

Two structurally different praseodymium-organic frameworks with permanent porosity



Osamah Alduhaish^a, Bin Li^a, Vladimir Nesterov^b, Hadi D. Arman^a, Khalid Alfooty^c, Abdullah M. Asiri^c, Hailong Wang^a, Banglin Chen^{a,c,*}

^a Department of Chemistry, University of Texas at San Antonio, San Antonio, TX 78249-0698, USA

^b Department of Chemistry, University of North Texas, 1155 Union Circle #305070, Denton, TX 76203-5017, USA

^c Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

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ABSTRACT

Two Praseodymium-organic frameworks, $[\text{Pr}_2(\text{NDC})_2(\text{NO}_3)_2(\text{DMA})_4]$ (**1**) and $[\text{Pr}_3(\text{NDC})_{4.5}(\text{DMF})_3(\text{H}_2\text{O})]$ (**2**) (H_2NDC = 2,6-naphthalenedicarboxylic acid; DMA = N,N-dimethylacetamide; DMF = N,N-dimethylformamide) have been synthesized and structurally characterized. The discrete $\text{Pr}_2(\text{COO})_4$ cluster and 1D $[\text{Pr}(\text{COO})_3]_n$ rod act as the secondary building units in MOF **1** and MOF **2**, respectively, leading to their different structures of 2D sheet and 3D rod-packing. Their permanent porosities have been also established.

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Compared with transition metal-organic frameworks, permanent porosities of lanthanide metal-organic frameworks (LnMOFs) are more difficult to establish [1]. This is because lanthanide ions have higher coordination numbers [2], so there are typically more solvent occupied sites within LnMOFs [3]. During the thermal/vacuum activation to remove the solvent molecules inside the pores and walls in order to establish their permanent porosities, the organic donors from organic linkers within LnMOFs easily occupy the in situ formed accessible lanthanide metal sites, leading to condensed and thus nonporous LnMOF structures. However, porous LnMOFs are highly in need in order to explore multifunctional LnMOF materials for sensing and heterogeneous catalysis, and as luminescent materials [4]. Although extensive research has been pursued to construct LnMOFs, those exhibiting gas sorption properties are still very rare.

Over the past several years, we have paid much effort to explore multifunctional LnMOF materials [5]. It is true that new organic linkers can guarantee the production of new LnMOFs; however, if some simple and commercially available organic linkers can be utilized to construct porous LnMOFs, the implementation of such new LnMOFs into their practical applications will be significantly facilitated [6]. Because of the rigidity and suitable length of 2,6-naphthalenedicarboxylic acid (H_2NDC), H_2NDC has been widely employed to construct porous

metal-organic frameworks transition metal ions/clusters [7]. However, thermally stable lanthanide-organic frameworks from H_2NDC are still rare [8]. In fact, only one of them has been established for its permanent porosity through gas sorption studies [8c]. With this in mind, we used H_2NDC to synthesize its Praseodymium-organic frameworks. Two new MOFs $[\text{Pr}_2(\text{NDC})_2(\text{NO}_3)_2(\text{DMA})_4]$ (**1**) and $[\text{Pr}_3(\text{NDC})_{4.5}(\text{DMF})_3(\text{H}_2\text{O})]$ (**2**) (DMA N,N-dimethylacetamide; DMF = N,N-dimethylformamide) were synthesized under slightly different solvothermal reactions between H_2NDC and praseodymium(III) salt. Herein we report their syntheses, structures and permanent porosities.

MOFs **1** and **2** were obtained by solvothermal reactions between H_2NDC and praseodymium(III) nitrate in the DMA/ CH_3CN and DMF, respectively (Supporting Information). The reaction conditions for the syntheses of these two MOFs are quite similar, so it appears that the solvent molecules play quite important roles for the formation of different LnMOFs.

Single crystal X-ray diffraction analysis result reveals that MOF **1** crystallizes in the orthorhombic system and *Pbca* space group (Supporting Information). In the crystal structure, the binuclear $\text{Pr}_2(\text{COO})_4$ clusters, as the discrete secondary building units, are bridged by organic dicarboxylates NDC to form a slightly distorted two-dimensional (2D) square grid $\{\text{Pr}_2(\text{NDC})_2\}$ (Fig. 1a and b). Except the coordinated NDC ligands on the Pr^{3+} ion, the two DMA molecules and a chelating nitrate ion also bind the metal ions, completing the eight-coordinated coordination sphere around the Pr(III) ions. The topology of MOF **1** can be best described as a simple (4,4)-connected

* Corresponding author.

E-mail addresses: hailong.wang@utsa.edu (H. Wang), banglin.chen@utsa.edu (B. Chen).

