

Three porous and robust metalloporphyrin frameworks exhibiting preferable gas storage



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ARTICLE INFO

Article history:

Received 3 November 2014

Received in revised form 24 December 2014

Accepted 14 March 2015

Available online 17 March 2015

Keywords:

Metal–organic frameworks

Metalloporphyrin frameworks

Crystal structure

Porous material

Adsorption

ABSTRACT

We have achieved success in obtaining three novel two-dimensional porous metalloporphyrin frameworks (MPFs) through solvothermal reactions, by using 5,15-di(4-pyridyl)-10,20-bis(3,4,5-trifluorophenyl) porphyrin (*trans*-Py₂(F₃-ph)₂Por) metalated with Fe (**1**), Co (**2**), and Ni (**3**) salts respectively. TGA reveals that they all have high thermal stabilities. Gas adsorption studies indicate that three MPFs have relatively preferable H₂ uptake capacities and the selective adsorption of CO₂ over N₂.

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Recently, metal–organic frameworks (MOFs) have received considerable attention due to their fascinating structural architectures and potential properties in catalysis, luminescence, gas storage and separation, and molecular magnetism [1–8].

Porphyrin is an important ligand in the construction of functional MOFs, because porphyrin macrocycle not only offers a rather rigid square planar building block, but also possesses prominent thermal stability, and excellent photophysical and electrochemical properties. Porphyrin-based MOFs have attracted immense research attention of researchers, and numerous metalloporphyrin framework (MPF) structures have been reported for the moment [9–14].

To build desired metalloporphyrin frameworks (MPFs) with fascinating framework topologies and intriguing properties, a variety of metal ions can be coordinated into the central of porphyrin plane with the axial positions left for further coordination, and in the meantime various coordinating groups can be introduced to the porphyrin peripheral positions. Aromatic carboxylic acids and N-heterocyclic groups such as imidazole and pyridine are among the most studied ligand types for the syntheses of metalloporphyrin frameworks (MPFs) [15–20]. Those multiple coordination sites in MPFs can obtain highly stable solids with well-defined porous systems. From the previous

research reports, it can be concluded that rigid ligands are much easier to construct distinctive structures than the flexible ones, especially for pyridyl-containing rigid ligands, which have attracted extensive attention [21–26]. Herein, we report three new MPFs, Fe[*trans*-Py₂(F₃-ph)₂Por]·Cl·2DMF (**1**), Co[*trans*-Py₂(Me₂N,F₂-ph)₂Por]·3DMF (**2**) and Ni[*trans*-Py₂(Me₂N,F₂-ph)₂Por]·3DMF (**3**), based upon 5,15-di(4-pyridyl)-10,20-bis(3,4,5-trifluorophenyl)porphyrin (*trans*-Py₂(F₃-ph)₂Por) ligand metalated with Fe, Co, and Ni ions, respectively (Scheme 1, ESI).

The three black block crystals were obtained by combining free-base *trans*-Py₂(F₃-ph)₂Por with Fe, Co, and Ni metal salts respectively in N,N-dimethylformamide (DMF) under solvothermal conditions for 72 h at 150 °C. The stoichiometric ratio of reactants and different types of metal salts were systematically changed in order to find an optimal synthesis condition (synthesis and characterization data, ESI).

Single-crystal X-ray structure determinations reveal that the crystal systems of three MPFs are all monoclinic, but the space group of **1** is C 2/c, **2** and **3** are isomorphous crystallized in the space group of P 21/c. Non-hydrogen atoms were all located successfully from Fourier maps, and hydrogen atoms were added at their geometrically proper positions. The solvent DMF molecules in **1**, **2** and **3** were highly disordered, which could not be entirely located successfully in the refinement cycles. In the article, all solvent molecules were ascertained combined with elemental analysis and thermogravimetric analysis. The detailed structure data are shown in Table S1.

