Inorganic Chemistry
Communication

Inorg. Chem. **2009,** *48,* 4649–4651 **4649**
DOI:10.1021/ic900486r

New Prototype Isoreticular Metal–Organic Framework Zn$_4$O(FMA)$_3$ for Gas Storage

Ming Xue,[†,‡] Yun Liu,[§,⊥] Roxanna M. Schaffino,[‡] Shengchang Xiang,[‡] Xiaojun Zhao,[†] Guang-Shan Zhu,[†] Shi-Lun Qiu,[†] and Banglin Chen*[,‡]

[†] *State Key Laboratory of Inorganic Synthesis & Preparative Chemistry, Jilin University, Changchun, China 130023,* [‡] *Department of Chemistry, University of Texas–Pan American, Edinburg, Texas 78539-2999,* [§] *NIST Center for Neutron Research, Gaithersburg, Maryland 20899-6100, and* [⊥] *Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742*

Received March 11, 2009

A new isoreticular metal–organic framework Zn$_4$O(FMA)$_3$·xG (**1**; FMA = fumarate; G = guest molecules) of a primitive cubic net was synthesized and structurally characterized. With intersecting pores of about 6.8 × 6.8 Å, the activated **1a** exhibits high gas adsorption with respect to H$_2$, CH$_4$, and CO$_2$.

The emergence of MOF-5 (or IRMOF-1, where IRMOF means isoreticular metal–organic framework) Zn$_4$O(BDC)$_3$ was certainly a breakthrough in the development of porous metal–organic frameworks (MOFs), highlighting not only the great promise to construct extraordinary highly porous materials but also the realization of the reticular chemistry on the synthesis of such solid materials in which the targeted MOF solids can be rationally designed by the deliberate choice of metal-containing secondary building units and organic linkers of certain symmetries.[1,2] In fact, a large number of such porous MOFs have been rationally designed and synthesized over the past decade with predictable structures and porosity for their functional applications in gas storage, gas separation, catalysis, and sensing.[3–29]

---

*To whom correspondence should be addressed. E-mail: banglin@utpa.edu.

(1) Li, H.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276.

(2) Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; O'Keeffe, M.; Yaghi, O. M. *Science* **2002**, *295*, 469.

(3) (a) Eddaoudi, M.; Moler, D. B.; Li, H.; Chen, B.; Reineke, T. M.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2001**, *34*, 319. (b) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (c) Ferey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.

(4) Chui, S.; Lo, S.; Charmant, J.; Orpen, A.; Williams, I. *Science* **1999**, *283*, 1148.

(5) Chen, B.; Ockwig, N. W.; Millward, A. R.; Contreras, D. S.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 4745.

(6) Zhao, X.; Xiao, B.; Fletcher, A. J.; Thomas, K. M.; Bradshaw, D.; Rosseinsky, M. J. *Science* **2004**, *306*, 1012.

(7) Ma, S.; Sun, D.; Simmons, J. M.; Collier, C. D.; Yuan, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 1012.

(8) Chandler, B. D.; Cramb, D. T.; Shimizu, G. K. H. *J. Am. Chem. Soc.* **2006**, *128*, 10403.

(9) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y.; Kim, K. *Nature* **2000**, *404*, 982.

(10) Dinca, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6766.

(11) Nelson, A. P.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T. *J. Am. Chem. Soc.* **2009**, *131*, 458.

(12) Kesanli, B.; Cui, Y.; Smith, M. R.; Bittner, E. W.; Bockrath, B. C.; Lin, W. *Angew. Chem., Int. Ed.* **2005**, *44*, 72.

(13) Hou, L.; Lin, Y.-Y.; Chen, X.-M. *Inorg. Chem.* **2008**, *47*, 1346.

(14) Zhang, J.-P.; Chen, X.-M. *J. Am. Chem. Soc.* **2008**, *130*, 6010.

(15) Lin, X.; Telepeni, I.; Blake, A. J.; Dailly, A.; Brown, C. M.; Simmons, J. M.; Zoppi, M.; Walker, G. S.; Thomas, K. M.; Mays, T. J.; Hubberstey, P.; Champness, N. R.; Schroder, M. *J. Am. Chem. Soc.* **2009**, *131*, 2159.

(16) Zhang, J.; Wu, T.; Zhou, C.; Chen, S.; Feng, P.; Bu, X. *Angew. Chem., Int. Ed.* **2009**, *48*, 2542

(17) Lan, A.; Li, K.; Wu, H.; Olson, D. H.; Emge, T. J.; Ki, W.; Hong, M.; Li, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2334

(18) Huang, G.; Yang, C.; Xu, Z.; Wu, H.; Li, J.; Zeller, M.; Hunter, A. D.; Chui, S. S.-Y.; Che, C.-M. *Chem. Mater.* **2009**, *21*, 541.

