



Short communication

Synthesis of two metal-porphyrin frameworks assembled from porphyrin building motifs, 5, 10, 15, 20-tetrapyrrolylporphyrin and their base catalyzed property

Weijie Zhang^a, Pingping Jiang^{a,*}, Ying Wang^a, Jian Zhang^b, Pingbo Zhang^a^a The Key Laboratory of Food Colloids and Biotechnology, School of Chemical and Material Engineering, Jiangnan University, China^b School of Chemistry and Environmental Science, Lanzhou City University, China

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ABSTRACT

Opening catalytically active sites in metal organic frameworks is an issue of fundamental importance for the development of effective and efficient catalysts. In this work, we first reported two metal metalloporphyrin–organic frameworks (MMPFs) with unoccupied pyridine groups as base catalysts. The reaction of Mn(II) and Co(II) with 5,10,15,20-tetrapyrrolylporphyrin produces two different metal metalloporphyrin–organic frameworks, $\{[(\text{MnTPyP})] \cdot \text{H}_2\text{O}\}_n$ (MMPF-Mn) and $\{[(\text{CoTPyP})]_n$ (MMPF-Co) (TPyP = 5,10,15,20-tetrapyrrolylporphyrin) under hydrothermal conditions. These two MMPFs have been fully characterized by single-crystal X-ray diffraction, powder XRD, elemental analysis and thermogravimetry (TG). MMPF-Mn displays a 3D network with a *nbo* topology, large and open hexagonal channels, MMPF-Co reveals a 1D single zigzag chain architecture. Interestingly, both MMPFs have a high thermal stability and opening basic pyridine group, which have been tested for the base catalyzed Knoevenagel condensation reaction. The catalytic study has demonstrated that MMPF-Mn catalysts having exposed pyridine group within 1D channel displayed an excellent performance for Knoevenagel condensation reaction. When MMPF-Mn was recycled four times, its catalytic activity remained with an inconspicuous decrease. We attribute MMPF-Mn showing a better performance than MMPF-Co to its active sites being aligned in extra-large cavity with an interior diameter of 20 Å.

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1. Introduction

Metal–organic frameworks (MOFs), also known as coordination polymers, is one of the most rapidly developing areas of chemical science [1]. MOFs as an interesting class of porous solids can be constructed from metal moieties and organic ligands, and have been explored for many practical applications, like gas storage, compound separation, chemical sensing, nonlinear optics, biomedical imaging, drug delivery, and heterogeneous catalysis [2–4]. In the reticular chemistry of MOFs where versatile custom-design organic linkers are used, e.g. metalloporphyrin-based ligands [5,6], MOFs allowing integration with a variety of functionalities are expected to form. Metal metalloporphyrin–organic frameworks (MMPFs) arouse intensive research interest, although MMPFs still remain in their premature stage.

In fact, the first porphyrin-based coordination polymer was reported by Robson and co-workers in 1991 [7], far earlier than the benchmarks of MOFs, HKUST-1 [8] and MOF-5 [9]. Metal–metalloporphyrin frameworks (MMPFs), as an important aspect of MOFs have been successfully developed by several groups with porphyrin ligand as building blocks [10–21]. The emergence of template-directed synthesis of MOFs in

which the porphyrin template is retained, which serves as a crystal engineering tool for the preparation of new MMPFs [22–25]. Their works not only enrich the domain of porous materials, but also been explored as candidates for a promising platform for the aforementioned applications. Then MMPFs and porphyrin-encapsulated MOFs have been intensely investigated for their various potential applications, like catalysis, sensor, gas capture and others [15,22–24,26–32]. However, compared with the fast-developing area of porphyrin chemistry, the field of MMPFs and their applications is still in its infancy. Although thousands of MOFs have been reported in recent years, the number of porphyrinic MOFs still remains relatively rare.

