOF-74 materials [23]. On the other hand, chemical similarities between Zn and Cd are well-known, as they belong to the same group in Periodic Table. Such behavior is not an exception and some isostructural MOF-based materials prepared with either

\* Corresponding author. Tel.: +34 915854795; fax: +34 915854760.  
E-mail address: [manuel.sanchez@icp.csic.es](mailto:manuel.sanchez@icp.csic.es) (M. Sánchez-Sánchez).

Zn or Cd [24–31] have been described, in spite of their quite different ionic sizes. Therefore, the choice of Cd to try to extend the M-MOF-74 family to the second transition metal row seems reasonable. Additionally, the acceptably good NMR properties of the  $^{111}\text{Cd}$  and  $^{113}\text{Cd}$  would open the possibility of studying the interaction between open metal sites and adsorbates/reactants, so far rather limited [32] by either the paramagnetic character of some metal ions M or by the low NMR sensitivity of some other M isotopes.

## 2. Experimental

### 2.1. Synthesis of the Cd-MOF-74 material

Cd-MOF-74 material was synthesized by solvothermal treatment of a clear solution of molar composition 2.6 Cd: 1.0 dhtp: 268 DMF, where dhtp represents the organic linker 2,5-dihydroxyterphthalic acid and DMF is the solvent N,N-dimethylformamide. In a typical procedure, a clear yellow solution of 0.200 g of dhtp (Aldrich) in 5.0 g of DMF (Aldrich) was added over other clear solution of 0.699 g of cadmium acetate dihydrate (Aldrich) in 15.0 g of DMF. The resultant clear solution was solvothermally treated at 125 °C for 20 h. A light yellow solid was obtained after such treatment, recovered by centrifugation and washed first with 20 mL of DMF and then two more times with 20 mL of methanol. The solid was kept submerged in methanol for 6 days; during these days, methanol covering the MOF sample was changed three times by fresh methanol.

For comparison purposes, a conventional Zn-MOF-74 material was prepared according to a described procedure [13].

### 2.2. Characterization techniques

Powder X-ray diffraction (XRD) patterns were acquired with a Philips X'PERT diffractometer using Cu K $\alpha$  radiation. Unit cell parameters were estimated with the XRD software CELREF from PXRD patterns registered with  $2\theta$  steps of  $0.01^\circ$  and radiation time of 100 s per point. The ten most intense non-overlapped reflections were selected and adjusted to the space group R-3 (No. 148) starting from the unit cell parameters determined by single-crystal X-ray diffraction of a Zn-MOF-74 material [13]. In order to get accurate  $2\theta$  values of the reflections, an internal standard of Si was physically mixed with the MOF-74 samples, and its reflection 111 (at  $2\theta$  of  $28.4^\circ$ ) of the former was taken as reference of  $2\theta$  position for the MOF-74 XRD reflections.

Theoretical PXRD pattern of Zn-MOF-74 was generated by Mercury software from the CIF file reported elsewhere [13]. Theoretical pattern of Cd-MOF-74 was obtained by Materials Studio software starting from the structure of Zn-MOF-74 and changing the Zn atoms by Cd ones, and considering the unit cell parameters estimated from the analysis of experimental PXRD pattern of Cd-MOF-74 sample. The CIF file of the Cd-MOF-74 structure, as well as that of Zn-MOF-74 published elsewhere [13], could be found in the Supporting information.

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra were recorded using a Thermo Nicolet Nexus 670 FTIR spectrometer equipped with a SensIR Technologies Durasampler horizontal ATR accessory and a liquid nitrogen-cooled MCT detector.

Thermogravimetric analyses (TGA) were registered in a Perkin-Elmer TGA7 instrument. TG analyses were carried out at a heating rate of 20 °C/min under air flow.

Nitrogen adsorption/desorption isotherms were measured at  $-196^\circ\text{C}$  in a Micromeritics ASAP 2020 device. Before the measurement, the previously calcined sample was degassed at 100 °C

under high vacuum for at least 18 h. Surface areas were estimated by BET method. Micropore and external surface areas were estimated by applying t-plot method.

