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

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Owing to their high surface area, permanent porosity and tunable pores, metal–organic frameworks (MOFs) have been used for catalysis, gas separation and storage, and drug delivery. Nonetheless, one big obstacle to the practical applications of MOFs is their stability, which includes water and chemical stability. To target stable MOFs, one effective method is the use of high-valence metal ions such as Fe3+, Al3+, Cr3+, Zr4+ and Hf4+ ions as the metal nodes. Compared with the traditional Cu2+, Zn2+ and Co2+ ions, the aforementioned 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, these high-valence metal ions tend to form highly connected inorganic clusters via the OH− and/or O2− bridges, which also significantly contributes to the stability of the frameworks. As for the Zr4+ ion, it prefers to form the classical 12-connected Zr6O4(OH)4 octahedron, the eight triangular faces are alternatively capped by four water and chemical stability. Thus, we present two ultra-stable metal–organic frameworks ([Zr6O4(OH)4(H2TBPP)3]n(solvent)) (FJI-H6) and ([Hf6O4(OH)4(H2TBPP)3]n(solvent)) (FJI-H7), which are isoostructural and both constructed from M6O4(OH)4(CO2)12 nodes (M = Zr, Hf) and porphyrin tetracarboxylic ligands (H4TBPP = 4′,4″,4‴,4‴′-tetratetakis[1,1′-biphenyl]-4-carboxylic acid)). As expected, both FJI-H6 and FJI-H7 have high water and chemical stability and can undergo a single-crystal-to-single-crystal (SCSC) transformation to embed Cu2+ ions into the open porphyrin rings. Interestingly, they both feature 2.5 nm cages. Notably, FJI-H6 has a high BET surface area of 5033 m2 g−1.

Results and discussion
Syntheses and structures of porphyrin Zr and Hf MOFs
Reaction of H6TBPP with ZrCl4 or HfCl4 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 isoostructural. Therefore, we chose FJI-H6 as the example in the following discussion. FJI-H6 crystallizes in the high symmetry space group Pm3m. In the Zr6O4(OH)4 cluster, six equivalent Zr4+ ions are in a square-antiprismatic O8 coordination environment and form a regular octahedron. In this Zr6 octahedron, the eight triangular faces are alternatively capped by four μ3-OH− and four μ3-O2− groups. Additionally, the twelve edges of the Zr6 octahedron are bridged by twelve carboxylate groups from twelve unique H2TBPP ligands. At the same time, each H2TBPP ligand, in which the peripheral four phenyl rings are coplanar with the inner porphyrin rings, links four independent Zr6O4(OH)4 clusters. Thus, a rarely seen (4,12)-connected ftw framework can be acquired. FJI-H6 has two

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kinds of polyhedral cages, i.e. a small octahedral cage and a large cubic cage. As seen in Fig. 1, the octahedral cage is constructed from two \( \text{Zr}_6\text{O}_4(\text{OH})_4 \) clusters and four \( \text{H}_2\text{TBPP} \) ligands, with a cavity diameter of ca. 1.5 nm. However, the cubic cage consists of eight \( \text{Zr}_6\text{O}_4(\text{OH})_4 \) clusters as the vertices and six \( \text{H}_2\text{TBPP} \) ligands as the sides. Significantly, the diameter of the cubic cage is approximately 2.5 nm, which is larger than that in PCN-221 (2.0 nm). Accordingly, the available volume is up to 78.6%. For \( \text{FJI-H6} \) the permanent porosity is 15 000 \( \text{Å}^3 \). Additionally, the window of the cubic cage is 1.2 nm \( \times \) 2.0 nm, which allows large organic molecules to freely get in and out.

Gas adsorption experiments and stability tests

Calculation by PLATON software reveals that in \text{FJI-H6} the free volume is up to 78.6%. For \text{FJI-H6} the permanent porosity is confirmed by an \( \text{N}_2 \) adsorption isotherm measured at 77 K. The sample exchanged with acetone exhibits a reversible type I isotherm and has a saturated uptake of 1346 cm\(^3\) g\(^{-1}\) at 1 atm (Fig. 2). When pre-treated with 8 M HCl, the value of the \( \text{N}_2 \) adsorption slightly increases to 1393 cm\(^3\) g\(^{-1}\), which indicates that \text{FJI-H6} is stable with respect 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\(^{-1}\)),\(^{14}\) NU-1000 (2320 m\(^2\) g\(^{-1}\)),\(^{15}\) PCN-223(Fe) (1600 m\(^2\) g\(^{-1}\)),\(^{16}\) PCN-94 (3377 m\(^2\) g\(^{-1}\)),\(^{17}\) NU-1100 (4020 m\(^2\) g\(^{-1}\)),\(^{18}\) and PCN-229 (4619 m\(^2\) g\(^{-1}\)),\(^{19}\) but less than those of the just reported NU-1103 (5164 m\(^2\) g\(^{-1}\)) and NU-1104 (5290 m\(^2\) g\(^{-1}\)).\(^{18}\) In addition, \text{FJI-H6} also has a high total pore volume of 2.16 cm\(^3\) g\(^{-1}\). The experimental BET surface area and pore volume are consistent with theoretical values calculated by Poreblazer (accessible surface area: 4695 m\(^2\) g\(^{-1}\); pore volume: 2.06 cm\(^3\) g\(^{-1}\)),\(^{14}\) which demonstrates that the sample is fully activated. Additionally, \text{FJI-H6} also shows good capacity for \( \text{H}_2 \) storage. The \( \text{H}_2 \) uptake reaches 172 cm\(^3\) g\(^{-1}\) at 1 atm and 77 K, and 108 cm\(^3\) g\(^{-1}\) at 87 K and 1 atm. Moreover, the adsorption heat of \( \text{H}_2 \) calculated by the Clausius–Clapeyron equation is 6.54 kJ mol\(^{-1}\) at zero coverage and decreases slowly with increasing \( \text{H}_2 \) loading. These values are comparable to those of famous MOF 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 \text{FJI-H7} the sample exchanged with acetone also exhibits a 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 \text{FJI-H7} is up to 3831 m\(^2\) g\(^{-1}\), which is among the highest reported for \( \text{Hf} \)-based MOFs.\(^{11}\)

