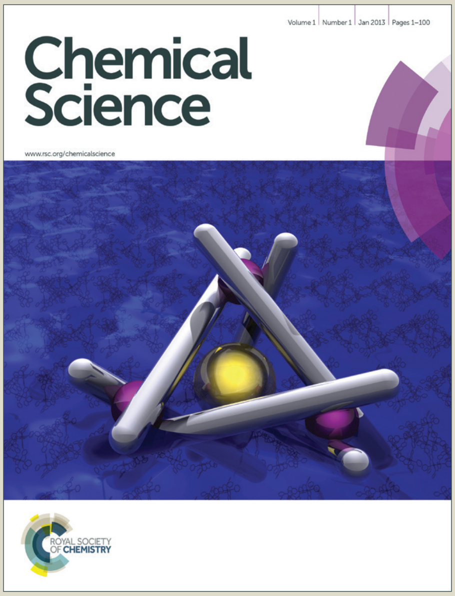

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Stable porphyrin Zr and Hf metal-organic frameworks featuring 2.5 nm cages: high surface areas, SCSC transformations and catalyses

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Two isostructural porphyrin Zr and Hf metal-organic frameworks (**FJI-H6** and **FJI-H7**) are designedly synthesized, which are constructed from 2.5 nm cubic cages. Notably, they both possess high water and chemical stability and can undergo single-crystal to single-crystal transformations to embed Cu^{2+} ions into the open porphyrin rings. Especially, **FJI-H6** has a high BET surface area of 5033 m^2g^{-1}. Additionally, they exhibit promising catalysis abilities of converting CO_2 and epoxides into cyclic carbonates at ambient condition.

Owing to the high surfaces, permanent porosity and tunable pores, metal-organic frameworks (MOFs) have been envisioned for catalysis,[1] gas separation and storage,[2] and drug delivery.[3] Nonetheless, one big obstacle to the practical applications of the MOFs is the stability, which includes water and chemical stability. To target the stable MOFs, one effective method is the usage of high-valence metal ions such as Fe^{3+}, Al^{3+}, Cr^{3+}, Zr^{4+} and Hf^{4+} ions as the metal nodes.[4] Compared with the traditional Cu^{2+}, Zn^{2+} and Co^{2+} ions,[5] the fore-mentioned trivalent or tetravalent metal ions will form stronger bonds with carboxylate groups according to the theory of hard and soft acids and bases. Therefore, the stability of the obtained frameworks will be strengthened. Furthermore, those high-valence metal ions tend to form high-connected inorganic clusters *via* the OH^- and / or O^{2-} bridges, which also have much contribution to the stability of the frameworks. As for the Zr^{4+} ion, it prefers to form the classical 12-connected $Zr_6O_4(OH)_4$ node. When assembled with linear carboxylate ligands, 3D fcu frameworks with ordered cubic cages (known as UiO series) can be obtained.[6] This kind of Zr-based MOFs often have high water and chemical stability, which even can serve as the water adsorbents.[7] Up to now, extensive investigation has been carried out to tune the porosity of the UiO series Zr-MOFs by selectively removing organic linkers[8] or functionalizing the ligands (pre-modification or post-synthetic methods).[9] However, there are several examples based on the assembly of the $Zr_6O_4(OH)_4$ clusters with the polycarboxylic ligands such as planar tetracarboxylic acids.[7b, 10] In addition, compared with Zr-based MOFs the Hf-based MOFs are also rare.[6f, 11] Herein, we present two ultra-stable metal-organic framework ($[Zr_6O_4(OH)_4(H_2TBPP)_3]_n$•$(solvent)_x$) (**FJI-H6**) and ($[Hf_6O_4(OH)_4(H_2TBPP)_3]_n$•$(solvent)_x$) (**FJI-H7**), which are isostructural and both constructed from the $M_6O_4(OH)_4(CO_2)_{12}$ nodes (M = Zr, Hf) and porphyrin tetracarboxylic ligands (H_6TBPP = 4',4''',4''''',4'''''''-(porphyrin-5,10,15,20-tetrayl)tetrakis([1,1'-biphenyl]-4-carboxylic acid)). As expected, both **FJI-H6** and **FJI-H7** have high water and chemical stability and can undergo the single-crystal-to-single-crystal (SCSC) transformation to embed Cu^{2+} ions into the open porphyrin rings. Interestingly, they both feature 2.5 nm cages. Especially, **FJI-H6** has a high BET surface area of 5033 m^2g^{-1}.

