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# A Pyrazolate-Based Porphyrinic MOF with Extraordinary Base-Resistance

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## Supporting Information Placeholder

**ABSTRACT:** Guided by a top-down topological analysis, a MOF constructed by pyrazolate-based porphyrinic ligand, namely PCN-601, has been rationally designed and synthesized, which exhibits excellent stability in alkali solutions. It is, to the best of our knowledge, the first identified MOF that can retain its crystallinity and porosity in saturated sodium hydroxide solution (~20 mol/L) at room temperature and 100 °C. This almost pushes base-resistance of porphyrinic MOFs (even if MOFs) to the limit in aqueous media and greatly extends the range of their potential applications. In this work, we also tried to interpret the stability of PCN-601 from both thermodynamic and kinetic perspectives.

## INTRODUCTION

As a novel class of porous materials, metal-organic frameworks (MOFs) have attracted great interest.<sup>1</sup> Their modular nature endows these materials with structural diversity and tunable functionality.<sup>2</sup> One feasible method to functionalize MOFs is to introduce different functional groups via the organic linkers.<sup>3</sup> Porphyrinic derivatives incorporated into MOFs as the organic linkers have been tremendously studied due to their important roles in lots of chemical and biological processes, and other applications such as anti-cancer drugs, catalysts, photosensitizer, pH sensors, etc.<sup>4</sup>

Owing to the fact that many applications of porphyrin involve harsh chemical conditions, chemical stability becomes crucial for porphyrinic MOFs.<sup>5</sup> Therefore, the development of highly stable porphyrinic MOFs is a sought-after goal to extend the scope of applications for these materials. One direct strategy to overcome the vulnerability of MOFs is to enhance the strength of coordination bonds between organic linkers and metal nodes. To realize it, one of the extensively-explored methods is to choose secondary building units (SBUs) formed with high-valent metal ions and carboxylate groups, like  $[Zr_6O_4(OH)_4(CO_2)_{12}]$ , and  $[M_3OX(CO_2)_6]$  ( $M = Al^{3+}$ ,  $Cr^{3+}$ , or  $Fe^{3+}$ ;  $X = OH^-$ ,  $F^-$ , or  $Cl^-$ ).<sup>6</sup>

With this strategy, several porphyrinic MOFs with high stability in acidic and neutral aqueous solutions have been obtained, such as PCN-22X ( $X = 2$ ,  $3$ ,  $4$ , and  $5$ ), PCN-600, and Al-PMOF.<sup>5,7</sup>

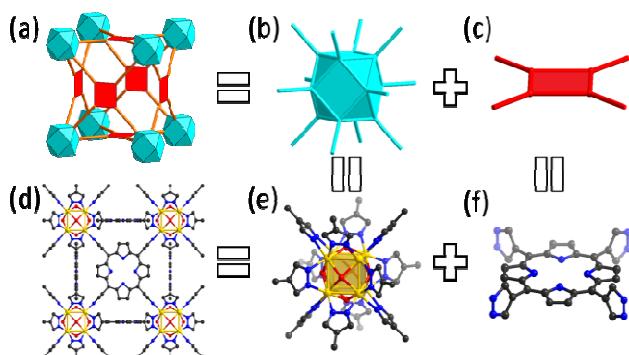
However, these acid-resistant MOF materials usually are fragile in basic aqueous solutions, which could severely hamper some of their applications.<sup>8</sup> A typical example is PCN-222 (or MOF-545).<sup>3e,5a</sup> It can even survive in concentrated hydrochloride acid, but decomposes easily in dilute alkali solution.<sup>5a</sup> Since azolate-based MOFs, especially pyrazolate-based ones (pyrazolate is shorten as Pz), have been demonstrated extremely stable under basic environments,<sup>9</sup> adopting Pz-based porphyrinic organic linkers thus becomes a promising way to obtain base-resistant porphyrinic MOFs.

