Synthesis, Structure, and Metalation of Two New Highly Porous Zirconium Metal−Organic Frameworks

William Morris,*,[†] Boris Volosskiy,[†] Selcuk Demir,[†] Felipe Gándara,[†] Psaras L. McGrier,[§] Hiroyasu Furukawa,[†] Duilio Cascio,[||] J. Fraser Stoddart,[§] and Omar M. Yaghi*,[†,⊥,¶,▽]

[†]Center for Reticular Chemistry, Center for Global Mentoring, and Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90095, United States

[§]Center for the Chemistry of Integrated Systems, Department of Chemistry, and Department of Material Science and Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States

[||]UCLA−DOE Institute of Genomics and Proteomics and Department of Biological Chemistry, David Geffen School of Medicine, University of California, Los Angeles, Los Angeles, California 90095, United States

[⊥]Materials Sciences Division, Lawrence Berkeley National Laboratory, California 94720, United States

[¶]Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, United States

[▽]Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon, Korea

Ⓢ *Supporting Information*

ABSTRACT: Three new metal−organic frameworks [MOF-525, $Zr_6O_4(OH)_4(TCPP-H_2)_3$; MOF-535, $Zr_6O_4(OH)_4(XF)_3$; MOF-545, $Zr_6O_8(H_2O)_8(TCPP-H_2)_2$, where porphyrin $H_4-TCPP-H_2 = (C_{48}H_{24}O_8N_4)$ and cruciform $H_4-XF = (C_{42}O_8H_{22})$] based on two new topologies, **ftw** and **csq**, have been synthesized and structurally characterized. MOF-525 and -535 are composed of $Zr_6O_4(OH)_4$ cuboctahedral units linked by either porphyrin (MOF-525) or cruciform (MOF-535). Another zirconium-containing unit, $Zr_6O_8(H_2O)_8$, is linked by porphyrin to give the MOF-545 structure. The structure of MOF-525 was obtained by analysis of powder X-ray diffraction data. The structures of MOF-535 and -545 were resolved from synchrotron single-crystal data. MOF-525, -535, and -545 have Brunauer−Emmett−Teller surface areas of 2620, 1120, and 2260 m²/g, respectively. In addition to their large surface areas, both porphyrin-containing MOFs are exceptionally chemically stable, maintaining their structures under aqueous and organic conditions. MOF-525 and -545 were metalated with iron(III) and copper(II) to yield the metalated analogues without losing their high surface area and chemical stability.

Recently, metal−organic frameworks (MOFs) based on the zirconium(IV) cuboctahedral secondary building unit (SBU), $Zr_6O_4(OH)_4(CO_2)_{12}$ (Figure 1A), and related expanded analogues with ditopic organic struts have been reported.[1] All of these MOFs have a face-centered-cubic (**fcu**) topology and high thermal and chemical stability.[1,2] Thus far, no other topologies have been reported for this important class of zirconium-based MOFs. Herein, we demonstrate that this 12-connected SBU (Figure 1A) can be linked with the deprotonated form of the 4-connected links (Figure 1B), tetracarboxyphenylporphyrin ($H_4-TCPP-H_2$) and a cruciform (H_4-XF), to make 3D MOFs (termed MOF-525 and -535,

respectively), which have a **ftw** topology (Figure 1C,D).[2] We also demonstrate how this SBU can be deployed as an 8-connector SBU (Figure 1E) by blocking four coordination sites on the zirconium atoms with water ligands and how linking this SBU with TCPP can form a MOF structure (MOF-545) with a **csq** topology (Figure 1F,G).[2] We show that the porphyrin-based MOF-525 and -545 exhibit the highest Brunauer−Emmett−Teller (BET) surface areas (2620 and 2260 m²/g, respectively) and pore diameters (20 and 36 Å, respectively) of any zirconium-containing MOFs.[1] Remarkably, these MOFs are also stable in aqueous media and in acidic solutions (pH = 5 for 24 h). MOF-525 and -545 were metalated in pre- and postsynthetic procedures; postsynthetic metalation of the porphyrin was possible because the porphyrin units do not incorporate zirconium(IV) during the synthesis.[3] The new MOFs described here expand the number and variety of known zirconium MOFs and extend the metrics of the pores and their surface areas beyond those previously reported for this emerging class of porous materials.