Results and discussion

Syntheses and structures of porphyrin Zr and Hf MOFs

Reaction of H_6TBPP with $ZrCl_4$ or $HfCl_4$ modulated by benzoic acid gives rise to dark red crystals of **FJI-H6** or **FJI-H7**. Single crystal X-ray structural analysis shows that **FJI-H6** and **FJI-H7** are isostructural.[12] Therefore, we choose **FJI-H6** as the example in the following discussion. **FJI-H6** crystallizes in the high-symmetry space group *P*m-3m. In the $Zr_6O_4(OH)_4$ cluster, six equivalent Zr^{4+} ions are in the square-antiprismatic O_8 coordination environment and form an regular octahedron. In the Zr_6 octahedron, eight triangular faces are alternatively capped by four μ_3-OH^- and μ_3-O^{2-} groups. Additionally, twelve edges of the Zr_6 octahedron are bridged by twelve carboxylate groups from twelve unique H_2TBPP ligands. At the same time, each H_2TBPP ligand, in which the peripheral four phenyl rings are well coplanar with the inner porphyrin rings, links four independent $Zr_6O_4(OH)_4$ clusters. Thus, a rarely-seen (4,12)-connected *ftw* framework can be acquired.[10a, 11b, 13] **FJI-H6** has two kinds of polyhedral cages, *i.e.* small octahedral cage and big cubic cage. As seen in Figure 1, the octahedral cage is constructed from two $Zr_6O_4(OH)_4$ clusters and four H_2TBPP ligands, with the cavity diameter of *c.a.* 1.5 nm. However, the cubic cage consists of eight $Zr_6O_4(OH)_4$ clusters as the vertices and six H_2TBPP ligands as the sides. In particular, the diameter of the cubic cage is approximately 2.5 nm, which is larger than that in the PCN-221 (2.0 nm).[11b] Accordingly, the available volume is 15000 $Å^3$. Additionally, the window of the cubic cage is 1.2 nm × 2.0 nm, which allows large organic molecules to freely get in and out.

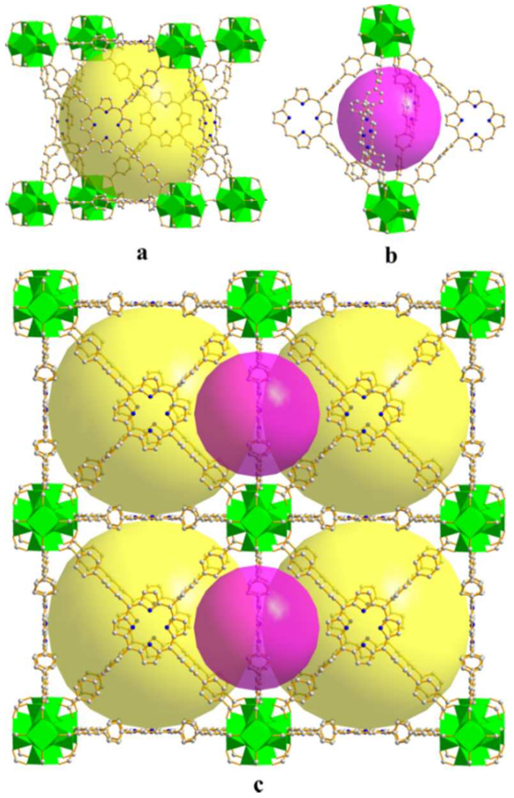


Figure 1 a) The large cubic cage constructed from six porphyrin ligands and eight $Zr_6O_4(OH)_4$ clusters. b) The small octahedral cage constructed from four porphyrin ligands and two $Zr_6O_4(OH)_4$ clusters. c) Packing of two kinds of cages.