(19) (a) Chen, B.; Ma, S.; Zapata, F.; Fronczek, F. R.; Lobkovsky, E. B.; Zhou, H.-C. *Inorg. Chem.* **2007**, *46*, 1233. (b) Chen, B.; Wang, L.; Zapata, F.; Qian, G.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **2008**, *130*, 6718. (c) Chen, B.; Zhao, X.; Putkham, A.; Hong, K.; Lobkovsky, E. B.; Hurtado, E. J.; Fletcher, A. J.; Thomas, K. M. *J. Am. Chem. Soc.* **2008**, *130*, 6411.

(20) (a) Rowsell, J. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **2006**, *128*, 1304. (b) Millward, A. R.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 17998. (c) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.

(21) Serre, C.; Mellot-Draznieks, C.; Surble, S.; Audebrand, N.; Filinchuk, Y.; Ferey, G. *Science* **2007**, *315*, 1828.

(22) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 4184.

(23) Noro, S.-I.; Kitagawa, S.; Kondo, M.; Seki, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 1433.

(24) Bourrelly, S.; Llewellyn, P. L.; Serre, C.; Millange, F.; Loiseau, T.; Ferey, G. *J. Am. Chem. Soc.* **2005**, *127*, 13519.

(25) Ma, S.; Eckert, J.; Forster, P. M.; Yoon, J. W.; Hwang, Y. K.; Chang, J.-S.; Collier, C. D.; Parise, J. B.; Zhou, H.-C. *J. Am. Chem. Soc.* **2008**, *130*, 15896.

(26) Fang, Q. R.; Zhu, G. S.; Jin, Z.; Ji, Y. Y.; Ye, J. W.; Xue, M.; Yang, H.; Wang, Y.; Qiu, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 6638. Xue, M.; Zhu, G. S.; Li, Y. X.; Zhao, X. J.; Jin, Z.; Kang, E. H.; Qiu, S. L. *Cryst. Growth Des.* **2008**, *8*, 2478. Xue, M.; Ma, S. Q.; Jin, Z.; Schaffino, R. M.; Zhu, G. S.; Lobkovsky, E. B.; Qiu, S. L.; Chen, B. *Inorg. Chem.* **2008**, *47*, 6825.

(27) Hermes, S.; Schroder, F.; Chelmowski, R.; Woll, C.; Fischer, R. A. *J. Am. Chem. Soc.* **2005**, *127*, 13744.

(28) Liu, B.; Shioyama, H.; Akita, T.; Xu, Q. *J. Am. Chem. Soc.* **2008**, *130*, 5390.

(29) Bauer, C. A.; Timofeeva, T. V.; Settersten, T. B.; Patterson, B. D.; Liu, V. H.; Simmons, B. A.; Allendorf, M. D. *J. Am. Chem. Soc.* **2007**, *129*, 7136.

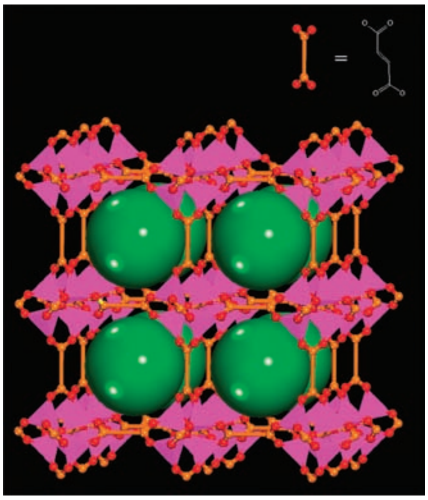

Figure 1. X-ray crystal structure of IRMOF **1** showing a cubic net of the intersecting pores of about 6.8 × 6.8 Å (Zn, pink; O, red).

