

# A Series of Highly Stable Mesoporous Metalloporphyrin Fe-MOFs

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**S** Supporting Information

**ABSTRACT:** A series of mesoporous metalloporphyrin Fe-MOFs, namely PCN-600(M) (M = Mn, Fe, Co, Ni, Cu), have been synthesized using the preassembled [Fe<sub>3</sub>O(OOCCH<sub>3</sub>)<sub>6</sub>] building block. PCN-600 exhibits a one-dimensional channel as large as 3.1 nm and the highest experimental pore volume of 1.80 cm<sup>3</sup>g<sup>-1</sup> among all the reported porphyrinic MOFs. It also shows very high stability in aqueous solutions with pH values ranging from 2–11 and is to our knowledge the only mesoporous porphyrinic MOF stable under basic aqueous conditions. PCN-600(Fe) has been demonstrated as an effective peroxidase mimic to catalyze the co-oxidation reaction.

As an emerging class of highly ordered porous materials, metal–organic frameworks (MOFs) have attracted great attention in the last two decades.<sup>1</sup> Their modular nature imparts structural diversity, tunable surface properties, and multiple functionalities within a single material. They have great potential applications in many fields, especially in gas storage/separation, sensing, and catalysis.<sup>2,3</sup> Linker modification is one of the most direct methods for MOF functionalization.<sup>4</sup> Porphyrinic ligand are such a category of versatile linkers that have been extensively explored. These porphyrin derivatives play key roles in many chemical and biological processes. They can also be used as anticancer drugs, catalysts, pH sensors, nonlinear optical materials, and DNA-binding or cleavage agents.<sup>5</sup> When MOFs work as platforms to immobilize porphyrin groups, their rigid structures with high surface area and porosity can not only make each porphyrin accessible by substrates but also prevent the dimerization of reaction centers, which will block the catalysis pathway.<sup>6a</sup> Because of the versatility of porphyrin and its promising combination with MOFs, extensive synthetic studies have been reported.<sup>7</sup>

The porphyrinic linkers are mostly carboxylate based.<sup>8</sup> When relatively soft Lewis acidic species are used as nodes, such as Zn<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup>, the weak coordinating bond makes the framework less resistant to the attack of reactive chemicals. This severely restricts the application of porphyrinic MOFs under harsh conditions. To overcome such a weakness, clusters formed with harder Lewis acidic metals were selected as nodes, leading to porphyrinic MOFs with significantly enhanced stability.<sup>9</sup> Porphyrinic zirconium MOFs are a class of representative examples showing extraordinary chemical stability. However, the multiple phases in porphyrinic Zr-

MOFs systems, caused by the diverse connectivity of Zr<sub>6</sub> clusters in one-pot solvothermal reactions, cause tremendous difficulty in phase purification. This has severely hampered their wide application and bulk production.<sup>10</sup> Therefore, chemically stable porphyrinic MOFs that are easily synthesized in a phase-pure form are highly desirable.

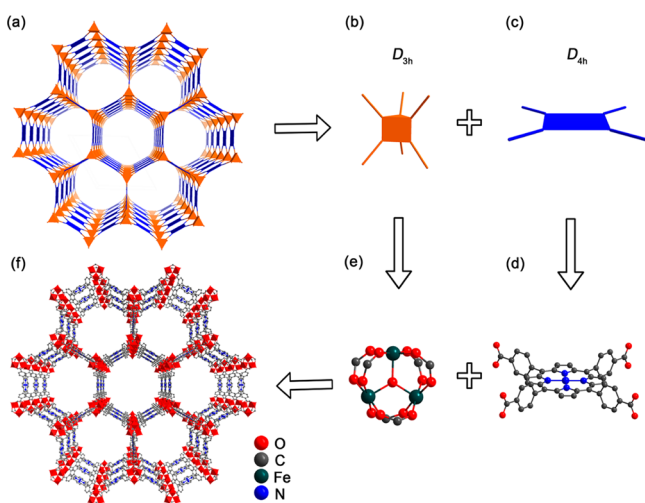
Fe(III) is an ideal alternative to Zr (IV) as the metal ion to construct nodes in MOFs due to its low toxicity, abundance, and, most importantly, its hard Lewis acidity, which results in stronger coordinating bonds with carboxylates and therefore more stable frameworks. Similar to those of the other stable MOFs, the synthesis and structure determination of Fe-MOFs have been long-standing challenges due to the difficulty of obtaining large single crystals and the unpredictable formation of inorganic building blocks.<sup>11</sup> However, the development of the kinetically tuned dimensional augmentation (KTDA) method provides us with the opportunity to target MOFs from designed inorganic building blocks and with a chosen topology, especially using the Fe<sub>3</sub>O(OOC)<sub>6</sub> cluster.<sup>12</sup>