Gas adsorption experiments and stability tests

Calculation by *PLATON* software[14] reveals that in **FJI-H6** the free volume is up to 78.6%. For **FJI-H6** the permanent porosity is confirmed by N_2 adsorption isotherm measured at 77 K. The sample exchanged with acetone exhibits reversible type I isotherm and has a saturated uptake of 1346 $cm^3\ g^{-1}$ at 1 atm (Figure 2). When pre-treated with 8 M HCl, the value of N_2 adsorption slightly increases and gets to 1393 $cm^3\ g^{-1}$, which indicates that **FJI-H6** is stable to the acid. From the above data, the calculated BET surface area of the sample exchanged with acetone is up to 5007 $m^2\ g^{-1}$ (5033 $m^2\ g^{-1}$for the sample pre-treated with 8 M HCl), which is much larger than those of PCN-222(Fe) (2200 $m^2\ g^{-1}$),[4b] NU-1000 (2320 $m^2\ g^{-1}$),[15] PCN-223(Fe) (1600 $m^2\ g^{-1}$),[10c] PCN-94 (3377$m^2\ g^{-1}$),[10b] NU-1100 (4020 $m^2\ g^{-1}$)[10a] and PCN-229 (4619 $m^2\ g^{-1}$),[13] but less than those of just reported NU-1103 (5646 $m^2\ g^{-1}$) and NU-1104 (5290 $m^2\ g^{-1}$).[10e] In addition, **FJI-H6** also has the high total pore volume of 2.16 $cm^3\ g^{-1}$. The experimental BET surface area and pore volume are consistent with theoretical ones calculated by *Poreblazer*[16] (accessible surface area: 4695 $m^2\ g^{-1}$; the pore volume: 2.06 $cm^3\ g^{-1}$)[14], which demonstrates that the sample is fully activated. Additionally, **FJI-H6** also shows good capacity of H_2 storage. The H_2 uptake reaches 172 $cm^3\ g^{-1}$ (1.54 wt%) at 1 atm and 77 K, and 108 $cm^3\ g^{-1}$ (0.94 wt%) at 87 K and 1 atm. Moreover, the adsorption heat of H_2 calculated by the Clausius–Clapeyron equation is 6.54 kJ mol^{-1} at zero coverage and decreases slowly along with the increasing H_2 loading. These values are comparable to those of the famous MOFs materials, such as HKUST-1 (6.6 kJ mol^{-1}),[17] MOF-5 (5.2 kJ mol^{-1}),[17] and NOTT-122 (6.0 kJ mol^{-1}).[18] As for **FJI-H7** the sample exchanged with acetone also exhibits reversible type I isotherm and has a saturated uptake of 1029 $cm^3\ g^{-1}$ at 1 atm. From the above data, the calculated BET surface area of **FJI-H7** is up to 3831 $m^2\ g^{-1}$, which is also among the highest of Hf-based MOFs reported.[11]

Since the $Zr_6O_4(OH)_4$ and $Hf_6O_4(OH)_4$ cluster are both highly connected with twelve carboxylate groups, **FJI-H6** and **FJI-H7** are expected to have high stability. To test their stability, we immersed the micro-crystal sample of **FJI-H6** or **FJI-H7** into the water with various pH values for 24 h (See Figure S2). The PXRD patterns of the resulting samples well match with the simulated one, which suggests that **FJI-H6** and **FJI-H7** retain their crystalline. Especially, **FJI-H6** has high stability to the acid. As seen in Figure 2, both the curves and the adsorption values for the sample in 1 M HCl do not deviate much from those of the untreated sample.

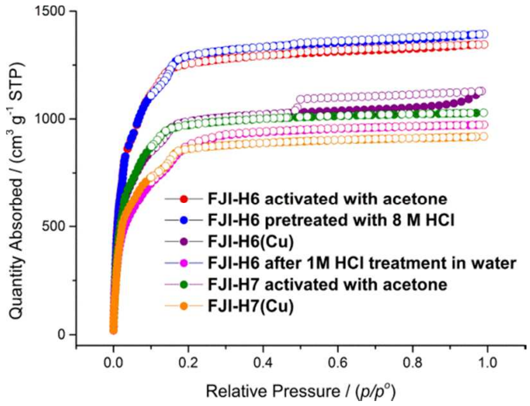
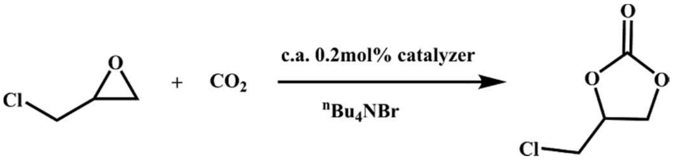


Figure 2 Experimental N_2 adsorption isotherms for **FJI-H6**, **FJI-H6(Cu)**, **FJI-H7** and **FJI-H7(Cu)**.

Incorporating Cu^{2+} ions into the open porphyrin rings *via* the SCSC transformations

Considering that in both **FJI-H6** and **FJI-H7** two nitrogen atoms of the porphyrin ring are un-deprotoned, we attempt to introduce the second kind of metal ions into the framework. Immersing the single-crystals of **FJI-H6** or **FJI-H7** into a solution of 0.5 M $Cu(NO_3)_2$ in N,N-dimethyl formamide (DMF) at 85 °C for 72 h results in metallated **FJI-H6(Cu)** or **FJI-H7(Cu)**. As anticipated, single crystal X-ray structural analysis definitely shows that in both **FJI-H6** and **FJI-H7** the Cu^{2+} ions have been embedded in the porphyrin rings. The Cu^{2+} ion is in the square planar N4 coordination environment with two axial sites exposed, which is typical for the divalent metal ions in the metal-porphyric complexes.[19] As we know, though there are several examples of exchanging metal ions in the porphrin MOFs it is the first observation of incorporating metal ions into the open porphyrin rings *via* the SCSC transformations in the porphyrin MOFs. N_2 adsorption measurements at 77 K for **FJI-H6(Cu)** also show type I isotherm. At 1 atm, **FJI-H6(Cu)** has the maximum N_2 adsorption of 1128 cm^3 g^{-1}, which is smaller than that of FJI-H6. Accordingly, the BET surface area of **FJI-H6(Cu)** is reduced to 3731 m^2 g^{-1}. Similarly, the maximum N_2 adsorption and BET surface area of **FJI-H7(Cu)** (918 cm^3 g^{-1} and 3195 m^2 g^{-1} respectively) are also lower than those of **FJI-H7**. The reason may be ascribed to the introduction of Cu^{2+} ions, which can slightly diminish the surface area.



