An Exceptionally Stable, Porphyrinic Zr Metal−Organic Framework Exhibiting pH-Dependent Fluorescence

Hai-Long Jiang,[†,‡,§] Dawei Feng,[†,§] Kecheng Wang,[†] Zhi-Yuan Gu,[†] Zhangwen Wei,[†] Ying-Pin Chen,[†] and Hong-Cai Zhou*,[†]

[†]Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States

[‡]Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China

Ⓢ *Supporting Information*

ABSTRACT: A reaction between a Zr^{IV} salt and a porphyrinic tetracarboxylic acid leads to a metal−organic framework (MOF) with two types of open channels, representing a MOF featuring a (4,8)-connected **sqc** net. The MOF remains intact in both boiling water and aqueous solutions with pH ranging from 1 to 11, a remarkably extensive pH range that a MOF can sustain. Given its exceptional stability and pH-dependent fluorescent intensity, the MOF can potentially be applied in fluorescent pH sensing.
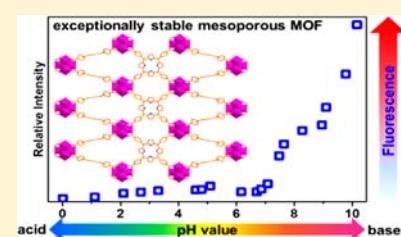
INTRODUCTION

In recent two decades, metal−organic frameworks (MOFs) have received tremendous attention due to their powerful attributes on structural and chemical versatility and tailorability.[1] The rational design in their construction promises these porous materials tailored to specific functional applications, such as gas storage/separation, catalysis, sensor, and drug delivery.[2−5] Despite this, stability has being recognized as a crucial issue on the way to practical applications of MOFs. Thermally, MOFs usually stabilize up to 250 °C and the best record demonstrates that the framework is able to maintain until even higher than 500 °C, which are robust enough as porous functional materials.[6] However, most MOFs are more or less sensitive to moisture, which could be one of the key limitations to meet the requirements of various applications. In addition, seldom were MOFs reported to be chemically resistant in an acidic or basic medium. On the basis of the previous reports, MOFs constructed by imidazole or pyrazolate derivatives are inclined to survive under alkaline conditions,[6d,7] while carboxylate-coordinated MOFs would withstand an acidic environment.[8]

To target the MOFs with both thermal and chemical stabilities, our group has aimed at zirconium(IV) carboxylates. According to "soft and hard acids and bases" theory, zirconium(IV) cation and carboxylate anion belong to hard acid and hard base, respectively, which makes the coordination bonds between zirconium and carboxylic oxygens very strong and potentially tolerable to attack of water, acid, and even base. However, the inert coordination bonds between Zr^{4+} cations and carboxylate anions make ligand exchange reactions extremely slow, which is unfavorable for defect repair in the process of crystal growth. Therefore, it is especially difficult to obtain single crystals of zirconium carboxylate MOFs and only a couple of them have been structurally characterized to

date.[6a,8b,9] During our persistent efforts in this research line, we have reported PCN-56 to -59 with UiO type structure that remains intact in dilute acid and base $(2 < pH < 11)^{9f}$ and PCN-222 survives in concentrated HCl solution[8b] recently. In this work, the assembly of zirconium(IV) and tetracarboxylic acids based on porphyrin center that could play multi-functionalities (such as light-harvesting, oxygen transportation, and catalysis, etc.[10]), leads to exceptionally stable Zr-MOFs, which are not only thermally stable (≥350 °C) but also retain frameworks in the aqueous solutions with pH ranges from 1 to 11. To our knowledge, this is the broadest pH range that a porphyrinic MOF can survive thus far. Remarkably, by perfectly combining the wide-pH-range stability and the dye characteristic of involved porphyrin center, our preliminary results have demonstrated that the resultant MOF could present pH-dependent fluorescence.

MATERIALS AND METHODS

Materials. Methyl 4-formylbenzoate was purchased from Oakwood Products, Inc. Pyrrole, propionic acid, *N,N*-dimethylformamide (DMF), *N,N*-diethylformamide (DEF), benzoic acid, acetone, zirconium(IV) chloride, glacial acetic acid, and zinc(II) chloride were purchased from Alfa Aesar. The tetrakis(4-carboxyphenyl)-porphyrin (H_2TCPP) and [5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrinato]-Zn(II) (Zn-TCPP) ligands were synthesized according to previous reports.[8b] All commercial chemicals were used without further purification unless otherwise mentioned.