The *stp-a* network contains six-connected trigonal prismatic nodes with *D*<sub>3h</sub> symmetry and four-connected square planar nodes with *D*<sub>4h</sub> symmetry (Figure 1a–c). The six-connected Fe<sub>3</sub>O(OOC)<sub>6</sub> binds the most commonly used four-connected porphyrinic linker, tetrakis (4-carboxyphenyl) porphyrin (TCPP) to form an *stp-a* network (Figure 1d–f). Herein, guided by topological analysis using the known connectivity of the organic linker and preformed cluster, we synthesized a series of highly stable mesoporous porphyrinic Fe-MOFs, namely PCN-600(M) (M = Mn, Fe, Co, Ni, Cu). PCN-600 exhibits one-dimensional (1D) channels as large as 3.1 nm and the highest experimental pore volume of 1.80 cm<sup>3</sup>g<sup>-1</sup> among all the reported porphyrinic MOFs. Remarkably, it also shows very high stability in aqueous solutions with pH values ranging from 2–11. Among them, PCN-600(Fe) has been demonstrated as an effective peroxidase mimic to catalyze the co-oxidation reaction.

Solvothermal reactions of M-TCPP (M = Mn, Fe, Co, Ni, Cu), [Fe<sub>3</sub>O(OOCCH<sub>3</sub>)<sub>6</sub>(OH)], and trifluoroacetic acid in *N,N*-dimethylformamide (DMF) at 150 °C for 12 h yielded needle-shaped single crystals of PCN-600. Although large single crystals with length around 0.3 mm have been obtained (Figure 3a), it was not feasible to determine the crystal structure by single-crystal X-ray diffraction (XRD) due to the

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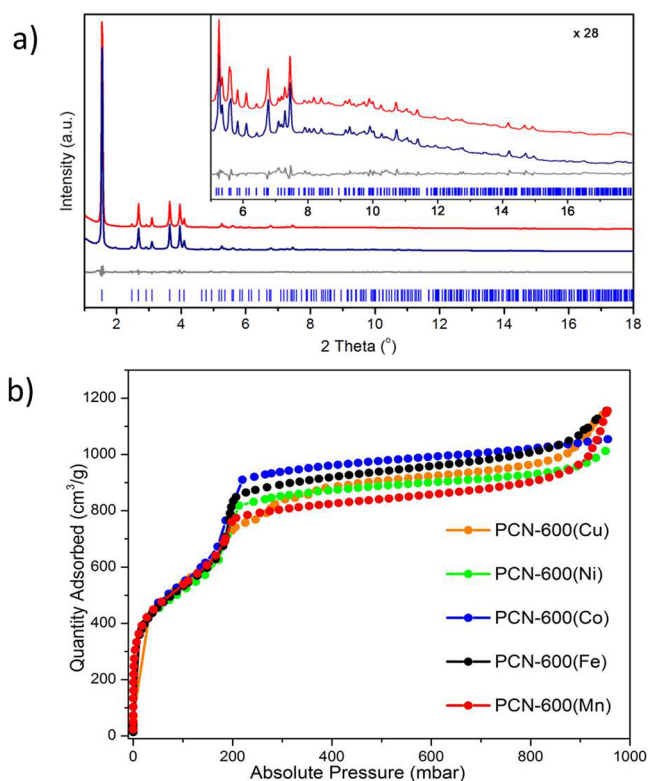