Scheme 1 Cycloaddition reactions of CO_2 with epoxide catalyzed by **FJI-H6(Cu)**, **FJI-H7** and **FJI-H7(Cu)**.

Cycloaddition reactions of CO_2 with epoxide

Recently, owing to the global warming, efficient CO_2 capture and storage is urgent to reduce the CO_2 emissions before the scientists find a practical clean energy. If we can convert this abundant inorganic waste into the usable organic chemicals utilizing reasonable reactions at ambient conditions, the above problem can be perfectly solved. One practical method is the synthesis of cyclic carbonates from the CO_2 and epoxides, which have extensive applications in degreasers, polar aprotic solvents and electrolytes in lithium ion batteries. Though many catalysts have been explored for the above reaction, metalloporphyrins show relatively high catalytic activity.[20] Hence, we have evaluated **FJI-H6**, **FJI-H6(Cu), FJI-H7** and **FJI-H7(Cu)** as heterogeneous catalysts for the cycloaddition reactions of CO_2 with epoxide. Typically, 25.5 mmol 3-chloropropylene oxide, 0.51 mmol (2.0 mol%) tetrabutylammonium bromide and 0.051 mmol (0.2 mol%) catalysts were added to a thick wall glass tube with a stirring bar. The tube was vacuumed and then purged with CO_2. The above circle was repeated for three times. Finally, the pressure of CO_2 was set as 1 atm. The mixture was stirred at 25 ^{o}C for 60 hours. Analysis of the resulting solution by gas chromatography indicated that 52.6%, 61.8%, 64% and 66.5% epoxide were converted into cyclic carbonate for **FJI-H6**, **FJI-H6(Cu)**, **FJI-H7** and **FJI-H7(Cu)** respectively. Though the yields are not very high compared with the homogeneous catalysts, it is also promising considering the low temperature and pressure. Compared with **FJI-H6** or **FJI-H7**, **FJI-H6(Cu)** or **FJI-H7(Cu)** has higher catalytic ability. The reason may be that as a lewis catalytic site the embedded Cu(II) ion in the porphyrin ring contributes to some extent. At the same time, the Hf-based MOFs **FJI-H7** and **FJI-H7(Cu)** have higher catalytic abilities than the corresponding Zr-based MOFs **FJI-H6** and **FJI-H6(Cu)** respectively since the Hf ion is more oxophilic than Zr ion and acts as a stronger lewis acid. Additionally, the PXRD patterns of **FJI-H6(Cu)**, **FJI-H7** and **FJI-H7(Cu)** after catalyses are also in good agreement with the simulated ones (See Figure S2), which further demonstrates that they all retain their framework. However, it's a pity that **FJI-H6** lost its crystallinity during the catalytic process.

Conclusions

In conclusion, we report the design and synthesis of two ultra-stable MOFs **FJI-H6** and **FJI-H7**, which both feature 2.5 nm cages. In particular, **FJI-H6** has a high BET surface area of 5033 m^2 g^{-1}. Due to the high connection of the $M_6O_4(OH)_4$ clusters (M = Zr and Hf), **FJI-H6** and **FJI-H7** are stable in the water with the pH values ranging from 0 to 10. Interestingly, they can undergo the single-crystal to single-crystal transformation to embed Cu^{2+} ions into the porphyrin rings, which also indicates their high chemical stability. Additionally, preliminary catalysis evaluation shows that **FJI-H6(Cu)**, **FJI-H7** and **FJI-H7(Cu)** exhibit promising catalysis capacity of converting CO_2 and epoxides into cyclic carbonates at low temperature and pressure. Consequently, **FJI-H6**, **FJI-H7** and their derivatives may be applied in catalysis due to their high surface area, ultra-high stability and easy post-modification. Further research is undergoing.

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Notes and references

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† Electronic Supplementary Information (ESI) available: General experimental, syntheses and characterization of the complexes mentioned in the manuscript, details of the single crystal diffraction experiments, PXRD, TG and additional figures. See DOI: 10.1039/b000000x/

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