Inorganic Chemistry
Communication
pubs.acs.org/IC

Porous Double-Walled Metal Triazolate Framework Based upon a Bifunctional Ligand and a Pentanuclear Zinc Cluster Exhibiting Selective CO_2 Uptake

Wen-Yang Gao,[†] Wuming Yan,[‡] Rong Cai,[‡] Le Meng,[†] Andrea Salas,[†] Xi-Sen Wang,[†] Lukasz Wojtas,[†] Xiaodong Shi,*[,‡] and Shengqian Ma*[,†]

[†]Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, Florida 33620, United States
[‡]Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506, United States

Supporting Information

ABSTRACT: The self-assembly of a custom-designed bifunctional ligand featuring both 1,2,3-triazolate and carboxylate donor groups with a pentanuclear zinc cluster generated in situ affords a double-walled metal triazolate framework (MTAF) material, MTAF-1 ($Zn_5(\mu_3\text{-}O)_2(C_9N_3H_5O_2)_5(H^+)_4(H_2O)_{17}(C_3H_7NO)_{10}$), which exhibits a surface area of 2300 m^2/g and demonstrates interesting selective CO_2 uptake performances.

Metal–organic frameworks (MOFs)[1] have been promoted into very promising candidates with potential applications in gas storage,[2] separation,[3] heterocatalysis,[4] sensor,[5] and other areas[6] because of their intriguing topologies and structural tunability.[7] Combining both metal ions and organic linkers as the building blocks, MOFs have been variously functionalized via judicious selections of the metal ions or clusters and the custom design of multifunctional organic ligands.[8] Carboxylate-based linkers have been predominantly employed for the construction of MOFs,[7b,8a,b] and recently there is an escalating interest in utilizing azolate-based ligands such as pyrazolate, 1,2,4-triazolate, 1,2,3-triazolate, and tetrazolate to generate functional MOFs with surfaces featuring exposed sites for various applications.[9] Among those, 1,2,3-triazolate-based ligands have rarely been developed[10] despite their interesting coordination nature and propensity to afford high thermal, moisture, and chemical stability.[11] Indeed, only six MOF structures constructed from multitopic 1,2,3-triazolate linkers have been reported,[10] and most of them possess limited surface areas, thus largely limiting their wide applications particularly in gas storage and CO_2 capture.[9]

To combine the merits of the 1,2,3-triazolate group with the diverse coordination nature of the carboxylate group, we designed a bifunctional organic linker, 4-(1,2,3-triazol-4-yl)-benzoate (tab; Figure 1a), which features both 1,2,3-triazolate and carboxylate donor groups. The self-assembly of the tab ligand with $Zn(NO_3)_2$ under solvothermal conditions affords a porous MOF, termed MTAF-1 (MTAF denotes a metal triazolate framework), that possesses a double-walled structure and a pentanuclear zinc cluster as the secondary building unit (SBU), as well as exhibits permanent porosity with a surface area of 2300 m^2/g and demonstrates interesting selective CO_2 uptake performances.

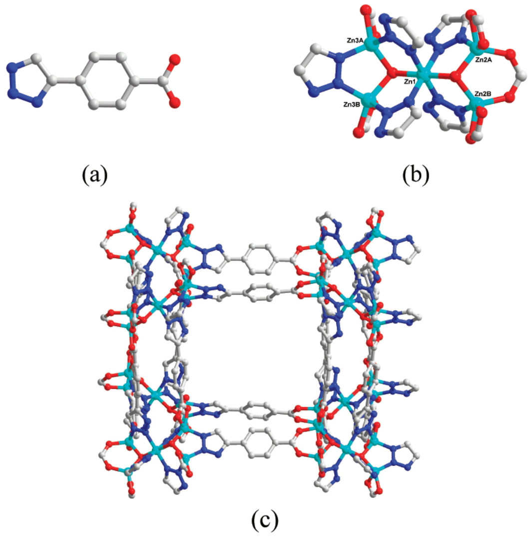


Figure 1. (a) tab; (b) pentanuclear zinc cluster SBU; (c) structure of MTAF-1.