Instrumentation. Powder X-ray diffraction (PXRD) was carried out with a BRUKER D8-Focus Bragg−Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178) at 40 kV and 40 mA. Elemental analyses (C, H, and N) were performed by Atlantic Microlab, Inc. (Norcross, Georgia). Thermogravimetric

analyses (TGA) were carried out on a Shimadzu TGA-50 thermal analyzer from room temperature to 650 °C at a ramp rate of 5 °C/min in a flowing nitrogen atmosphere. Fourier transform infrared (IR) measurements were performed on a SHIMADZU IR Affinity-1 spectrometer. Nuclear magnetic resonance (NMR) data were collected on a Mercury 300 spectrometer. Scanning Electron Microscope (SEM) images and Energy Dispersive Spectrometer (EDS) analyses were taken by FEI Quanta 600 FE-SEM. The fluorescence spectra were recorded by a PTI QuantaMaster series spectrofluorometer. The pure PCN-225 obtained was employed for fluorescent pH sensing studies. Prior to the fluorescent experiments, 2 mg of PCN-225 was soaked in 2.55 mL aqueous solutions with different acidity-basicity and the mixtures were ultrasonicated for some time to reach good dispersion. The final pH values for all solutions were remeasured by a pH-meter after fluorescent experiment. Gas sorption measurements were conducted using a Micrometritics ASAP 2020 system at different temperatures.

Synthesis of PCN-225. $ZrCl_4$ (25 mg), H_2TCPP (10 mg), benzoic acid (550 mg) and 5 drops of acetic acid in 2 mL of DEF were ultrasonically dissolved in a Pyrex vial. The mixture was heated in 120 °C oven for 12 h. After cooling down to room temperature, a purple powder was harvested by filtration (10 mg, 70% yield). Anal. Calcd (%) for PCN-225: C, 48.18; H, 2.86; N, 4.68%. Found: C, 48.78; H, 2.99; N, 4.32%.

Synthesis of PCN-225(Zn). $ZrCl_4$ (60 mg), Zn-TCPP (50 mg), and benzoic acid (3 g) in 9 mL of DEF were ultrasonically dissolved in a Pyrex vial. The mixture was heated in a 120 °C oven for 12 h. After cooling down to room temperature, violet crystals were harvested by filtration (10 mg, 70% yield). Anal. Calcd (%) for PCN-225(Zn): C, 45.76; H, 2.56; N, 4.45%. Found: C, 46.44; H, 2.86; N, 4.05%.

Sample Activation. Before the gas sorption experiment, as-synthesized PCN-225 and PCN-225(Zn) samples were washed with DMF followed by acetone and then immersed in acetone for around 2 days and exchanged once with fresh acetone during the period. The mixture was finally centrifuged and the acetone was removed by decanting. The sample was dried first by N_2 sweeping and then by using the "outgas" function of the adsorption instrument for 10 h at 100 °C prior to gas adsorption/desorption measurement.

Single Crystal X-ray Crystallography. Single crystals of PCN-225 suitable for single-crystal X-ray diffraction have been obtained in our experiments. As their similar structures evidenced by powder X-ray diffraction patterns and smaller crystals of PCN-225(Zn), only single crystal data of PCN-225 were collected.

Single crystal X-ray data of PCN-225 were collected on a Bruker Smart Apex diffractometer equipped with a low temperature device and a fine-focus sealed-tube X-ray source (Mo−Kα radiation, λ = 0.71073 Å, graphite monochromated). The data frames were collected using the program APEX2 and processed using the program SAINT routine within APEX2. The data were corrected for absorption and beam corrections based on the multiscan technique as implemented in SADABS. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement using the SHELXTL software package.[11a] Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Hydrogen atoms on carbon and nitrogen were calculated in ideal positions with isotropic displacement parameters set to 1.2 × Ueq of the attached atoms, while hydroxide hydrogen atoms were not added into the structure. In the structure, free solvent molecules were highly disordered, and attempts to locate and refine the solvent peaks were unsuccessful. Contributions to scattering due to these solvent molecules were removed using the SQUEEZE routine of PLATON;[11b] the structures were then refined again using the data generated. The contents of the solvent region are not represented in the unit cell contents in the crystal data. Crystallographic data and structural refinements for PCN-225 are summarized in Table S1 (Supporting Information, SI).