Since the \( \text{Zr}_6\text{O}_4(\text{OH})_4 \) and \( \text{Hf}_6\text{O}_4(\text{OH})_4 \) clusters are both highly connected with twelve carboxylate groups, \text{FJI-H6} and \text{FJI-H7} are expected to have a high stability. To test their stabilities, we immersed a microcrystalline sample of \text{FJI-H6} or \text{FJI-H7} into water with various \( \text{pH} \) values for 24 h (see Fig. S2†). The PXRD patterns of the resulting samples match well with the simulated ones, which suggests that \text{FJI-H6} and \text{FJI-H7} retain their crystallinity. In particular, \text{FJI-H6} has high stability in acid. As seen in Fig. 2, the curves and the adsorption values for the sample treated with 8 M HCl do not deviate much from those of the untreated sample.

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

Considering that in both \text{FJI-H6} and \text{FJI-H7} two nitrogen atoms of the porphyrin ring are not deprotonated, we attempted to introduce a second kind of metal ion into the framework. Immersing single-crystals of \text{FJI-H6} or \text{FJI-H7} into a solution of 0.5 M \( \text{Cu(NO}_3)_2 \) in \( \text{N}_2\text{N}-\text{dimethyl formamide (DMF)} \) at 85 °C for
72 h results in metallated FJI-H6(Cu) or FJI-H7(Cu). As anticipated, single crystal X-ray structural analysis definitively 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 a square planar N4 coordination environment with two axial sites exposed, which is typical for divalent metal ions in metal-porphyrin complexes. We believe that, although there are several examples of exchanging metal ions in porphyrin MOFs, this is the first observation of incorporating metal ions into open porphyrin rings via SCSC transformations in porphyrin MOFs. N$_2$ adsorption measurements at 77 K for FJI-H6(Cu) also show a 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.

**Cycloaddition reactions of CO$_2$ with epoxides**

Recently, owing to global warming, efficient CO$_2$ capture and storage is urgently needed to reduce CO$_2$ emissions before scientists find a practical clean energy. If we can convert this abundant inorganic waste into 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 CO$_2$ and epoxides, which have extensive applications as 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. Hence, we have evaluated FJI-H6, FJI-H6(Cu), FJI-H7 and FJI-H7(Cu) as heterogeneous catalysts for the cycloaddition reaction of CO$_2$ with epoxides (Scheme 1). Typically, 25.5 mmol 3-chloropropylene oxide, 0.51 mmol (2.0 mol%) tetrabutylammonium bromide and 0.051 mmol (0.2 mol%) catalyst were added to a thick-walled glass tube with a stirring bar. The tube was placed under vacuum and then purged with CO$_2$. The above cycle was repeated three times. Finally, the pressure of CO$_2$ was set as 1 atm. The mixture was stirred at 25 °C for 60 hours. Analysis of the resulting solution by gas chromatography indicated that 52.6%, 61.8%, 64% and 66.5% of the epoxide was converted into the resulting solution by gas chromatography indicated that compared with homogeneous catalysts, it is nevertheless 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).

Compared with FJI-H6 or FJI-H7, FJI-H6(Cu) or FJI-H7(Cu) has a higher catalytic ability. The reason may be that, as a Lewis catalytic site, the embedded Cu(n) 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 activities than the corresponding Zr-based MOFs FJI-H6 and FJI-H6(Cu), respectively since the Hf ion is more oxophilic than the 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 in good agreement with the simulated ones (see Fig. S2†), which further demonstrates that they all retain their framework. However, it is a pity that FJI-H6 lost its crystallinity during the catalytic process.

**Conclusions**

In conclusion, we report the design and synthesis of two ultrastable 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 connectivity of the M$_6$O$_4$(OH)$_4$ clusters (M = Zr and Hf), FJI-H6 and FJI-H7 are stable in water with pH values ranging from 0 to 10. Interestingly, they can undergo a 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 catalytic capacity for 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 ongoing.

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**Notes and references**


Just prior to the submission of this manuscript, a similar strategy was reported by H. C. Zhou and his coworkers *J. Am. Chem. Soc.*, 2015, **137**, 413, whose work focuses on tuning the porosity of Zr-based MOFs through ligand design and variation. During the submission and revision of this manuscript, Xu, H. B. and his coworkers discussed the ligand and heteroatom effect for optimizing ORR catalysts *J. Am. Chem. Soc.*, 2015, **137**, 2235; R. Q. Snurr and his coworkers synthesized a series of Zr-based MOFs employing a linker expansion approach and provided insight into the applicability of BET theory *J. Am. Chem. Soc.*, 2015, **137**, 3585. However, our work focuses not only on the synthesis of Hf and Zr-based MOFs, but also on the SCSC transformations and catalyses of the Zr and Hf-based MOFs.