Indeed, by introducing various functional peripheral substituents at the β -pyrrolic and/or *meso*-positions or adding different central metals to the porphyrin core, porphyrin can exhibit multi-functional properties. These macrocycles often possess approximate D_{4h} symmetry, a point group rarely encountered in organic chemistry. The peripheral substituents at *meso*-positions like pyridine or carboxylate group can serve as base or acid catalytic sites. On the other hand, the porphyrin core can also allow pre-metalation, metalation *in situ* or postmetalation by numerous metal ions generating metalloporphyrins-based networks. Therefore, such porphyrins are exotic ligands for building frameworks, which might prove inaccessible using other types of ligands with different connectivity and symmetry.

* Corresponding author.

Taking into account the above mentioned aspects, this work was focused on the preparation of novel MMPFs and their catalytic properties. In this work, two different MMPFs have been prepared *via* the reaction of Mn(II) and Co(II) with 5, 10, 15, 20-tetrapyridylporphyrin, named MMPF-Mn and MMPF-Co. The single-crystal X-ray analysis showed that the pyridine group of MMPF-Mn and MMPF-Co were not fully occupied. These results inspired us to test MMPFs as basic catalysts for the first time. Remarkably, due to the presence of basic sites (unoccupied pyridine), MMPF-Mn shows significant reusability, and excellent ability to perform Knoevenagel condensation reaction.

Here, two different MMPFs, $\{[(\text{MnTPyP})] \cdot \text{H}_2\text{O}\}_n$ (MMPF-Mn) and $\{[(\text{CoTPyP})] \cdot \text{H}_2\text{O}\}_n$ (MMPF-Co) were synthesized as follows. MMPF-Mn was synthesized with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (1.97 mg, 0.01 mmol) and TPYP (6.8 mg, 0.01 mmol) in DMF *via* a hydrothermal method. Deep-purple crystals of MMPF-Mn were obtained in 58% yield based on the Mn, 7 days later after slowly cooling down from 150 °C to room temperature. In addition, MMPF-Co was prepared in a similar manner as that of MMPF-Mn except the $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was instead of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, and purple crystals of MMPF-Co in 54% yield were obtained based on the Co.

X-ray crystallographic data reveals that MMPF-Mn crystallizes in a rhombohedral space group of R-3 (Table S1). As seen in Fig. 1a,c and S1a (seen in supporting information), the net of MMPF-Mn is significantly distorted from its ideal *nbo* topology, creating large, open hexagonal channels. The structure of MMPF-Mn consists of a 3D framework with large cavities. The secondary building blocks consist of the cyclic metalloporphyrins hexamer. Each metal center is coordinated octahedrally by four nitrogen atoms of the porphyrin (average bond lengths:

Mn–N 2.10 Å) and two nitrogen atoms of the *trans* pyridyl groups of other two TPYPs (Mn–N 2.42 Å). The TPYP building block is engaged in a *trans*- $\mu_{1,3}$ coordination mode. Notable features of the MMPF-Mn structure are the hexameric cage, which has an extra-large cavity with an interior diameter of 20 Å, and the functional pyridine windows which are suitable for base catalysis. Interestingly, an intriguing feature of MMPF-Mn structure is the presence of the highly ordered solvent molecules trapped in the channels. As anticipated, the hexagonal channels have the dimensions of (17 × 20 Å). Although the pendant pyridyl groups protrude into the window, this metalloporphyrinate has an extremely open structure due to the long N–N distance (10.46 Å) between the pyridyl groups and the high projection angle (about 70°).

MMPF-Co crystallized in the monoclinic $P_{21/c}$ space group (Table S1). The 1D single zigzag chain is a common structural motif found in 1D Zn-porphyrin coordination solids [17]. This motif requires a metallated porphyrin because the only connection point is the metal node in the center of the porphyrin. In this work, Co-metallated TPYPs are linked through their cobalt metal centers to one of the pyridyl arms of a neighboring Co-TPYP, as illustrated in Fig. 1b,d. The resulting geometry is the zigzag pattern (Fig. S1b). To be more precise, the Co atom is located within the porphyrin ring with an average Co–N distance of ca. 1.98 Å. The fifth coordination site around the metal is occupied by the nitrogen atom of the pyridine belonging to the consecutive unit, with a Co–N distance of ca. 2.16 Å. This pyridine unit is almost perpendicular to the mean plane of the porphyrin. The Co center is located in the porphyrin mean plane toward the nitrogen atom of the pyridine group of the consecutive tecton. Among the two pyridines of the tecton, only one is engaged in the