RESULTS AND DISCUSSION

Solvothermal reactions of zirconium(IV) chloride, tetrakis(4-carboxyphenyl)porphyrin (H_2TCPP), acetic acid, and benzoic acid in N,N-diethylformamide (DEF) at 120 °C yielded single crystals of $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(H_2TCPP)_2$ (denoted as PCN-225, PCN stands for "porous coordination network"). The similar reaction afforded polycrystalline powder of $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(ZnTCPP)_2$ (denoted as PCN225(Zn)) in the presence of $ZnCl_2$ while without acetic acid in the reactants. Powder X-ray diffraction (XRD) studies have revealed that both MOFs have similar framework topology and the only difference should be the replacement of two hydrogen atoms in each porphyrin center in PCN-225 with one Zn atom in PCN-225(Zn). Therefore, the structure of PCN-225 will be discussed below as a representative.

PCN-225 crystallizes in the tetragonal $I4_1/amd$ space group. There are two unique Zr atoms and both are coordinated by eight oxygen atoms, in which Zr_1 coordinates four μ_3-oxygens and the other four carboxylate oxygens from four H_2TCPP ligands; Zr_2 connects three hydroxide oxygens, three μ_3-oxygens, and two carboxylate oxygens from two H_2TCPP ligands. In the Zr_6 core of PCN-225, one Zr−O bond is around 2.05 Å that is shorter than 2.13 Å in UiO-66 and another Zr−O bond is 2.23 Å, which is longer than 2.13 Å. Since the Zr−O bond is an average length due to the symmetry in UiO-66 and the Zr_6 has lower symmetry in PCN-225, those two types of μ_3 oxygen could be differentiated into O^{2-} and OH^-. Therefore, the terminal oxygens have to be 4-OH and 4 H_2O. The average length of the bonds between Zr and terminal oxygens is 2.18 Å, which is shorter than Zr−H_2O bond (2.21 Å) in PCN-222, which suggests shorter bonds (Zr−OH) existing in PCN-225. This is consistent with our assignment. Therefore, the cluster formula in PCN-225 is assigned to be $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(COO)_8$.

Six Zr atoms connect eight μ_3-oxygen atoms to form a $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4$ cluster core, around which four −OH and four H_2O groups are attached as terminal groups with the eight bridging hydroxide oxygens in the same plane. As displayed in Figure 1a, each edge of Zr_6 octahedron is bridged by one carboxylate from a H_2TCPP ligand to afford an 8-connected Zr_6 core. It is worthy to note that the only 8-connected Zr_6 cluster was reported in PCN-222 most recently,[8b] while the other ZrO_x motifs are 12-connected Zr_6 clusters[6a,9a−f] and zirconium oxide chains[9g] in all Zr-carboxylate MOFs. Interestingly, for the cluster core in PCN-225, the six Zr atoms combine an exact octahedron (Figure 1b), while the eight μ_3-oxygens capped on the triangular faces of the Zr_6 octahedron form a highly distorted polyhedron, in which all three oxygens are in a unique plane (Figure 1c). In comparison, both Zr_6 octahedron and $(\mu_3\text{-}O)_8$ cube are idealized in PCN-222 (Figures 1d, e). As a result, the cluster symmetry in D_{4h} in PCN-222 reduces to D_{2d} in PCN-225, which could further induce lower symmetry in the framework of PCN-225.