**Figure 1.** (a) The **stp-a** network, (b)  $D_{3h}$  symmetric six-connected and (c)  $D_{4h}$  four-connected nodes, and (d, e) corresponding nodes commonly seen in MOFs and PCN-600.

crystal's small size in the other two dimensions. However, since the **stp-a** topology is an example of a repeating net using  $D_{3h}$  and  $D_{4h}$  nodes, the structure model of **PCN-600** with a space group of  $P6/mmm$  can be constructed by using Material Studio 6.0.<sup>13</sup> The unit cell parameters of  $a = b = 31.27 \text{ \AA}$  and  $c = 16.95 \text{ \AA}$  are obtained through the indexing of the experimental high-resolution powder X-ray diffraction (PXRD) patterns. The predicted structure is ultimately validated with Rietveld refinements using the PXRD data collected from a synchrotron source (Figure 2a, details in Supporting Information, Section 3). The 3D framework of **PCN-600** can also be viewed as iron-carboxylate layers, which form a honeycomb-like 2D lattice in the  $ab$  plane, inherently pillared by TCPP ligands giving rise to a 3-D framework. The 3D framework contains very large hexagonal 1D channels with a diameter of 3.1 nm along the  $c$  axis, which is one of the largest reported in MOFs.

Due to the large ligand and pore size, direct activation of **PCN-600** was unsuccessful. The activation procedures were performed under supercritical carbon dioxide, after applying a dilute acid solution for preactivation treatments. The porosity of **PCN-600** was confirmed by nitrogen adsorption experiments at 77 K (Figure 2b). A type IV isotherm of **PCN-600(Fe)** exhibits a steep increase at  $P/P_0 = 0.2$ , suggesting its mesoporosity.  $N_2$  uptake of  $1150 \text{ cm}^3 \text{ g}^{-1}$  (Gas uptake has been converted to the volume under 273 K, 1 atm throughout) and a Brunauer–Emmett–Teller (BET) surface area of  $2270 \text{ m}^2 \text{ g}^{-1}$  were observed for **PCN-600(Fe)**. The experimental total pore volume is  $1.80 \text{ cm}^3 \text{ g}^{-1}$ , which is noticeably lower than the value of calculated pore volume ( $2.28 \text{ cm}^3 \text{ g}^{-1}$ ). A density functional theory (DFT) simulation from the  $N_2$  sorption curve indicates that there is only one type of pores. These 2.6 nm pores are assigned to the hexagonal channels, which is consistent with the crystallographic data when we take van der Waals contact into account. **PCN-600** with other metal ions in the porphyrin center shows similar type IV  $N_2$  sorption isotherms and gave  $N_2$  uptake, surface area, and total pore volume of up to  $1170 \text{ cm}^3 \text{ g}^{-1}$ ,  $2350 \text{ m}^2 \text{ g}^{-1}$ , and  $1.79 \text{ cm}^3 \text{ g}^{-1}$ , respectively (Figure 2b).