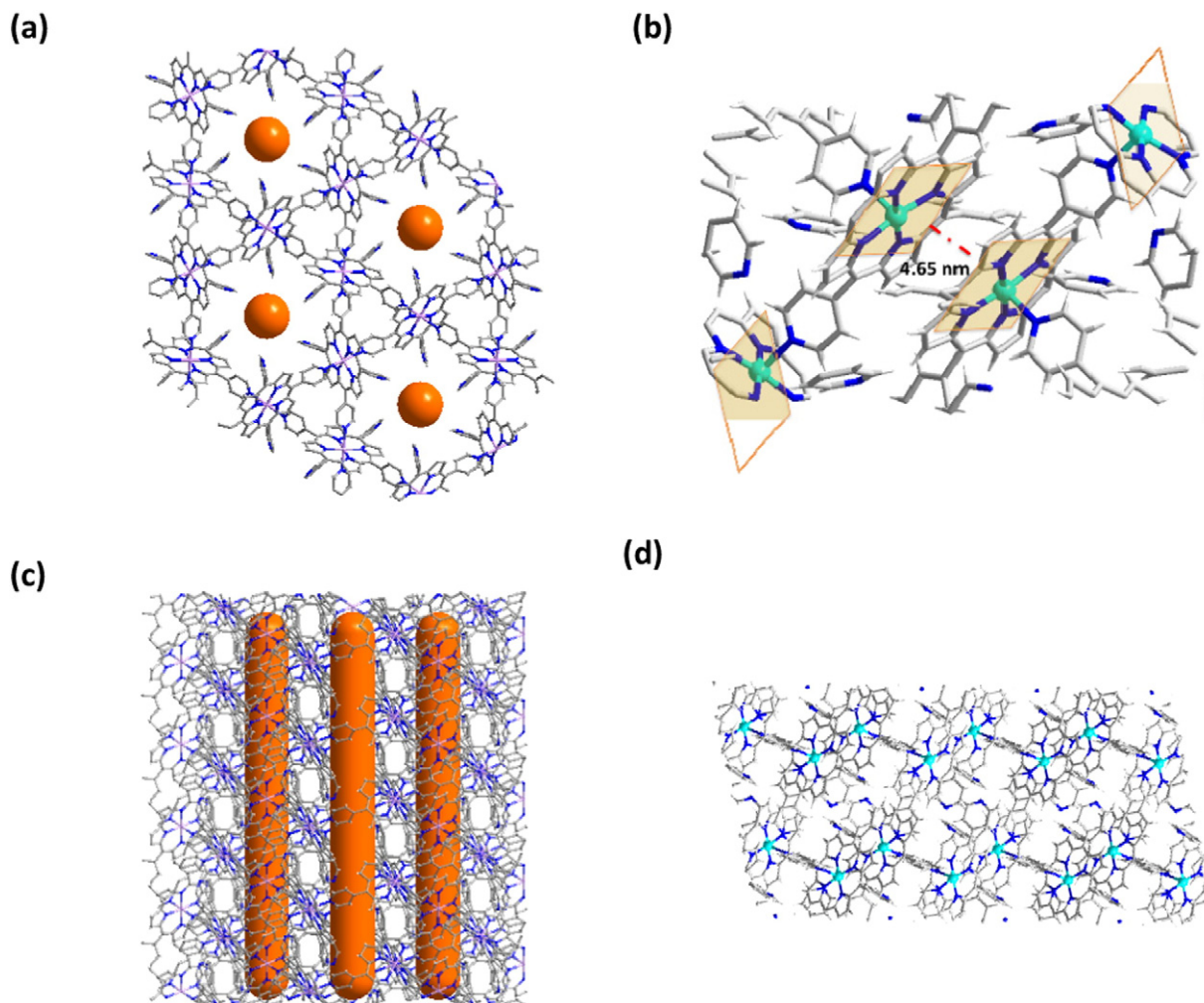


Fig. 1. Perspective view of framework structure of MMPF-Mn (a,c) and MMPF-Co (b,d).

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