In the H_2TCPP ligand, the peripheral benzene rings have 60.84° dihedral angle deviated from the porphyrin central plane and each carboxylic acid links to one Zr_6 cluster. Therefore, the H_2TCPP ligand is in a 4-connected mode to interconnect with Zr_6 clusters, giving rise to a three-dimensional (3D) structure with exactly the same two types of channels along either a or b-axes, while all pores are blocked along the c-axis. The small channel with size of 0.8 × 1.5 nm^2 in quadrangle shape is surrounded by two Zr_6 clusters and two ligands, whereas the
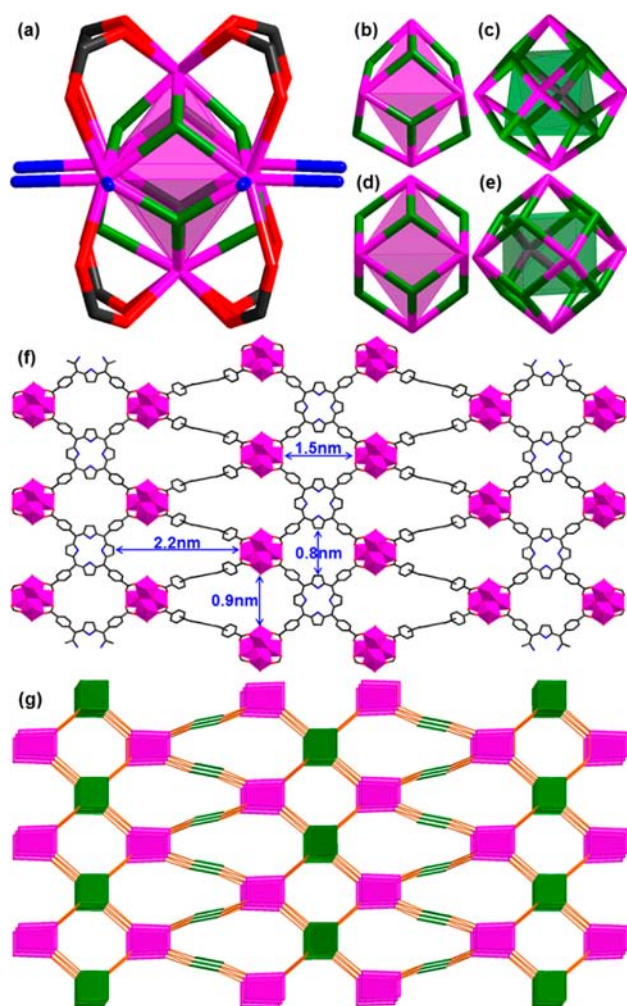
Figure 1. (a) $Zr_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(OH)_4(H_2O)_4(COO)_8$ cluster. The oxygen atoms from μ_3-OH/-O, −OH/H$_2$O and −COO groups are shown in green, blue and red, respectively. (b, c) Irregular $Zr_6(\mu_3$-O)$_4(\mu_3$-OH)$_4$ cluster core in PCN-225, in which six Zr atoms combine an idealized octahedron shaded in pink (b) whereas eight μ_3 oxygen atoms form a highly distorted polyhedron highlighted in green (c). (d, e) Idealized $Zr_6(\mu_3$-OH)$_8$ cluster core in PCN-222, where the Zr$_6$ octahedron and $(\mu_3$-O)$_8$ cube are drawn in pink and green, respectively. (f) View of the structure of PCN-225 along the *b*-axis with two types of channels. The Zr, O, C, N atoms are shown in pink, red, gray and blue, respectively. H atoms are omitted for clarity. (g) Schematic representation of the unprecedented (4,8)-connected **sqc** net for PCN-225 framework, in which Zr$_6$ cluster and H$_2$TCPP ligand are simplified as purple cubic and green square nodes, respectively.

larger one with size of 0.9 × 2.2 nm^2 in pear-like shape is comprised of three Zr$_6$ clusters and three ligands (Figure 1f). The solvent-accessible volume in PCN-225 is as high as 68.1% calculated using the PLATON routine.[12] As described above, the cluster and ligand can be respectively regarded as 8- and 4-connected nodes; thus in a topological view, the whole network can be extended to a 3D (4,8)-connected **sqc** net with the point symbol of $(4^4 \bullet 6^2)_2 (4^8 \bullet 6^{16} \bullet 8^4)$ (Figure 1g). There have been a few (4,8)-connected MOFs reported and they are almost concerned with **flu**, **scu** and **alb** nets.[13] As far as we know, PCN-225 and PCN-225(Zn) represent the first MOFs with a (4,8)-connected **sqc** net.

Thermogravimetric (TG) analyses in the N$_2$ stream show that the frameworks of both MOFs start to decompose around