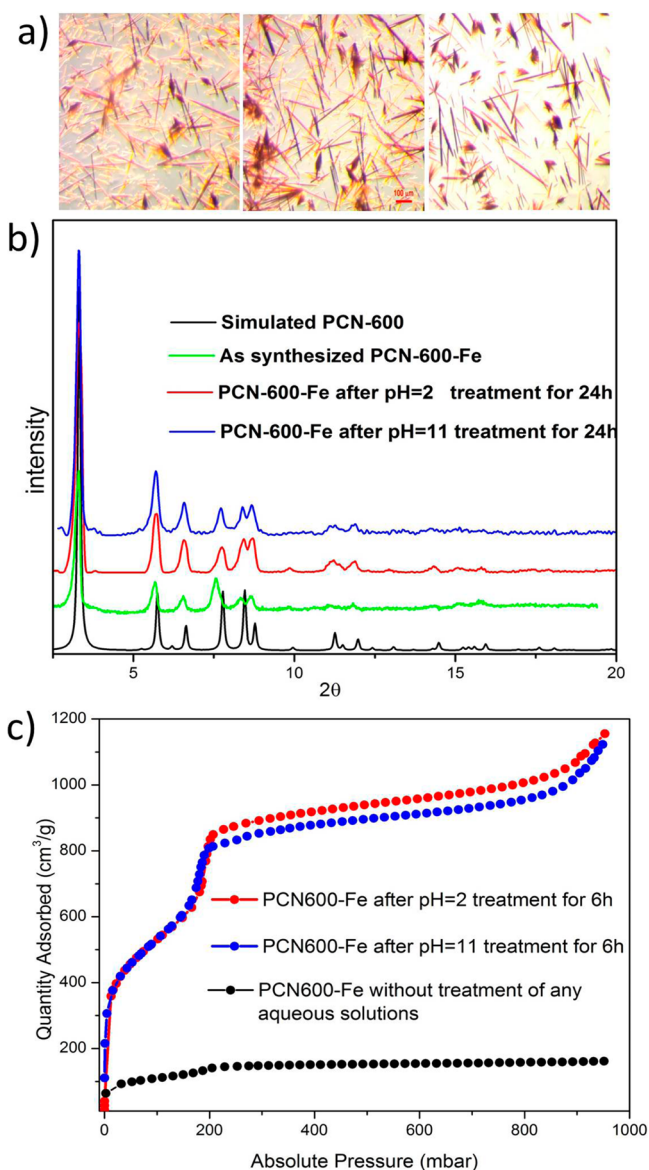
Although the supercritical carbon dioxide activation requirement implies that **PCN-600** is not highly mechanically stable, this will not lower its high potential in many applications in



**Figure 2.** (a) Rietveld refinement of PXRD for **PCN-600(Fe)**. The curves from top to bottom are simulated (red), observed (blue), and difference profiles (gray), respectively; the bars below curves indicate peak positions. (b)  $N_2$  adsorption isotherms of **PCN-600** series; the desorption branches are omitted for clarity.

water-mediated systems, since the collapse of frameworks is mainly due to the surface tension during liquid–gas phase transition.<sup>14</sup> However, when **PCN-600** is used as a heterogeneous catalyst in solution, it does not need to undergo any phase change and is therefore stable under those conditions. This is a representative example of how a MOF's mechanical robustness and chemical stability are not always related. **PCN-600** has very high chemical stability relative to all known MOFs. The PXRD patterns show the frameworks remain intact upon immersion in solutions with pH = 2 and 11 for 24 h, indicating that no framework collapse or phase transition happens during the stability test (Figure 3a,b). More importantly, the  $N_2$  sorption isotherms of samples after treatments of solutions with pH = 2 and 11 further confirmed that **PCN-600** can survive these conditions (Figure 3c). The chemical stability of **PCN-600** mainly comes from its  $\text{Fe}_3\text{O}(\text{OOC})_6$  cluster.  $\text{Fe}^{3+}$ , with high charge density, can form very strong coordination bonds with carboxylate groups, which makes the MOF highly resistant to the attack of water, dilute acid, and base. Compared to the only reported mesoporous porphyrinic MOF, **PCN-222** (or **MOF-545**), which only shows stability in acidic aqueous solutions,<sup>6a</sup> **PCN-600** maintains good crystallinity in both acid and base aqueous media.