Herein, we demonstrate how rational top-down strategy based on topological analysis guides us to obtain a Pz-based porphyrinic MOF with excellent base-resistance, namely PCN-601, which is constructed by  $[Ni_8(OH)_4(H_2O)_2Pz_{12}]$  (denoted as  $[Ni_8]$ ) nodes and 5,10,15,20-tetra(1*H*-pyrazol-4-yl)porphyrin ( $H_4TPP$ ) ligands (Figure 1). Experimental data confirms PCN-601 is immune to the attack of  $H_2O$  and  $OH^-$  in aqueous solutions, even at high temperature. As far as we know, it is the first identified MOF that can retain crystallinity and porosity in saturated NaOH solution at room temperature (RT) and 100 °C.

## EXPERIMENTAL SECTION

**General information.** The commercial chemicals are used as purchased unless mentioned otherwise. Detailed chemical sources are listed in the Supporting Information.

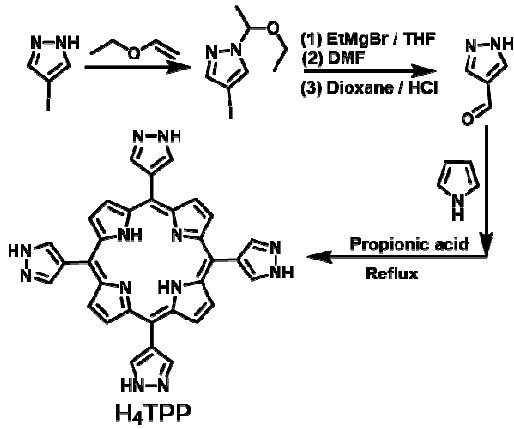
**Instrumentation.** High resolution powder X-ray powder diffraction (PXRD) was performed on a PANalytical X'Pert PRO diffractometer equipped with a Pixel detector and using Cu  $K\alpha 1$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The powder samples were placed in a 0.4 mm diameter glass capillary that was spun during the experiment. Other PXRD was carried out with a BRUKER D8-Focus



**Figure 1.** Structural analysis of PCN-601. (a) **ftw-a** topology; (b)  $O_h$  symmetric 12-connected node; (c)  $D_{4h}$  symmetric 4-connected node; (d) PCN-601 (Ni atoms in the porphyrin center are omitted for clarity.); (e)  $[Ni_8]$  cluster moiety; (f)  $TPP^{4+}$  ligand.

Bragg-Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube ( $\lambda = 1.54178 \text{ \AA}$ ) at 40 kV and 40 mA.  $N_2$  adsorption-desorption isotherms were measured using a Micrometrics ASAP 2420 system at 77 K. The UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. X-ray absorption spectroscopy (XAFS) measurements were performed in the transmission mode at the beam-line 14W1 in Shanghai Synchrotron Radiation Facility (SSRF).

**Synthesis of  $H_4TPP$ .** The synthesis procedure is shown in Scheme 1 and details in the Supporting Information section 2.



**Scheme 1.** Synthesis of  $H_4TPP$  ligand.

**Synthesis of PCN-601.**  $Ni(AcO)_2 \cdot 4H_2O$  (800 mg),  $H_4TPP$  (400 mg),  $Et_3N$  (2 mL), and water (8 mL) in 80 mL of  $N,N$ -dimethylformamide (DMF) were ultrasonically dissolved in a 150 mL high pressure vessel. The mixture was heated at 75 °C for 4 days. After cooling down to room temperature, reddish crystalline powder in colorless solution was obtained. The scanning electron microscope (SEM) image indicates that the crystal size of obtained powder is around 100 nm (Figure S2 in the Supporting Information). Thermogravimetry analysis reveals that the thermal stability of PCN-601 can be held up to 300 °C, from which it begins to decompose (Figure S3 in the Supporting Information).

**Rietveld Refinement and Crystallographic Data of PCN-601.** The Rietveld refinement of PCN-601 against PXRD data was performed using Topas V4.2. Background was fitted with a 21<sup>th</sup> order Chebychev polynomial. The refinement was conducted