350 °C and the weight loss before 300 °C could be mainly attributed to the isolated *N,N*-diethylformamide (DEF) molecules and coordinated hydroxide groups/water molecules. Strikingly, both MOFs also exhibit amazing chemical stability and powder XRD results have suggested that they remain stable not only in boiling water but also in aqueous solutions with pH values in the range of 0−12 (Figure 2 and Section 3 in the SI).
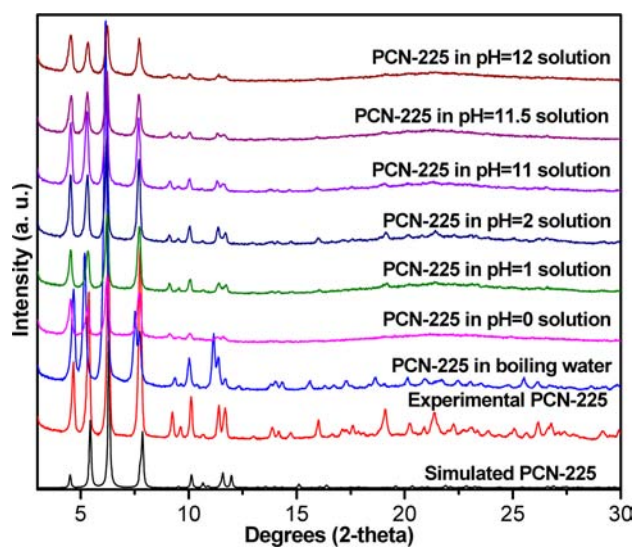

Figure 2. Powder X-ray diffraction (XRD) profiles for simulated and experimental PCN-225 and PCN-225 samples soaked in boiling water and aqueous solutions with pH values of 0, 1, 2, 11, 11.5, and 12 for 12 h.

The powder XRD profiles are almost unaltered, revealing the retained crystallinity. To further demonstrate the stability of PCN-225, we have conducted N$_2$ sorption upon soaking MOF in the solutions with different pH values. N$_2$ adsorption isotherms indicate that the porosity of PCN-225 is perfectly maintained in pH = 1−11 solutions as well as boiling water. Only slight decrement has been found in pH = 0 solution and less than half of the porosity loss has been observed in pH = 12 solution, which indicates the relative stability in a wider pH range. Although some MOFs have been reported to have water tolerance or chemical stability in acidic or basic media, very few MOFs were found to be resistant to both acid and base. To our knowledge, NO$_2$-tagged UiO-66 was reported to have short-period (2 h) stability in both acid and basic solutions,[9a] and a microporous pyrazolebased Ni-MOF with pore size of 1 nm was demonstrated to be stable in solutions with a pH range of 2−14.[6d] The enlarged pore sizes usually weaken the framework stability and make their collapse easier under harsh conditions. Therefore, PCN-225 is one of the most stable MOFs with large pore sizes that can survive in an extensive pH range.

The permanent porosity of both MOFs has been confirmed by nitrogen and argon sorption experiments at 77 and 87 K, respectively (Figure S7, SI). The N$_2$ uptakes fall in 450−500 cm^3/g (STP) and the similar Brunauer−Emmett−Teller (BET) surface areas are 1902 and 2080 m^2/g, respectively for PCN-225 and PCN-225(Zn). These values are among the highest reported for porphyrinic MOFs and the porosity is hardly preserved upon removal of solvent molecules in previously reported porphyrinic MOFs.[14] The slightly higher Ar uptakes than N$_2$ should be attributed to the smaller molecule diameter of argon that allows it to occupy pore spaces more efficiently.

The similar H_2 uptakes for PCN-225 and PCN-225(Zn) are 1.80 and 1.76 wt %, which are comparable to most of MOFs and at the high end among those for Zr-MOFs with the high weight of Zr element. The slightly lower isosteric heat of H_2 adsorption for PCN-225 than that of PCN-225(Zn) should be ascribed to the absence of exposed zinc(II) centers (Section 6 in the SI).