The synthesis and activation of MOF-525 is described in the Supporting Information.[4] To confirm the homogeneous nature of the sample, scanning electron microscopy (SEM) was performed, which revealed cuboctahedron crystallites of 1−5 μm size.[5] Crystalline products from the MOF-525 synthesis were not suitable for single-crystal analysis because of their microcrystalline size, as revealed by SEM. Problems of limited crystallite size have been readily overcome by analysis of the powder X-ray diffraction (PXRD) data. On the basis of the connectivity of the building units, initial structure matches were generated using nets that appear in the reticular chemistry structural resource (RCSR), a procedure used frequently to resolve covalent organic framework structures.[2,5] Only three topologies combine 12,4-connected components in the RCSR database: **ith**, **shp**, and **ftw**.[2] The **ith** topology was excluded
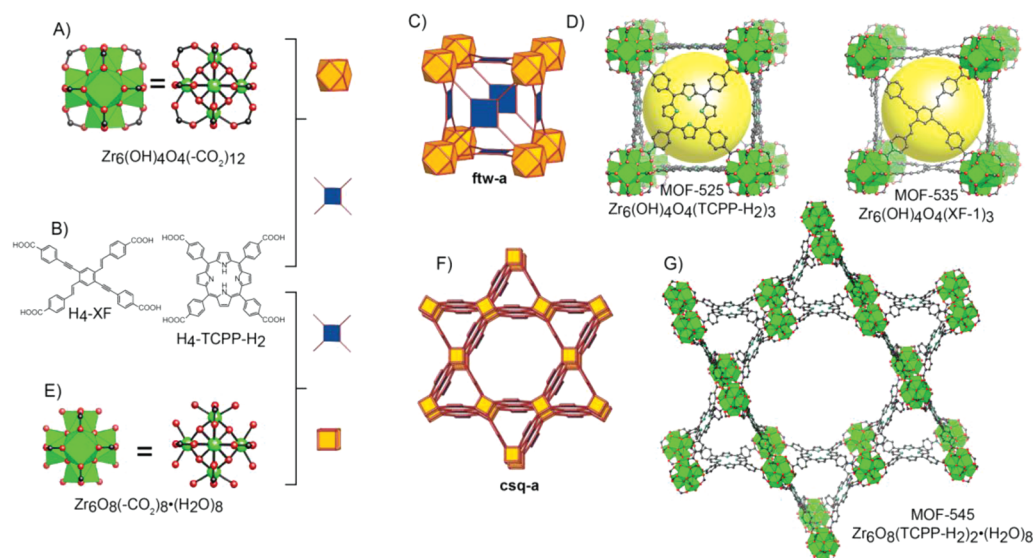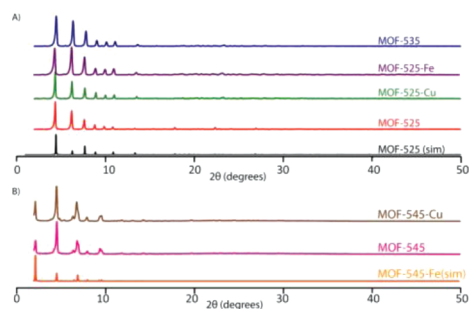
Figure 1. Crystal structures of MOF-525, -535, and -545: (A) cube octahedral unit, $Zr_6(OH)_4O_4(CO_2)_{12}$; (B) links used in MOF-525 and -545 [H_4-TCPP-H_2 = $C_{48}H_{30}N_4O_8$] and MOF-535 {H_4-XF = $C_{42}H_{24}O_8$}; (C) **ftw** topology; (D) MOF-525 and -535; (E) cube unit, $Zr_6O_8(CO_2)_8(H_2O)_8$; (F) **csq** topology; (G) MOF-545. Pores in the frameworks are illustrated by yellow spheres. Atom colors: zirconium, green; carbon, black; nitrogen, dark green; oxygen, red. Hydrogen atoms are omitted.

because it incorporates tetrahedra, a geometry not accessible with the porphyrin binding unit. Furthermore, the **shp** topology was excluded because the geometry of the 12-coordinate unit is not cuboctahedron, the cluster shape that is predominant in other zirconium-based MOFs. Therefore, a structure with the **ftw** topology was calculated, replacing the cuboctahedron units with the zirconium metal oxide units, $Zr_6O_4(OH)_4$ (Figure 1A), and the square units with TCPP-H_2 (Figure 1B). The structure was constructed in the space group $Pm\bar{3}m$ (No. 221) with an optimized unit cell parameter of 19.39 Å (Figure 1D). The calculated PXRD pattern of the calculated structure was shown to be coincident with the experimental PXRD pattern for MOF-525 (Figure 2A). To confirm the correctness of the