Scanning Electron Microscopy (SEM) studies were carried out in an Ultra-high Resolution FEI-NOVA NanoSEM 230 FESEM instrument.

All Nuclear Magnetic Resonance (NMR) spectra were acquired in a Bruker AV-400-WB spectrometer operating at 100.61 MHz for  $^{13}\text{C}$  NMR spectra and at 88.80 MHz for  $^{113}\text{Cd}$  NMR spectra, under magic-angle spinning (MAS) technique. A 4-mm probe and a spinning rate of 10 kHz were used during the acquisition of all spectra.  $^1\text{H}$  to  $^{13}\text{C}$  cross-polarization MAS NMR spectra were acquired applying a  $\pi/2$  pulse of 3  $\mu\text{s}$  over the  $^1\text{H}$  channel, using a contact time of 3.5 ms and a pulse delay of 5 s. In the acquisition of  $^1\text{H}$  to  $^{113}\text{Cd}$  cross-polarization MAS NMR spectra, the  $^1\text{H}$   $\pi/2$  pulse length was 2.8  $\mu\text{s}$ , the contact time of 9.0 ms and the pulse delay of 5 s.  $^{13}\text{C}$  chemical shifts were referenced to TMS, whereas the  $^{113}\text{Cd}$  ones were referenced respect to the signal of the secondary reference  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  ( $\delta^{113}\text{Cd}$  of  $-100$  ppm against the primary reference 0.1 M aqueous solution of  $\text{Cd}(\text{ClO}_4)_2$ ).

## 3. Results

### 3.1. Structural characterization by powder XRD

In order to reach the objective of preparing Cd-based MOF-74-like materials, we systematically studied different Cd sources and different reported methods of synthesis of MOF-74/CPO-27-M/M $_2$ -(dhtp)/M $_2$ (dobdc) materials. However, the aim of this article is not to report and discuss the failed conditions that do not lead to pure Cd-MOF-74. Nevertheless, it is pertinent to point out that the key point to obtain high-quality Cd-MOF-74 materials seemed to be the use of Cd acetate as Cd source. The use of nitrate source,  $\text{Cd}(\text{NO}_3)_2$ , which is the most commonly-used anion source for any M-MOF-74/CPO-27 materials, systematically led to samples with impurities and/or poor in the desirable phase MOF-74 compared to its analogous samples prepared with Cd acetate. Some examples of the convenience of using acetate versus nitrate as Cd source are given in Supporting information.

Fig. 1 shows the powder X-ray diffraction (PXRD) patterns of the Cd-MOF-74 sample and a Zn-MOF-74 sample prepared according to the literature [13]. Similarities between both patterns are evident, suggesting that the MOF crystallized from our Cd-dhtp

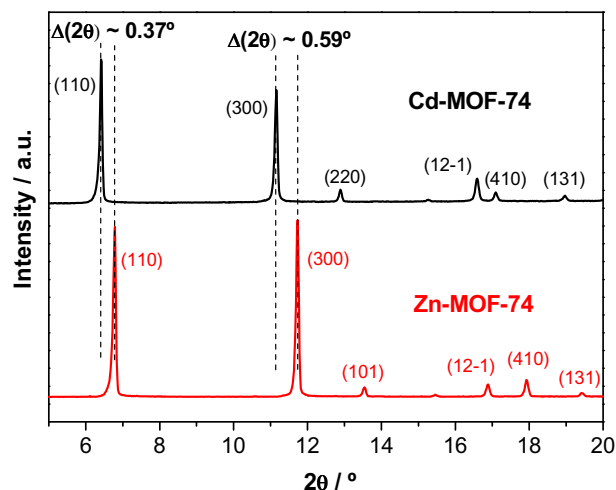


Fig. 1. PXRD patterns of the Cd and Zn-MOF-74 materials. Miller indexes of the most intense reflections are labelled in both patterns. The difference in  $2\theta$  values of the reflections 110 and 300 between both patterns is indicated.

Download English Version:

<https://daneshyari.com/en/article/6533319>

Download Persian Version:

<https://daneshyari.com/article/6533319>

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