Fluorescent pH sensors have certain advantages over electrodes and present widespread applications spanning from environmental analysis, bioanalytical chemistry to medical diagnostics, etc. Encouraged by the wide-pH-range stability, in the combination of fluorescent porphyrin dye involved in the framework, the pH-dependent fluorescence of PCN-225 has been explored (Figure 3a). The weak fluorescence emission of H_2TCPP ligand at 725 nm (λ = 415 nm) is owing to the conjugated double bond system and the high mobility of the π-electrons. Similarly, the excitation of PCN-225 at 415 nm gives an emission peak at ~725 nm, which could be assigned to the intraligand transitions. Interestingly, the fluorescence intensity of PCN-225 is strongly correlated with pH value of the dispersed solution in our experimental pH range (0−10.2), in which the most acidic solution gave weakest fluorescence while the highest intensity was obtained with pH = 10.2 solution. Significantly, although the intensity almost rises along with pH increasing in the whole experimental range (0−10.2), it is not a simple linear relationship between pH value and fluorescent intensity (Figure 3b), which is in good agreement with our simulated results (Section 11 in the SI). When the pH is below 5, which is characteristic of protonation of the pyrrole ring, rising the pH leads to a very slightly increase in emission intensity. At high acidity, proton in the aqueous solution attach to the pyridine-type nitrogen atoms in the porphyrin center to afford the protonated nitrogens, which destroy the π-electron conjugated double-bond system of porphyrin and thus result in significant fluorescence quenching (Figure 3c).[15] In comparison, when the pH is higher than 7, PCN-225 presents much stronger fluorescence that is in close association with pH. The fluorescence enhancement and slight blue-shift in basic solution are assumed to arise from deprotonation of imino group of porphyrin involved in the PCN-225 framework (Figure 3c).[15a] So far, only one Eu-based MOF has been reported as a pH senor in the pH range of 5−7.5.[16] Our preliminary results indicate pH-dependent fluorescence response of PCN-225 in a much wider pH range due to the exceptional chemical stability, which suggests that PCN-225 could be promising MOF for pH sensing, especially in the pH range of 7−10.

CONCLUSION

In summary, zirconium-porphyrin frameworks, PCN-225 and PCN-225(Zn), have been developed as the first MOFs with a (4,8)-connected **sqc** net. They exhibit exceptional chemical stability in aqueous solutions with pH ranging from 1 to 11, which, to our knowledge, is the most extensive pH range that a porphyrinic MOF can survive. Remarkably, given the wide-pH-range stability and that the central core region of porphyrin free base is subject to protonation−deprotonation equilibrium upon varying the pH, the fluorescence intensity of PCN-225 is in close correlation with pH variation, of which 7 < pH < 10 is the most sensitive range for intensity response. The results indicate that PCN-225 is promising for pH sensing. Furthermore, the ready installation of exposed metal sites in the porphyrin center in PCN-225, combined with its high stability, should raise their
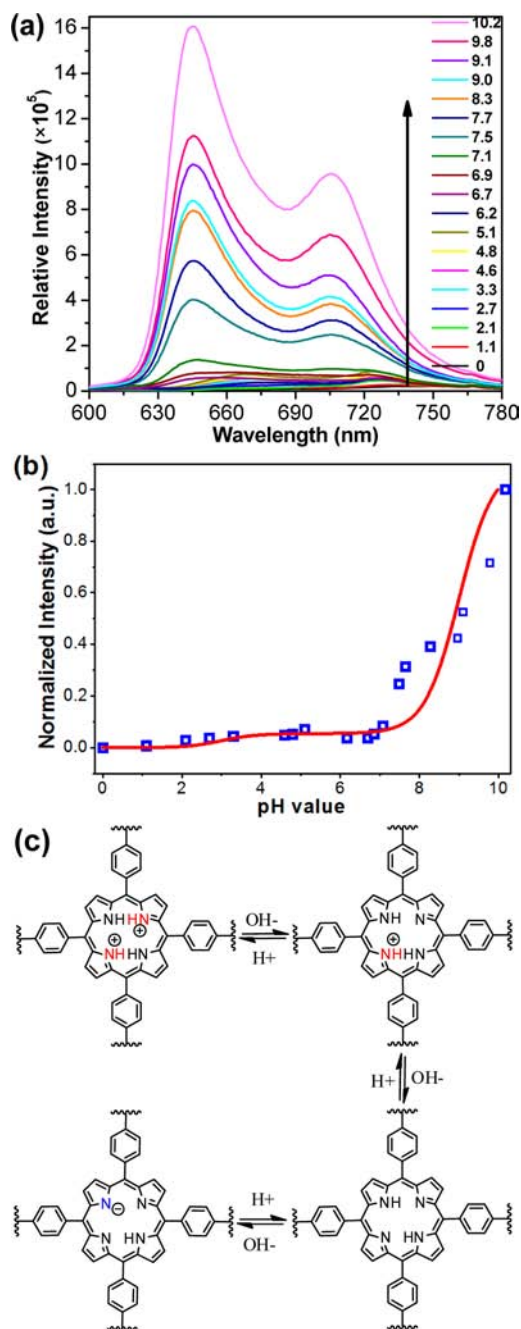