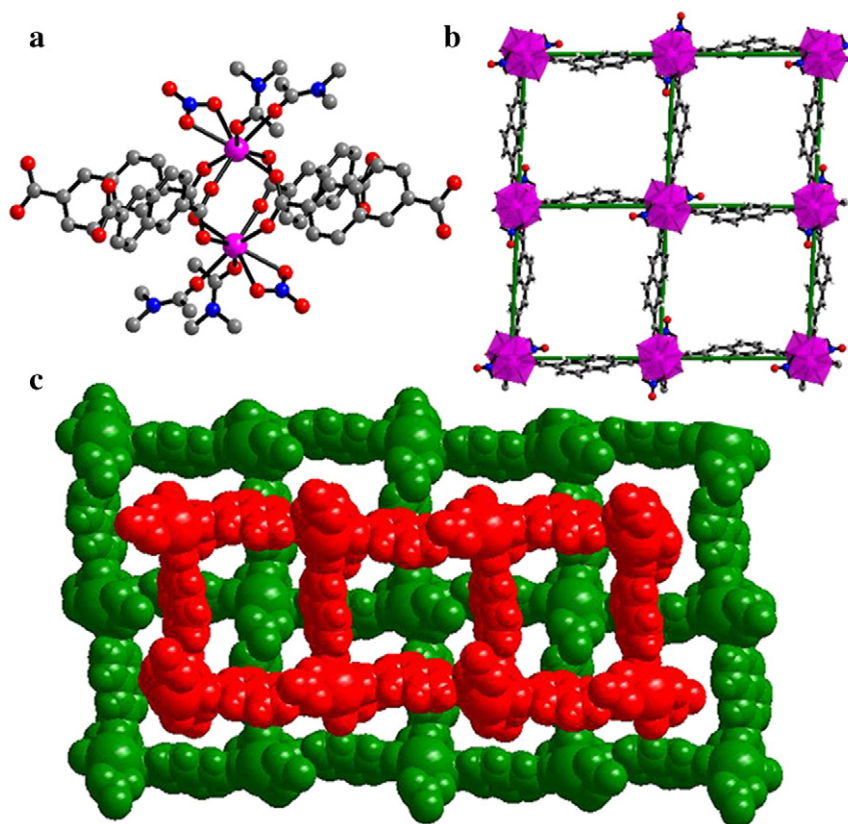


Fig. 1. X-ray crystal structure of MOF **1** indicating (a) the coordination geometry for Pr(III) atoms (the hydrogen atoms and solvent molecules are omitted for clarity), (b) 2D square grid, and (c) the framework packing of **1** along a axis, respectively.

net (Fig. 1b), which is very common [9]. The adjacent 2D square grids are packed in stagger mode in their framework packing (Fig. 1c). The coordination modes of NDC ligands to Pr^{3+} ions are shown in Scheme 1a and b.

MOF **2** belongs to the triclinic system and $P-1$ space group. There are three Pr(III) ions, four and half NDC ligands, two coordinated DMF molecules, and one coordinated water molecule in the asymmetric unit of **2**. As shown in Fig. 2a and b, there are three kinds of crystallographically independent Pr(III) ions in MOF **2**. Pr1 and Pr2 ions are located in an eight-coordinated environment built from seven oxygen atoms of NDC ligands and one oxygen atom from DMF and water molecule, respectively. Pr3 ion is seven-coordinated by six oxygen atoms of NDC ligands and one oxygen atom of DMF molecule. Unlike the structure of MOF **1** in

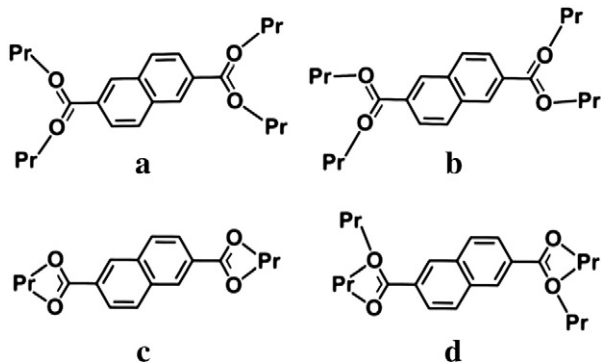
which the discrete $\text{Pr}_2(\text{COO})_4$ acts as the isolated secondary building unit, the structure of MOF **2** has the 1D $[\text{Pr}(\text{COO})_3]_n$ rod as the infinite secondary building unit. These adjacent 1D rods are further connected by the NDC ligands to form two kinds of rhombic channels: one of the channels are filled by the NDC ligand binding one group of diagonal Pr(III) ions (Fig. 2c), while another one has the pore size of about $4.0 \times 4.0 \text{ \AA}$ (Fig. 2d). These two building units construct the three-dimensional framework of **2**, (Fig. 2e). In this MOF, the NDC ligands exhibit all the four coordination modes shown in Scheme 1. The structures of **1** and **2** are different from the reported ones in the literature because they have been synthesized in different solvents [8].

The acetone-exchanged MOFs **1** and **2** were activated under high vacuum at 60°C for 24 h to generate the activated **1a** and **2a**. The CO_2 gas sorption isotherm at 196 K (Fig. 3) indicates that these two frameworks have certain degree of permanent porosities. They have Brunauer–Emmett–Teller (BET) surface area of 68 and $84 \text{ m}^2 \text{ g}^{-1}$, respectively, for **1a** and **2a**. These values are slightly lower than the reported ones in other lanthanide-NDC frameworks [8c].

In summary, we realized two new lanthanide metal-organic frameworks from a simple and commercially available organic linker. They exhibit structurally different packing. Given the fact that very few porous LnMOFs have been constructed, the establishment of the permanent porosities of these two new LnMOFs are still encouraging. We are now exploring further to establish more porous LnMOFs from some very simple and commercially available organic linkers for their diverse applications.

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Scheme 1. Schematic coordination modes of NDC ligand in MOFs 1–2.

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