Figure 2. PXRD data for MOF-525, -535, and -545: (A) PXRD patterns of the calculated **ftw** structures of MOF-525 (black), MOF-525 (red), MOF-525-Cu (green), MOF-525-Fe (purple), and MOF-535 (blue); (B) PXRD patterns of the calculated **csq** structures of MOF-545-Fe (orange), MOF-545 (pink), and MOF-545-Cu (brown).

calculated structure, a Pawley refinement was first carried out; this agreed with the calculated unit cell (R_{wp} = 8.34).[4] Second, a Rietveld refinement was performed on the activated sample to confirm the structure and atom positions within the MOF-525 structure.[4] The final refined unit cell parameters for MOF-525 are a = 19.393(3) Å, R_p = 8.98 wR_p = 12.28.[4] This result supports the structural assignment of MOF-525 and leads to its cubic structure and its pore diameter of 20 Å. Each cube is

comprised of eight corner-sharing $Zr_6O_4(OH)_4$ units and six face-sharing porphyrin units, where each porphyrin is bridging four $Zr_6O_4(OH)_4$ units.

MOF-535 synthesis is described in the Supporting Information.[4] Single crystals of the as-synthesized MOF-535 were analyzed by synchrotron X-ray diffraction, revealing a primitive cubic unit cell with a = 19.41 Å. The metal oxide units were clearly located in the space group $Pm\bar{3}m$, the expected space group for the **ftw** topology. These metal oxide units are connected by 12 carboxylates from XF. The exact positions of the atoms in the ligand could not be successfully located, which is indicative of disorder in the relative orientation of the linkers with respect to the SBUs (Figure 1E).[4] This fact is also reflected in the relatively high final residual values (R1 = 0.2874 and 0.1860 after the *SQUEEZE* routine was applied). Nevertheless, XF displays a conformational flexibility that allows formation of this network type, as indicated by formation of the metal oxide unit with the carboxylic groups of XF and their disposition within a cubic $Pm\bar{3}m$ symmetry.[6]

MOF-545 synthesis is described in the Supporting Information.[4] The initial X-ray diffraction study, carried out using synchrotron radiation, revealed that MOF-545 crystals were twinned, preventing full characterization of the structure. However, after replacement of H_4-TCPP-H_2 with H_4-TCPP-FeCl, no twinning was observed in the MOF-545-Fe crystals and the structure could be solved. MOF-545-Fe crystallizes in the hexagonal space group $P6/mmm$ (No. 191) with unit cell parameters a = 42.545 Å and c = 16.96 Å. In the SBU of MOF-545, 4 of the 12 carboxylates found in the SBU of MOF-525 have been replaced by terminating water ligands (Figure 1E). In order to maintain the charge balance, eight μ_3-oxo atoms complete the SBU with the formula $Zr_6O_8(CO_2)_8(H_2O)_8$. The geometry of the simplified SBU is now a cube, which combines with the tetratopic link to give the **csq** topology of MOF-545. The structure of MOF-545-Fe contains hexagonal and triangular 1D channels that have a diameter of 36 and 8 Å, respectively. The structure of MOF-545 was shown to be

analogous to that of MOF-545-Fe by comparison of the PXRD data (Figure 2B).

To assess the porosity of MOF-525, -535, and -545, argon adsorption isotherms at 87 K were measured for the guest-free materials.[4] The argon isotherms for each MOF clearly showed a reversible argon adsorption indicative of permanent porosity.[4] Surface area analysis of MOF-525, -535, and -545 by the BET method gave surface areas of 2620, 1120, and 2260 m^2/g, respectively. MOF-525 has the highest surface area reported for a zirconium-based MOF.[1] The step position observed in the argon isotherm of MOF-545 supports the mesoporous size of the large hexagonal pore.[4]

The chemical stability of MOF-525 and -545 was evaluated by immersing the activated structures in methanol, water, and acidic conditions [water:acetic acid = 50:50 (v/v)] for 12 h. Upon reactivation of these MOFs by immersion into acetone followed by evacuation at 30 mTorr, the crystallinity and porosity of the materials were completely recovered.[4]