The coordination environment of **1** and **2** is illustrated in Fig. 1. The **2** and **3** are isomorphous with highly similar cell parameters, so we take

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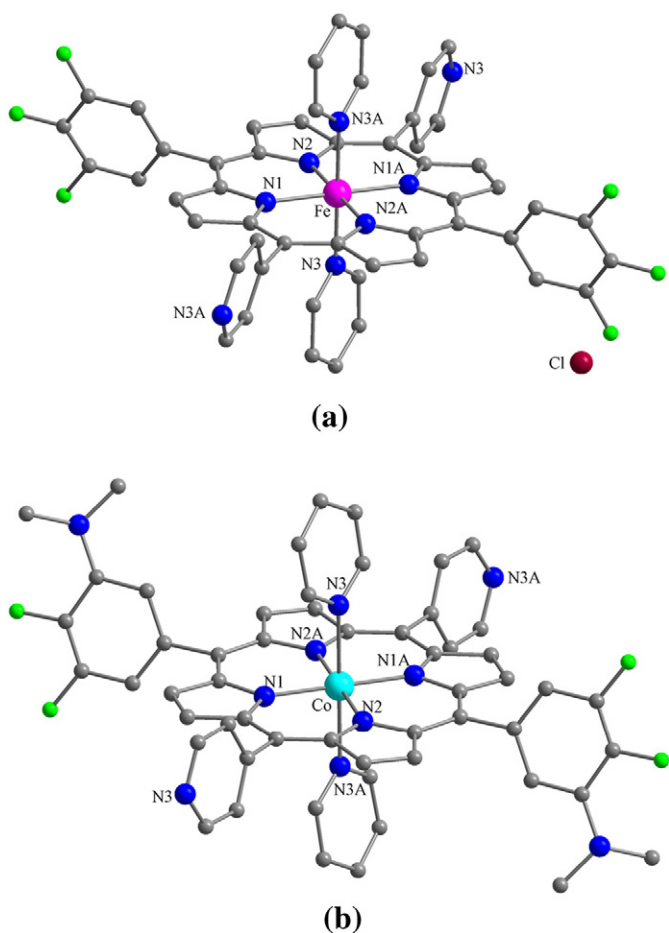


Fig. 1. Illustrations of the coordination environment: a (1), b (2). Color code: C (gray), N (blue), F (green), Fe (pink), Co (turquoise).

the structure of **2** for example to discuss crystal structure in detail, and only discuss related points for **3**. As we can see, metal ions, located in the center of the porphyrin square, are all hexacoordinated with octahedral coordination geometry. Each metal ion coordinates with four pyrrolyl nitrogen atoms in equatorial plane from the porphyrin core and two pyridyl nitrogen atoms in the axial sites from neighboring porphyrin ligands, thus a stable 2D porphyrin grid network is obtained. That is, every porphyrin moiety interlinks four neighboring porphyrin ligands in the grid through four metal-pyridine coordination bonds by engaging all two pyridyl sites of the porphyrin.

It must be noted that the central Fe^{3+} ion causes the positive framework of **1**, and the counter Cl^- ion compensates the charge of the framework. The Cl^- ions in **1** lie in the pores and do not take part in the coordination of metalloporphyrin frameworks. The DMF can be decomposed into *N,N*-dimethylamine and formic acid at high temperature. In **2** and **3**, one fluoride ion in trifluorophenyl group is replaced by dimethylamino substitution due to nucleophilic substitution reaction [27–29]. As far as we know, **3** is the first example of Ni-based MPFs that Ni^{2+} ion adopts a scarce six-coordinated octahedral configuration, which is different from usual four-coordinated plane geometry in reported Ni(II) metalloporphyrin frameworks [30–32].

It can be seen from Table S2, the bond lengths of Fe (Co, Ni)–N in equatorial plane are almost similar in three structures, and the bond lengths of Co–N (Py) and Ni–N (Py) in axial location are also almost the same, but much longer than that of Fe–N (Py). So Fe^{3+}

ion in **1** forms a proximate octahedral configuration, while Co^{2+} and Ni^{2+} ions exhibit elongated octahedral configurations in **2** and **3** (Fig. 1). It can be attributed to the valence state of the central metal ions, the iron ion is +3 valence state, while Co and Ni metal ions are all +2 valence, simultaneously dimethylamino substitutions may also disturb the axial coordination of the central metal ions.