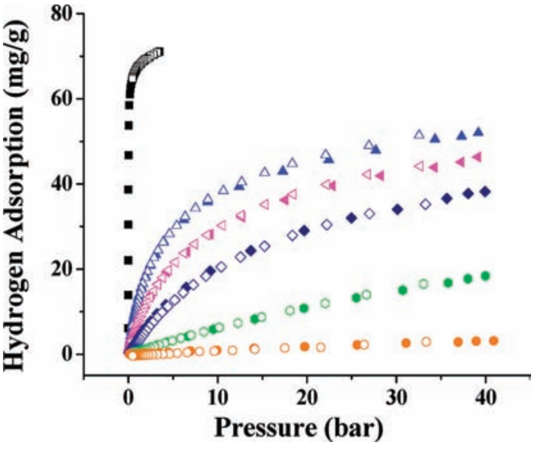

Figure 2. Excess H_2 sorption isotherms at 30 K (black), 77 K (blue), 87 K (magenta), 100 K (navy), 150 K (green), and 300 K (orange) (adsorption, filled; desorption, open).

With the improved synthesis of IRMOF-1 by the well-established solvothermal methodology, IRMOF-1 has been one of the most examined prototype MOFs for their practical applications. IRMOF-1 is certainly a very good material for gas storage because of its high porosity;[20] while making use of the pore space to immobilize catalytic nanoparticles and initiate polymerization, IRMOF-1 has been explored as the template to design new catalysts and porous carbon materials, respectively.[27,28] To incorporate the expanded bicarboxylates, a series of IRMOFs of diverse porosity have also been developed.[20] The longer bicarboxylates typically led to interpenetrated IRMOFs and quite flexible noninterpenetrated ones, which are basically not very porous except for IRMOF-20. However, the limited availability of thieno[3,2-*b*]thiophene-2,5-dicarboxylate has limited IRMOF-20 to be further explored as another important prototype MOF.[20] To assemble a readily available and very cheap bicarboxylate, fumarate (FMA),[19a,21] into IRMOF of a cubic net, herein we report a new noninterpenetrated IRMOF $Zn_4O(FMA)_3$ of high rigidity and porosity as established by gas adsorption isotherms, highlighting its promise as another straightforward prototype IRMOF to explore new functional materials in the near future.

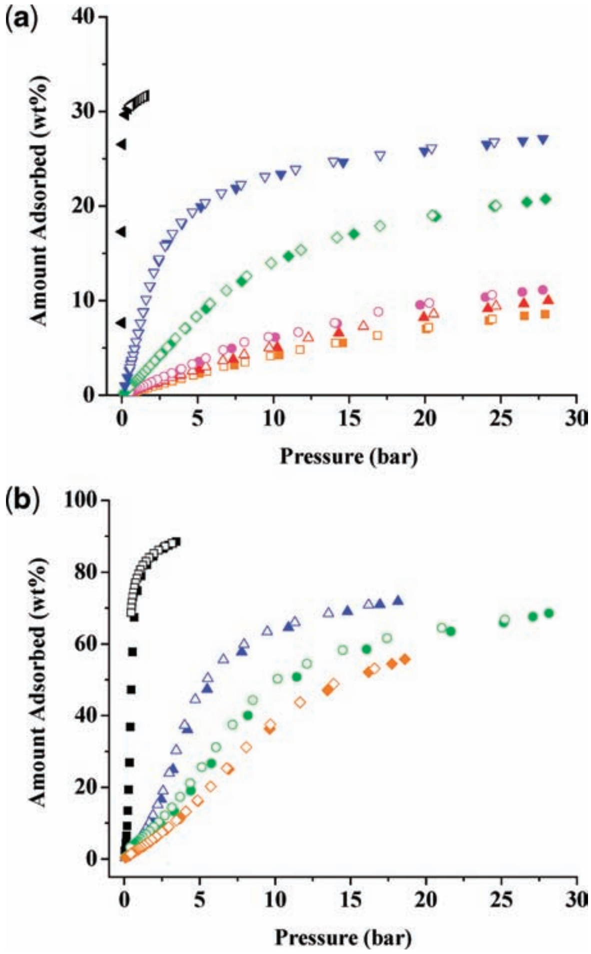

Figure 3. (a) CH_4 sorption isotherms at 125 K (black), 200 K (blue), 240 K (green), 280 K (magenta), 290 K (red), and 300 K (orange) and (b) CO_2 sorption isotherms at 220 K (black), 280 K (blue), 300 K (green), and 310 K (orange) (adsorption, filled; desorption, open).

1 was synthesized by the solvothermal reaction of H_2FMA and $Zn(NO_3)_2 \cdot 6H_2O$ in *N*,*N*-diethylformamide (DEF) at 100 °C for 24 h as light-yellow cubic crystals. It was formulated as $Zn_4O(FMA)_3 \cdot 4.5DEF \cdot 2H_2O$ by elemental microanalysis and single-crystal X-ray diffraction studies,[30,31] and the phase purity of the bulk material was independently confirmed by powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA).