The incorporation of active metal sites into MOF materials has been shown to enhance their gas adsorption and catalytic properties.[7] For the incorporation of a porphyrin binding unit into MOF-525 and -545, H_4-TCPP-H_2, the porphyrin units are known for enabling metal complexation into MOFs.[3,8] Although many MOFs that contain porphyrin units have been synthesized, few have both accessible porphyrin binding sites and permanent porosity.[3,9] Metalated porphyrins are known to be catalytically active and adsorb gases selectively.[10] Both porphyrin-containing topologies have high porosity, chemical stability, and accessible porphyrin sites; therefore, they are potentially applicable for catalysis and gas adsorption, but first they must be metalated. Two methods have been used to obtain a metalated porphyrin: pre- and postmetalation. Primarily, premetalation has been achieved using H_4-TCPP-Cu and H_4-TCPP-FeCl under synthetic conditions similar to those of MOF-525 and -545 to form MOF-525-Cu $[Zr_6O_4(OH)_4(TCPP-Cu)_3]$, MOF-545-Fe $[Zr_6O_8(TCPP-FeCl)_2(H_2O)_8]$, and MOF-545-Cu $[Zr_6O_8(TCPP-Cu)_2(H_2O)_8]$.[5]

Premetalation was not successful for isolation of a pure iron analogue of MOF-525 with H_4-TCPP-FeCl. Therefore, postmetalation of the open porphyrin sites of MOF-525 was used to quantitatively introduce iron into the porphyrin of MOF-525. To achieve this, iron chloride (200 mg, 1.6 mmol) was dissolved in N,N-dimethylformamide (DMF; 40 mL) and MOF-525 (100 mg) was added to the solution and heated to 100 °C for 12 h. The excess of metal salts and DMF were removed by activation conditions analogous to those of MOF-525.

Analysis of the PXRD patterns showed that the metalated analogues of MOF-525 and -545 have the same structures as their nonmetalated analogues (Figure 2A,B). Analysis of the nitrogen isotherms of each MOF revealed BET surface areas comparable to those of the nonmetalated analogues.[4] To confirm that each MOF was quantitatively metalated, the samples were digested in 2 M NaOH, and a UV−vis spectroscopy study was performed; in no case was free porphyrin observed in the digested material.[4]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format and full synthetic and analytical details. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: w.morris29@gmail.com (W.M.), yaghi@berkeley.edu (O.M.Y.).

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) (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) Morris, W.; Doonan, C. J.; Yaghi, O. M. Inorg. Chem. 2011, 50, 6853. (c) Schaate, A.; Roy, P.; Preube, T.; Lohmeier, S. J.; Godt, A.; Behrens, P. Chem.—Eur. J. 2011, 17, 9320.

(2) (a) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. Acc. Chem. Res. 2005, 38, 176. (b) RCSR can be accessed at http://rcsr.anu.edu.eu/.

(3) (a) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. Nature 1994, 369, 727. (b) Farha, O. K.; Shultz, A. M.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. J. Am. Chem. Soc. 2011, 133, 5652.

(4) See the Supporting Information for additional information on the synthesis, activation, and structure refinement.

(5) Côté, A. P.; El-Kaderi, H. M.; Furukawa, H.; Hunt, J. R.; Yaghi, O. M. J. Am. Chem. Soc. 2007, 129, 12914.

(6) Wilson, J. N.; Smith, M. D.; Enkelmann, V.; Bunz, U. H. F. Chem. Commun. 2004, 1700.

(7) Britt, D.; Furukawa, H.; Wang, B.; Glover, T. G.; Yaghi, O. M. Proc. Natl. Acad. Sci. U.S.A. 2009, 106, 20637.

(8) (a) Suslick, K. S.; Bhyrappa, P.; Chou, J. H.; Kosal, M. E.; Nakagaki, S.; Smithenry, D. W.; Wilson, S. R. Acc. Chem. Res. 2005, 38, 283. (b) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. J. Am. Chem. Soc. 2009, 131, 4204. (c) Barron, P. M.; Wray, C. A.; Hu, C.; Guo, Z.; Choe, W. Inorg. Chem. 2010, 49, 10217. (d) Wang, X.; Meng, L.; Cheng, Q.; Kim, C.; Wojtas, L.; Chrzanowski, M.; Chen, Y.; Zhang, P.; Ma, S. J. Am. Chem. Soc. 2011, 133, 16322.

(9) 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.

(10) Stephenson, N. A.; Bell, A. T. J. Mol. Catal. A: Chem. 2007, 275, 54.

6445

dx.doi.org/10.1021/ic300825s | Inorg. Chem. 2012, 51, 6443−6445