Figure 3. (a) pH dependent fluorescence of PCN-225 in the aqueous solutions with pH ranging from 0 to 10.2 measured under excitation of 415 nm. (b) Blue points showed fluorescence emission at 725 nm at different pH, matching the simulation fluorescence intensity (red line). (c) Protonation and deprotonation processes of porphyrin involved in PCN-225 framework in experimental acidic and basic media (pH = 0− 10.2).

potential for a variety of applications, especially catalysis, light-harvesting, sensor, and so on.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Full details for characterization results, discussions, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

■ **AUTHOR INFORMATION**

Corresponding Author
zhou@mail.chem.tamu.edu

Author Contributions
§H.-L.J. and D.F. contributed equally to this work.

Notes
The authors declare no competing financial interest.

■ **REFERENCES**

(1) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217. (c) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695. (d) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213. (e) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 673.

(2) (a) Wu, H.; Zhou, W.; Yildirim, T. *J. Am. Chem. Soc.* **2009**, *131*, 4995. (b) Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo, T. K. *Science* **2010**, *330*, 650. (c) Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch, E. D.; Herm, Z. R.; Bae, T.-H.; Long, J. R. *Chem. Rev.* **2012**, *112*, 724. (d) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782. (e) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869. (f) Gu, Z.-Y.; Yang, C.-X.; Chang, N.; Yan, X.-P. *Acc. Chem. Res.* **2012**, *45*, 734−745.

(3) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Ma, L.; Abney, C.; Lin, W. *Chem. Soc. Rev.* **2009**, *38*, 1248. (c) Farrusseng, D.; Aguado, S.; Pinel, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 7502. (d) Corma, A.; García, H.; Llabrés i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606. (e) Jiang, H.-L.; Xu, Q. *Chem. Commun.* **2011**, *47*, 3351. (f) Zhang, Z.; Zhang, L.; Wojtas, L.; Eddaoudi, M.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2012**, *134*, 928.

(4) (a) Chen, B.; Xiang, S.; Qian, G. *Acc. Chem. Res.* **2010**, *43*, 1115. (b) Jiang, H.-L.; Tatsu, Y.; Lu, Z.-H.; Xu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 5586. (c) Takashima, Y.; Martinez, V.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. *Nat. Commun.* **2011**, *2*, 168. (d) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105.

(5) (a) An, J.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8376. (b) Rocca, J. D.; Liu, D.; Lin, W. *Acc. Chem. Res.* **2011**, *44*, 957. (c) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Férey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232.

(6) (a) Cavka, J. H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K. P. *J. Am. Chem. Soc.* **2008**, *130*, 13850. (b) Banerjee, D.; Borkowski, L. A.; Kim, S. J.; Parise, J. B. *Cryst. Growth Des.* **2009**, *9*, 4922. (c) Ibarra, I. A.; Yang, S.; Lin, X.; Blake, A. J.; Rizkallah, P. J.; Nowell, H.; Allan, D. R.; Champness, N. R.; Hubberstey, P.; Schröder, M. *Chem. Commun.* **2011**, *47*, 8304. (d) Colombo, V.; Galli, S.; Choi, H. J.; Han, G. D.; Maspero, A.; Palmisano, G.; Masciocchi, N.; Long, J. R. *Chem. Sci.* **2011**, *2*, 1311.

(7) (a) Park, K. S.; Ni, Z.; Côté, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 10186. (b) Huang, X. C.; Lin, Y. Y.; Zhang, J. P.; Chen, X. M. *Angew. Chem., Int. Ed.* **2006**, *45*, 1557.

(8) (a) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040. (b) Feng, D.; Gu, Z.-Y.; Li, J.-R.; Jiang, H.-L.; Wei, Z.; Zhou, H.-C. *Angew. Chem., Int. Ed.* **2012**, *51*, 10307.