As expected, the framework is composed of octahedral Zn_4O units that are bridged by FMA dianions to form a 3D primitive cubic (α-Po) structure with intersecting pores of ca. 6.8 × 6.8 Å (Figure 1). **1** is very robust, as is clearly shown in the PXRD of the solvent-exchanged and activated ones. TGA studies indicate that the activated **1a** is thermally stable up to about 300 °C. The Langmuir and Brunauer−Emmett−Teller surface areas are 1618 and 1120 m^2/g, respectively,

---

(30) Synthesis of **1**: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.279 g, 1.0 mmol) and H_2FMA (0.116 g, 1.0 mmol) was suspended in DEF (100 mL) and heated in a vial (400 mL) at 100 °C for 24 h. The light-yellow cubic crystals formed were collected and washed with DEF (0.34 g, 85%). Elem anal. Calcd for $Zn_4(FMA)_3 \cdot 4.5DEF \cdot 2H_2O$ ($C_{34.5}H_{59.5}N_{4.5}O_{19.5}Zn_4$): C, 37.48; H, 5.43; N, 5.70. Found: C, 37.55; H, 5.14; N, 5.75.

(31) Crystal data for **1**: $C_{12}H_6O_{13}Zn_4$, cubic, space group $Fm\bar{3}m$, a = 21.639(3) Å, V = 10133(2) Å^3, Z = 8, D_{calc} = 0.812 g/cm^3, μ = 1.895 mm^{-1}, T = 293 K, $F(000)$ = 2416. R1 [$I > 2\sigma(I)$] = 0.0688, wR2 (all data) = 0.1649. CCDC 715031.

based on the N_2 adsorption at 77 K (Figures S1−S3 in the Supporting Information).

High-pressure gas sorption measurements were carried out at various temperatures to explore the potential of **1** as a gas storage material. As shown in Figure 2, IRMOF **1** takes up quite a large amount of H_2 gas of 71 mg/g at 30 K and 3.5 bar and of 52 mg/g at 77 K and 39 bar. These feature **1** as very few high storage MOF materials ever reported. Given the comparatively low surface area of **1**, such high hydrogen storage capacities are remarkable.[32] As expected, **1** can only adsorb a very small amount of H_2 gas at room temperature (0.32 wt %) even at 40 bar. IRMOF **1** takes up a moderate amount of methane (CH_4) and carbon dioxide (CO_2) of 8.6 and 69 wt %, respectively, at 28 bar and 300 K (Figure 3).

The coverage-dependent adsorption enthalpies of IRMOF **1** to H_2, CH_4, and CO_2 were calculated based on the virial method,[20,32] a well-established and reliable methodology from fits of their adsorption isotherms at variable temperatures. **1** exhibits adsorption enthalpies to H_2 of about 4 kJ/mol (4.2 kJ/mol at the coverage of 2.85 mmol/g), comparable to those of other typical MOFs, indicating that there are no specific strong binding sites within IRMOF **1** for H_2 adsorption. The adsorption enthalpies of **1** to CH_4 and CO_2 are 12.0 kJ/mol at the coverage of 5.8 mmol/g and 16.1 kJ/mol at the coverage of 8.8 mmol/g, respectively, which are not specifically high, although the pores of **1** are smaller than those of MOF-5. Because of the very open structure with intersecting pores of 6.8 × 6.8 Å and large cavities of about 8.5 Å within **1**, there exists no strong pore confinement effect to enhance their interactions with the small molecules examined here.

In conclusion, a new prototype cubic IRMOF $Zn_4O(FMA)_3$ (**1**) was rationally designed and structurally characterized, exhibiting rigid structure and high porosity with a Langmuir surface area of 1618 m^2/g. IRMOF **1** can take up 5.2 wt % H_2 at 77 K and 39 bar, 7.1 wt % H_2 at 30 K and 3.5 bar, 8.6 wt % CH_4 at 300 K and 28 bar, and 69 wt % CO_2 at 300 K and 28 bar. The straightforward synthesis of this new IRMOF together with the readily available and cheap raw material of fumaric acid will certainly motivate us to explore its new functions. We are currently examining its potential as the template for the synthesis of porous carbon materials.

Acknowledgment. This work was supported by Award CHE 0718281 from the NSF (B.C.), the State Basic Research Project (2006CB806100), and the Outstanding Young Scientist Foundation of NSFC (Grant 20625102).

Supporting Information Available: X-ray data in CIF format, TGA, and PXRD. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(32) Thomas, K. M. *Dalton Trans.* **2009**, 1487.