Single-crystal X-ray structure determinations show that three crystals are all novel two-dimensional (2D) homologous serial metalloporphyrin frameworks (MPFs), and the 2D porphyrin layers form square open pores with sizes of approximately $9.7 \times 9.7 \text{ \AA}$ for **1** (Fig. 2(a)), $9.9 \times 9.9 \text{ \AA}$ for **2** (Fig. 3(a)), and $10.0 \times 10.0 \text{ \AA}$ for **3** respectively along the *a* axis. In the same way, there are only small differences between **2** and **3** in structures, so we only explain the structure of **2** in detail. Despite the existence of such open channels, the layers in all three MPFs are non-interpenetrated, and packing diagrams exhibit that the 2D networks are stacking in a parallel fashion. The inter-layer distance of adjacent layers is 11.7 \AA for **1** (Fig. 2(b)), 13.1 \AA for **2** (Fig. 3(b)), and 13.2 \AA for **3**, respectively. As can be seen from Fig. 2(b), each layer in **1** is not eclipsed but staggered by $(1/2, 1/2)$ relative to adjacent layers, so the pore size of **1** is reduced to some extent. Viewing from the *a* axis, it is observed that the 2D porphyrin sheet of **1** forms an ABAB stacking pattern, while adjacent layers of **2** and **3** are completely overlapped with one another, they stack in AA fashion (Fig. 3(b)), thus infinite one-dimensional channels are built along the *a* axis. From the topology diagrams (Fig. S4, ESI), it can be seen more clearly that **1** forms an ABAB stacking pattern, while **2** and **3** stack in AA fashion. Due to the different stacking patterns, the solvent-free 2D frameworks indicate that three MPFs are porous and have void volume of 20.9% ($916.4 \text{ \AA}^3/4392.1 \text{ \AA}^3$) for **1**, 27.4% ($641.1 \text{ \AA}^3/2342.0 \text{ \AA}^3$) for **2**, and 27.7% ($657.6 \text{ \AA}^3/2370.6 \text{ \AA}^3$) for **3**, based on PLATON analyses.

The phase purity of the bulk complexes was confirmed by comparing the powder X-ray diffraction patterns (PXRD) of samples and simulated ones from the single-crystal X-ray data (Fig. S5, S6, and S7, ESI). The evacuated samples were gained through being heated under vacuum at $80 \text{ }^\circ\text{C}$ for 10 h. The PXRD analyses of complexes **1**, **2** and **3** show that most of sharp diffraction peaks are retained even after being heated under vacuum at $80 \text{ }^\circ\text{C}$ for a long time. This indicates the phase purity of three complexes, so we may definitely come to the conclusion that the structures of three crystals are extremely robust and porous even being heated and evacuated.

To study the thermal stabilities of three novel MPFs, thermogravimetric analysis (TGA) was carried out in the temperature range of $25\text{--}800 \text{ }^\circ\text{C}$ under a flow of N_2 with a heating rate of $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Data are shown in Fig. S8, thermogravimetric analysis of **1** reveals that the lattice DMF molecules can be completely removed in the temperature range of $93\text{--}160 \text{ }^\circ\text{C}$ with a weight loss of 15.6%, which is the equivalent of losing two lattice DMF molecules trapped in the channels, and then the curve is followed by a relatively steady platform up to $500 \text{ }^\circ\text{C}$, after this, the framework starts to decompose. For **2**, the TGA curve reveals the weight loss of 21.1% at $283 \text{ }^\circ\text{C}$ corresponding to the removal of three solvated DMF molecules and then is almost flat until $415 \text{ }^\circ\text{C}$, followed by a significant skeleton decomposition. The TGA curve for **3** displays a weight loss of 20.7% from 25 to $212 \text{ }^\circ\text{C}$, which can be attributed to the removal of three lattice DMF molecules, and is followed by a gravity platform until $400 \text{ }^\circ\text{C}$, and then the framework starts to decompose. The thermal behaviors characterized by TGA display that all three materials exhibit high thermal stabilities of the frameworks.

A major challenge for MPFs is the stability of pore structure. The three samples were heated at $80 \text{ }^\circ\text{C}$ for 10 h in vacuum, and their PXRD patterns are almost the same as the simulated ones, which indicate that the porous frameworks are maintained even being heated and evacuated for a long time. In order to further verify three complexes are permanent porous materials, N_2 , H_2 and CO_2 gas adsorption

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