(9) (a) Kandiah, M.; Nilsen, M. H.; Usseglio, S.; Jakobsen, S.; Olsbye, U.; Tilset, M.; Larabi, C.; Quadrelli, E. A.; Bonino, F.; Lillerud, K. P. *Chem. Mater.* **2010**, *22*, 6632. (b) Schaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P. *Chem.—Eur. J.* **2011**, *17*, 6643. (c) Schaate, A.; Roy, P.; Preuße, T.; Lohmeier, S. J.; Godt, A.; Behrens, P. *Chem.—Eur. J.* **2011**, *17*, 9320. (d) Morris, W.; Volosskiy, B.; Demir, S.; Gándara, F.; McGrier, P. L.; Furukawa, H.; Cascio, D.; Stoddart, J. F.; Yaghi, O. M. *Inorg. Chem.* **2012**, *51*, 6443. (e) Bon, V.; Senkovskyy, V.; Senkovska, I.; Kaskel, S. *Chem. Commun.* **2012**, *48*, 8407. (f) Jiang, H.-L.; Feng, D.; Liu, T.-F.; Li, J.-R.; Zhou, H.-C. *J. Am. Chem. Soc.* **2012**, *134*, 14690. (g) Guillerm, V.; Ragon, F.; Dan-Hardi, M.; Devic, T.; Vishnuvarthan, M.; Campo, B.; Vimont, A.; Clet, G.; Yang, Q.; Maurin, G.; Férey, G.; Vittadini, A.; Gross, S.; Serre, C. *Angew. Chem., Int. Ed.* **2012**, *51*, 9267.

(10) Kadish, K. M., Smith, K. M., Guilard, R., Eds. *The Porphyrin Handbook*; Academic Press: San Diego, 2000−2003.

(11) (a) *APEX2 v2012.2.0* and *SAINT v7.68A* data collection and data processing programs, respectively; Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2012. Sheldrick, G. M. *SADABS v2008/1 semi-empirical absorption and beam correction program*; University of Göttingen: Germany, 2008. (b) Sheldrick, G. M., *SHELXTL*, Version 6.14; Structure Determination Software Suite; Bruker AXS: Madison, WI, 2003.

(12) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

(13) (a) Chun, H.; Kim, D.; Dybtsev, D. N.; Kim, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 971. (b) Lan, Y. Q.; Li, S. L.; Li, Y. G.; Su, Z. M.; Shao, K. Z.; Wang, X. L. *CrystEngComm* **2008**, *10*, 1129. (c) Wen, L.; Cheng, P.; Lin, W. *Chem. Sci.* **2012**, *3*, 2288. (d) Jiang, H.-L.; Lin, Q.-P.; Akita, T.; Liu, B.; Ohashi, H.; Oji, H.; Honma, T.; Takei, T.; Haruta, M.; Xu, Q. *Chem.—Eur. J.* **2011**, *17*, 78. (e) Lan, Y.-Q.; Jiang, H.-L.; Li, S.-L.; Xu, Q. *Inorg. Chem.* **2012**, *51*, 7484. (f) He, Y.; Zhang, Z.; Xiang, S.; Fronczek, F. R.; Krishna, R.; Chen, B. *Chem.—Eur. J.* **2012**, *18*, 613.

(14) (a) Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 5652. (b) Lee, C. Y.; Farha, O. K.; Hong, B. J.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 15858. (c) Burnett, B. J.; Barron, P. M.; Hu, C.; Choe, W. *J. Am. Chem. Soc.* **2011**, *133*, 9984. (d) Yang, X.-L.; Xie, M.-H.; Zou, C.; He, Y.; Chen, B.; O'Keeffe, M.; Wu, C.-D. *J. Am. Chem. Soc.* **2012**, *134*, 10638. (e) Fateeva, A.; Devautour-Vinot, S.; Heymans, N.; Devic, T.; Grenèche, J.-M.; Wuttke, S.; Miller, S.; Lago, A.; Serre, C.; Weireld, G. D.; Maurin, G.; Vimont, A.; Férey, G. *Chem. Mater.* **2011**, *23*, 4641. (f) Wang, X.-S.; Chrzanowski, M.; Gao, W.-Y.; Wojtas, L.; Chen, Y.-S.; Zaworotko, M. J.; Ma, S. *Chem. Sci.* **2012**, *3*, 2823.

(15) (a) Manna, B. K.; Bera, S. C.; Rohatgi-Mukherjee, K. K. *Spectrochim. Acta, Part A* **1995**, *51*, 1051. (b) Thyagarajan, S.; Leiding, T.; Årsköld, S. P.; Cheprakov, A. V.; Vinogradov, S. A. *Inorg. Chem.* **2010**, *49*, 9909.

(16) (a) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. *Chem. Rev.* **2012**, *112*, 1126. (b) Harbuzaru, B. V.; Corma, A.; Rey, F.; Jordá, J. L.; Ananias, D.; Carlos, L. D.; Rocha, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6476.