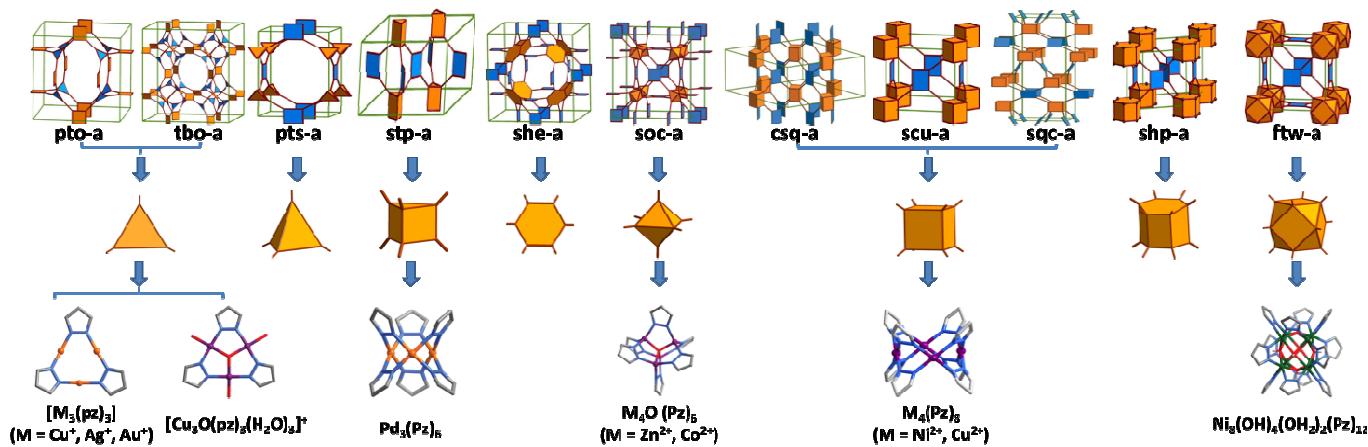
using a Thompson-Cox-Hastings pseudo-Voight peak profile function, followed by refinement of unit cells and zero-shift. The rigid bodies were applied on the porphyrin ligand. The unit cell parameters were determined directly from the high solution PXRD pattern by TREOR.<sup>10</sup> 30 diffraction peaks were used to index (Table S1 in the Supporting Information). The diffraction intensities were extracted by Le Bail fitting using JANA2006. We applied charge-flipping iterations on the extracted intensities using the software Superflip.<sup>11</sup> From the best electron density maps with the lowest R-values, the space group ( $Pm-3m$ ) and the position of Ni and O were determined. Other framework atoms were located from the difference Fourier maps, the occupancy were confirmed by ICP and EA (Figure S5 and Table 1, details in the Supporting Information section 6).

**Table 1.** Crystallographic data, experimental conditions for PXRD data collection, and the Rietveld refinement result of PCN-601.

Chemical formula	$Ni_{9.77}C_{56.64}N_{21.24}O_{10.92}H_{43.75}$
Formula weight	1734.20
Density (calculated)	0.785
Crystal system	cubic
Space group	$Pm-3m$
$a/\text{\AA}$	15.4292(9)
Z	1
Temperature /K	298(2)
X-ray source	$Cu K\alpha 1$
Wavelength / $\text{\AA}$	1.540596
$2\theta$ range /°	4.502-60.012
Number of reflections	146
Number of data points	4271
Refinement method	Rietveld refinement
$R_p$	0.0427
$R_{wp}$	0.0566
$R_{exp}$	0.0321
GOF	1.765
$R_{bragg}$	0.0130

**Gas adsorption of PCN-601.** The reddish powder of PCN-601 obtained through solvothermal reaction was washed with deionized (DI) water for several times to remove excess inorganic salt. Then the sample was washed with acetone for 3 times. After being soaked in acetone for additional 12 h, the sample was activated at 100 °C under vacuum for 12 h. Then, its  $N_2$  uptake was measured at 77 K.

**PXRD measurements for stability test of PCN-601.** After washed with DI water, as-obtained PCN-601 samples, 10 mg for each batch, were immersed in about 3.5 mL aqueous solution of 0.01 mmol/L HCl, 0.1 mmol/L HCl, 0.1 mol/L NaOH, 1 mol/L NaOH, 10 mol/L NaOH, and saturated NaOH (the solution is



**Figure 2:** Top-down topological analysis: binodal edge-transitive topologies with planar 4-connected nodes (top line), the nodes assigned to SBUs in corresponding nets (middle line), and reported Pz-based SBUs with the same symmetries and connectivities to corresponding nodes (bottom line).<sup>9b-d,12,13</sup> For the simplification of figure and the absence of reported planar 4-connected Pz-based SBU, the 5 topologies derived from uninodal edge-transitive nets with only 4-connected planar nodes are omitted here: **ssb-a**, **ssa-a**, **rhr-b**, **nbo-b** and **lvt-b**. Some pictures are reproduced with permission from Refs. 9b and 12, Copyright 2012 American Chemical Society.