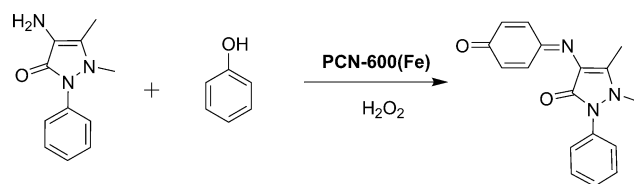
The integration of excellent chemical stability, large open channels, and high concentration of porphyrins, which can work as active centers in many enzymes, inspired us to explore **PCN-600(Fe)** as a biomimetic catalyst. The enzyme mimetic activity was evaluated by catalysis of co-oxidation of phenol and 4-aminoantipyrine (4-AAP) in the presence of  $\text{H}_2\text{O}_2$ , which is



**Figure 3.** (a) Pictures of PCN-600(Fe) under optical microscope. As-synthesized (left), after treatment with pH = 2 solution for 24 h (middle) and after treatment with pH = 11 solution for 24 h (right). (b) PXRD pattern of PCN-600(Fe) and the samples treated with aqueous solutions of pH = 2 and 11. (c) N<sub>2</sub> adsorption isotherms for PCN-600(Fe) at 77 K, showing the framework stability of PCN-600(Fe) upon treatment with aqueous solutions of pH = 2 and 11 (When the crystals are immersed in acid or base solution, the H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> could help to decompose the coordination compounds that are stuck in channels and make them removable by water and DMF; see in Figures S3 and S11a. Similar behavior can also be observed in PCN-222, MIL-101, and MIL-53).<sup>6</sup>

also used for phenol and cholesterol estimation. The addition of PCN-600(Fe) and H<sub>2</sub>O<sub>2</sub> to the substrate solution led to the appearance of a red color and gave a maximum absorbance at 500 nm, which originates from the formation of quinone-imide (Scheme 1). A control experiment was performed to compare the peroxidase activity of PCN-600(Fe) with wild-type cytochrome c (Cyt c) from bovine hearts, and their catalytic activities were analyzed by determining apparent steady-state kinetic parameters. With the suitable range of H<sub>2</sub>O<sub>2</sub> concentrations, typical Michaelis–Menten curves were ob-

### Scheme 1. Reaction catalyzed by PCN-600(Fe)



tained for PCN-600(Fe) and Cyt c (Table 1). The results show PCN-600(Fe) has a much smaller Michaelis–Menten constant

**Table 1.** Comparison of Catalytic Activity of PCN-600(Fe) and Cyt c

catalyst	PCN-600(Fe)	Cyt c
$K_m$ (mM)	6.37	89.4
$V_{max}$ (mM·min <sup>-1</sup> )	0.042	0.013
$k_{cat}$ (min <sup>-1</sup> )	0.66	9.59
$k_{cat}/K_m$ (min <sup>-1</sup> ·mM <sup>-1</sup> )	0.10	0.11

( $K_m$ ) indicating that PCN-600(Fe) has a higher affinity for substrate than Cyt c. This may be caused by the following advantages of a MOF catalyst: First, the distribution of active sites throughout the framework is ensured by the highly ordered structure of a MOF. Second, the porphyrinic cores are well exposed to substrate in the channel. Third, the mesopore, acting as a nano-reactor, can mediate the reactivity by providing a confined environment.<sup>16</sup> The relatively low  $k_{cat}$  of PCN-600(Fe) is presumably caused by the slower diffusion rate of the product in the MOF channel than that of the enzyme.<sup>15</sup> However, the  $k_{cat}/K_m$  allows direct comparison of the catalytic efficiency.

In summary, we have demonstrated that PCN-600(Fe) is a mesoporous MOF with exceptional chemical stability and extraordinary porosity. With the catalytically active sites located on the inner wall of the 1D channel of 3.1 nm, PCN-600(Fe) shows good activity for the co-oxidation of phenol and 4-AAP. The high density of active centers, large open channels, and excellent chemical stability of PCN-600(Fe) suggest its intriguing potential in enzyme-mimetic catalysis and other applications, especially those requiring basic conditions.

## ■ ASSOCIATED CONTENT

### Supporting Information

Full details for sample preparation and characterization, crystallographic data of the precursor, CIF files, as well as, N<sub>2</sub> adsorption, thermal stability, chemical stability, and catalytic activity tests. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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