concentrated with NaOH at 20 °C, which means the concentration is around 109 g NaOH/100 g H<sub>2</sub>O or 20 mol/L) at room temperature or 100 °C for 24 hours. The treated samples were washed with DI water (3 times) and acetone (3 times). The powders were dried under vacuum at 100 °C for 10 h before PXRD measurements.

**N<sub>2</sub> uptakes for stability test of PCN-601.** Two batches of samples (about 100 mg for each) were immersed in 35 mL of 0.1 mM HCl solution (at room temperature) and saturated NaOH solution (at 100 °C) for 24 hours, respectively. After being washed with water (3 times) and acetone (3 times), the samples were degassed on ASAP 2420 adsorption system for 10 h at 100 °C. These samples were then measured for N<sub>2</sub> adsorption at 77 K.

**UV-vis spectra for stability test of PCN-601.** Two batches of samples (about 5 mg for each) were immersed in 3.5 mL of 0.1 mM HCl solution (at room temperature) and saturated NaOH solution (at 100 °C) for 24 hours, respectively. After being washed with DI water (3 times), the samples were soaked in DMF for 24 hours. The clear solutions were taken for UV-vis spectrum measurements. The standard solution of H<sub>4</sub>TPP was prepared by dissolving 1 mg of H<sub>4</sub>TPP in 20 mL of DMF.

## RESULTS AND DISCUSSION

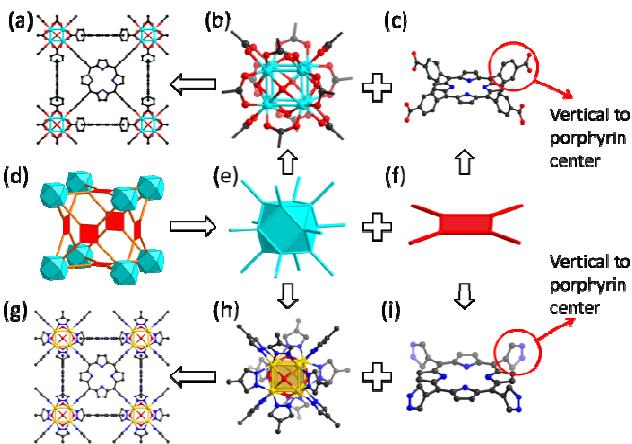
Despite of the well-known high robustness of Pz-based MOFs, researchers have faced great difficulty in synthesizing these materials. Because, unlike carboxylate-based MOFs, it is much more difficult to obtain single crystals or even highly crystalline powders of Pz-based MOFs, which makes structure determination challenging.<sup>9g,13</sup> To alleviate such challenges and obtain our desired product, a top-down strategy based on topological analysis is applied here. Firstly, we find out the possible topologies and structures which can theoretically incorporate our desired organic linkers. After limiting our preferred products to certain networks, we then rationally choose suitable SBUs and porphyrinic ligands with proper symmetry and geometry, which can fit into targeted structures. Finally, a synthetic condition which can generate our selected SBU is adopted to obtain our expected frameworks. In this way, the time consuming explorative synthet-

ic work can be minimized and matched structure can be easily identified by comparison with the proposed framework.

In the first step of the top-down strategy, to make searching of suitable topologies easier, we start from the simplest situation by restricting ourselves to MOFs containing only one kind of SBU, one kind of organic linker, and one kind of connecting edge, which are defined as binodal edge-transitive nets.<sup>9a</sup> Since tetratopic porphyrinic ligands are most frequently adopted in MOFs due to their relative ease of synthesis, we further zoom into binodal edge-transitive nets with planar 4-connected node. Herein, we enumerated the reported topologies that satisfy our requirements (Figure 2, top line), analyzed the nodes that can be assigned to SBUs in corresponding nets (Figure 2, middle line, the planar 4-connected node is assigned to porphyrinic linker in each topology), and listed the reported Pz-based SBUs with the same symmetries and connectivities to corresponding nodes (Figure 2, bottom line). Through this top-down analysis, eight candidate structures with different topologies (**pto-a**, **tbo-a**, **stp-a**, **soc-a**, **csq-a**, **scu-a**, **sqc-a**, and **ftw-a**) constructed by six kinds of SBUs are generated. Among these SBUs,  $[Ni_8(OH)_4(H_2O)_2Pz_{12}]$  (shorten as  $[Ni_8]$  below), a 12-connected cluster with  $O_h$  symmetry, is very intriguing to us.<sup>13</sup> Because it owns the highest connectivity in reported Pz-based SBUs, which empirically can increase the robustness of MOFs.<sup>5c</sup> Thus, a **ftw-a** network constructed by  $[Ni_8]$  and Pz-based tetratopic porphyrinic ligand becomes our target.

After determination of the topology and the SBU of our desired MOF, the next step is to consider the geometry details of Pz-based tetratopic porphyrinic ligand. Because the ligand is assigned to the 4-connected node with  $D_{4h}$  (or 4/mmm) symmetry in a **ftw-a** topology, therefore, only two possibilities are left here: the 4 peripheral Pz groups could be either perpendicular or parallel to the porphyrin center. To determine which type of ligands we should use, we picked PCN-221 as a reference for analysis (Figure 3). Because it is also a porphyrinic MOF with **ftw-a** topology.<sup>14</sup> In PCN-221, the SBU is both symmetrically and geometrically equivalent to  $[Ni_8]$ . Although when the  $[Zr_8O_6(CO_2)_{12}]^{8+}$  (denoted as  $[Zr_8]$ ) is simplified into a topological node, it is compatible with two topologically identical tetratopic porphyrinic

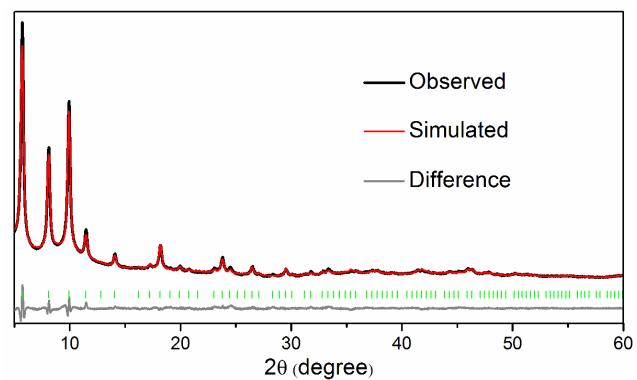
linkers with  $D_{4h}$  symmetry,<sup>5c</sup> in the real MOF construction only one type of linker fits when the spatial arrangement of  $[Zr_8]$  and porphyrinic linker is taken into account (Figure S4 in the Supporting Information). Therefore, to construct MOF isostructural to PCN-221, the ligand we use should also be geometrically equivalent to the ligand in PCN-221, which is tetrakis(4-carboxyphenyl) porphyrin ( $H_4TCPP$ ). As four peripheral benzoates are perpendicular to porphyrin center in TCPP<sup>4-</sup> (Figure 3c), we finally choose to construct our targeted MOF with  $H_4TPP$ , in which four Pz groups are forced vertical to the porphyrin center because of the steric hindrance of pyrrole rings (Figure 3i).



**Figure 3.** Topological and geometrical analysis of PCN-221 and PCN-601: (a) PCN-221; (b)  $[Zr_8O_6(CO_2)_{12}]^{8+}$  cluster moiety; (c) TCPP<sup>4-</sup>; (d) ftw-a topology; (e)  $O_h$  symmetric 12-connected node; (f)  $D_{4h}$  symmetric 4-connected node; (g) PCN-601 (Ni atoms in the porphyrin center are omitted for clarity); (h)  $[Ni_8]$  cluster moiety; (i) TPP<sup>4-</sup> ligand.

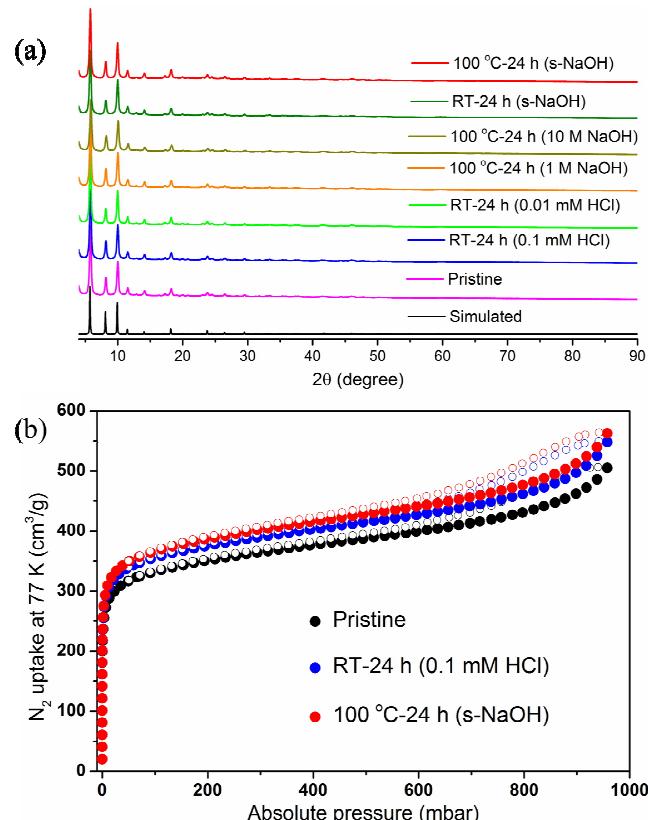
In order to obtain our hypothetic structure, the last step here is to explore synthetic condition to generate the desired cluster.  $[Ni_8]$ , as isolated cluster, has been synthesized with  $Ni(AcO)_2 \cdot 4H_2O$ , pyrazole, and a weak base in MeOH.<sup>13c</sup> Ideally, if we can conduct the synthesis under similar condition, it is quite possible to obtain our designed structure. However, given the low solubility of  $H_4TPP$  in MeOH, the solution for the synthesis of our targeted MOF needs to be optimized. Considering the deprotonation of  $H_2O$  and Pz groups during the formation of  $[Ni_8]$  and the high pKa values of these two species, we propose weak base might be feasible during synthesis of our desired MOF. After dozens of trials, crystalline powder of PCN-601 was finally obtained through the solvothermal reaction of  $H_4TPP$ ,  $Ni(AcO)_2 \cdot 4H_2O$ , water, and triethylamine ( $Et_3N$ ) in DMF.

Guided by the predicted structure, the model of PCN-601 with a space group of  $Pm\bar{3}m$  was constructed by Material Studio 6.0.<sup>15</sup> The unit cell parameter of  $a = b = c = 15.43 \text{ \AA}$  was obtained through indexing experimental high resolution powder X-ray diffraction (PXRD) data. The predicted structure was ultimately validated with Rietveld refinements (Figure 4). In addition, XAFS analysis of PCN-601 sample also suggests that Ni atom lies in a high symmetrical position such as octahedral center, being consistent with the refined structure (Figure S6 in the Supporting Information).

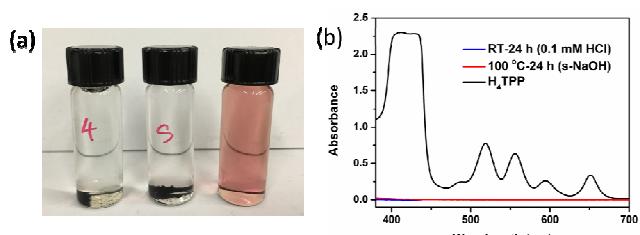


**Figure 4.** Rietveld refinement of PXRD data for PCN-601. The curves are simulated (red), observed (blue), and difference profiles (grey), respectively; the bars below curves indicate peak positions.

$N_2$  adsorption/desorption isotherm of PCN-601 at 77 K was performed, after washing and activation of the as-synthesized powder (Figure 5b and S8). A Brunauer-Emmett-Teller (BET) surface area of  $1309 \text{ m}^2 \text{ g}^{-1}$  and a  $N_2$  uptake of  $505 \text{ cm}^3 \text{ g}^{-1}$  were observed (Figure S9 in the Supporting Information). Evaluation of a density functional theory (DFT) simulation from the  $N_2$  sorption curve suggested the pore size distribution curve reached the maximum around 1.1 nm. The very low distributions of pores with larger diameters are possibly caused by the space between nanoparticles and the existence of defects in crystals (Figure S10 in the Supporting Information).<sup>16</sup>



**Figure 5.** (a) PXRD patterns for simulated, pristine PCN-601, and PCN-601 samples treated under different conditions; (b)  $N_2$  adsorption/desorption isotherms at 77 K of pristine PCN-601 and acid and base treated PCN-601 samples.



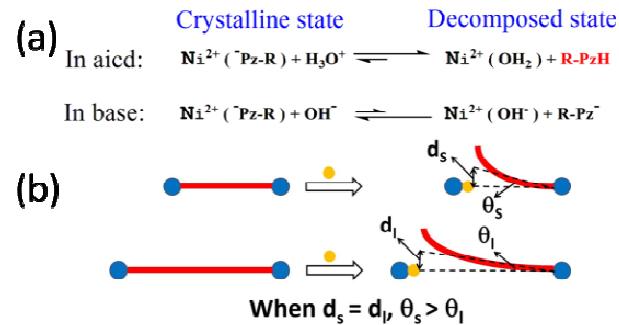
**Figure 6.** (a) DMF solutions with immersed PCN-601 samples being treated under 0.1 mM HCl solution at room temperature for 24 h (left) and saturated NaOH at 100 °C for 24 h (middle), respectively. In the right vial it is the standard solution of  $\text{H}_4\text{TPP}$  in DMF (1 mg/20 mL); (b) UV-vis spectra of different DMF solutions from the vials in Figure 6a.

Chemical stability of PCN-601 was then tested by treating its samples under different conditions. It was found that the PXRD patterns of all treated PCN-601 remain intact, which indicated there was no phase transition or framework collapse during treatments (Figure 5a). Moreover,  $\text{N}_2$  adsorption isotherms of PCN-601 treated under the harshest conditions further confirmed its viability in these environments (Figure 5b). Though it is not very obvious, the  $\text{N}_2$  uptake of PCN-601 after treatments is slightly higher than that of untreated sample. We propose that it could be explained by the removal of unknown coordination species trapped inside of the framework in as-synthesized samples during the treatment of acid or base solutions, which causes a slight increase of porosity of PCN-601. Such situation has also been observed in some other MOFs, like PCN-222, PCN-600, MIL-101 and MIL-53.<sup>5d</sup> Additionally, UV-vis adsorption spectra suggested that the ligand of PCN-601 did not leak into DMF solution even the samples were treated under the harshest conditions, which also proved the intactness of PCN-601 in stability tests (Figure 6).

We propose the extreme robustness of PCN-601 in basic aqueous media could be explained from both thermodynamic and kinetic perspectives. In basic condition, the decomposition procedure of PCN-601 could be considered as a competition between  $\text{Pz}^-$  and  $\text{OH}^-$  (or  $\text{H}_2\text{O}$ ) for  $\text{Ni}^{2+}$ . Compared to  $\text{OH}^-$  and  $\text{H}_2\text{O}$ ,  $\text{Pz}^-$  has higher crystal field splitting parameter.<sup>17</sup> According to crystal field theory, the coordination between  $\text{Ni}^{2+}$  and  $\text{Pz}^-$  can provide more crystal field stabilization energy than that between  $\text{Ni}^{2+}$  and  $\text{OH}^-$  (or  $\text{H}_2\text{O}$ ). This thermodynamically endows PCN-601 with strong resistance to the attack of  $\text{H}_2\text{O}$  and  $\text{OH}^-$  even under extremely basic condition (details in the Supporting Information section 10). However, in acidic solution, the major driving force of MOF decomposition becomes the competition between  $\text{H}^+$  and  $\text{Ni}^{2+}$  for  $\text{Pz}^-$ . Because of high  $\text{pK}_a$  value of pyrazole, the equilibrium is more inclined to the decomposed state (Scheme 2a). Therefore, both comparative acid-lability and extreme base-resistance of PCN-601 are related to its different thermodynamic behaviors in acid and base.

From kinetic aspect, the decomposition of MOFs in solution could be generally considered as a successive substitution reactions, during which defects are generated through replacing coordination moieties of ligands with small molecules or ions, akin to  $\text{H}_2\text{O}$  and  $\text{OH}^-$ .<sup>18</sup> Respect to the ligand, when one coordination site is displaced from the metal node, it might still stay around because of the restriction from other attached “arms” of ligands.

This generates a very high “effective concentration” of coordination moiety around the defect site. Therefore the rate of reverse reaction for the dissociated site to re-attach to the metal nodes is extremely fast,<sup>19</sup> which results in immediate structure reparation. When the connectivity of ligand is higher, this effect will become stronger, because the ligand could tolerate the displacements of more coordination sites and still keep a high rate of defect repair. We call this as “three-dimensional (3D) chelating effect” because of its similarity to the chelating effect in soluble coordination compound. Similar conclusion can be drawn if SBU is considered as the leaving moiety, where high connectivity of SBU will also enhance the stability of framework. Overall, when the connectivities of the ligand and SBU are high, partially ligand dissociation can hardly result in collapse of the whole framework because of the fast structure reparation. Therefore, such 3D chelating effect can contribute to the kinetic inertness of MOFs with highly connected SBUs and ligands. Besides the 3D chelating effect, activation energy is another critical factor in decomposition reaction of MOFs. Scheme 2b is a model to compare decomposition processes of two isoreticular MOFs with short and long ligands, noted as MOF-s and MOF-l respectively. For simplification, we first assume SBUs in these two MOFs are ideally rigid. No matter the substitution reactions undergo association or dissociation mechanism, ligands coordinated to SBUs need to be bent in transition states. When the displacements of terminals of ligands in transition states are equal in these two MOFs ( $d_s = d_l$ ), apparently the shorter ligand will be bended more severely ( $\theta_s > \theta_l$ ), which leads to a higher activation energy. As a result, MOFs becomes comparatively inert.<sup>20</sup> On the other hand, both rigidities of SBUs and ligands should also be taken into account in real situations. Reasonably, SBUs and ligands with higher connectivity will be stiffer, which makes MOFs constructed by them more stable.<sup>3c</sup> Given the facts that  $\text{TPP}^{4-}$  is the shortest porphyrinic ligands in reported porphyrinic MOFs and both  $[\text{Ni}_8]$  and  $\text{TPP}^{4-}$  have high connectivities, it is quite natural for PCN-601 to be kinetically stable.



**Scheme 2.** (a) Thermodynamic stability of PCN-601 in acid and base conditions; (b) Kinetic stability of MOFs with different length of ligands:  $d_s$  and  $d_l$  are the displacements of terminals of ligands in transition states,  $\theta_s$  and  $\theta_l$  are the bending angles of ligands in transition states.

In summary, guided by a top-down topological analysis, we rationally designed and synthesized PCN-601. Its stability has been carefully explored. PXRD and  $\text{N}_2$  adsorption suggested its crystallinity and porosity were perfectly maintained in saturated NaOH solution (20 mol/L) at RT and 100 °C. This not only pushes base-resistance of porphyrinic MOFs to the limit in aqueous media, but also greatly extends the scope of applications for these

1 materials. We also proposed thermodynamic and kinetic factors  
2 that might induce extraordinary robustness of PCN-601 in basic  
3 conditions. The extreme robustness in alkali aqueous media indeed  
4 endows PCN-601 with unique advantages in many applications,  
5 like pH sensing, catalysis, and photodynamic therapy, which may have high requirement to base-resistance of  
6 MOFs.<sup>3e,5b,8</sup> The exploration of PCN-601's performances in these  
7 applications are undergoing now.

## 9 ASSOCIATED CONTENT

### 10 Supporting Information

11 Full details for the synthesis and characterizations of the MOF,  
12 SEM, FT-IR, UV-vis, crystallographic data of the refined  
13 structure (CIF), N<sub>2</sub> isotherms, BET calculation, pore size  
14 distribution, XAFS analysis, and thermal and chemical stability  
15 check in the Supporting Information. This material is available  
16 free of charge via the Internet at <http://pubs.acs.org>.

## 17 AUTHOR INFORMATION

### 18 Author Contributions

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### 23 Notes

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