The tab ligand employed herein was obtained by the Huisgen cycloaddition, which is described as a case of "click" chemistry and is sweepingly utilized in various fields of chemistry ranging from biorelated applications to materials.[12]

Colorless block crystals of MTAF-1 were formed by reacting the tab ligand with $Zn(NO_3)_2\cdot6H_2O$ in *N*,*N*-dimethylformamide (DMF) at 135 °C for 60 h. Single-crystal X-ray diffraction analysis reveals that MTAF-1 crystallizes in the space group *I*4*cm*.[13] It adopts the $Zn_5(\mu_3\text{-}O)_2(CO_2)_5(C_2N_3)_5$ cluster as the SBU, which can also be considered as two trigonal-prismatic SBUs of $Zn_3(\mu_3\text{-}O)(CO_2)_3(C_2N_3)_2$ and $Zn_3(\mu_3\text{-}O)(CO_2)_2(C_2N_3)_3$ fused through a six-coordinated Zn atom. The central six-coordinated Zn atom (Zn1) connects with two μ_3-O atoms and four N atoms from four 1,2,3-triazolate groups of four different tab ligands. The other four Zn atoms are five-coordinated and divided into two types (Zn2 and Zn3). Zn2 is coordinated with one μ_3-O atom, three O atoms from two carboxylate groups of two different tab ligands, and one N atom from the 1,2,3-triazolate group of another tab ligand; in

Received: January 30, 2012
Published: March 26, 2012

contrast, Zn_3 links with a μ_3-OH atom, two N atoms from two 1,2,3-triazolate groups of two different tab ligands, and two carboxylate O atoms from one carboxylate group of another tab ligand. Each pentanuclear zinc cluster SBU is connected by 10 organic ligands embraced with 5 carboxylate groups and 5 1,2,3-triazolate groups to afford a rare double-walled three-dimensional (3D) framework (Figure 1c). The double-walled structure of MTAF-1 is different from the double-interpenetrating MOFs and is also distinct from the other double-walled MOF constructed from the binary ligands.[14] Indeed, MTAF-1 represents the first example of a double-walled MOF based upon a unitary organic linker, and this kind of double-walled arrangement has prevented the formation of interpenetration and can enhance the robustness of the framework.

Topologically, MTAF-1 can be described as a noninterpenetrating pcu network. The pentanuclear zinc cluster SBUs are bridged by tab ligands to form rectangular channels of 11.583 Å × 9.947 Å (atom-to-atom distance) along the *a* or *b* axis (Figure 2, left) and square channels of 9.984 Å × 9.984 Å (atom-to-atom distance) along the *c* axis (Figure 2, right). MTAF-1 is highly porous and has a solvent-accessible volume of 72% calculated using *PLATON*.[15]

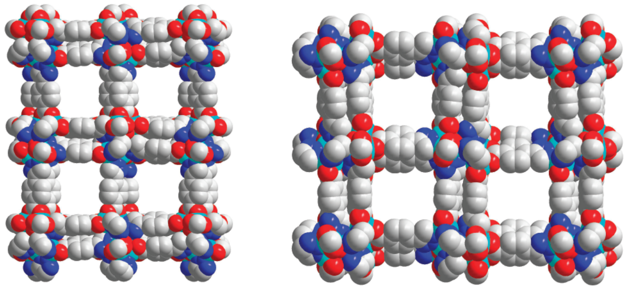


Figure 2. Space-filling mode of MTAF-1 viewed from the *a* or *b* direction (left) and the *c* direction (right).

The phase purity of MTAF-1 was confirmed by powder X-ray diffraction (PXRD) studies. Thermogravimetric analysis (TGA) of the fresh MTAF-1 sample reveals a weight loss of about 42% from 30 to ~220 °C corresponding to the loss of guest solvent molecules of 10 DMF and 17 H_2O trapped in the channels; it is followed by a steady plateau from ~220 to 420 °C before complete decomposition of the framework (Figure S2 in the Supporting Information, SI). The thermal stability of up to ~420 °C was further confirmed by TGA studies on the solvent-free MTAF-1 sample (Figure S2 in the SI), highlighting the robustness of the double-walled framework.

To assess the permanent porosity of MTAF-1, we performed gas adsorption studies on the activated sample. As shown in Figure 3, the N_2 adsorption isotherm at 77 K reveals that MTAF-1 exhibits an uptake capacity of 514 cm^3/g at the saturation pressure with typical type I adsorption behavior, as was expected for microporous materials. Derived from the N_2 adsorption data, MTAF-1 possesses a Brunauer–Emmett–Teller surface area of 2020 m^2/g (P/P_0 = 0.01–0.15), corresponding to a Langmuir surface area of 2300 m^2/g (P/P_0 = 0.9). Ar adsorption at 87 K (Figure S3 in the SI) reveals similar surface area values for MTAF-1, further validating its permanent porosity and framework robustness in the absence of guest solvent molecules. The surface area of MTAF-1 also surpasses those of other MOFs constructed from pyrazolate-, 1,2,4-triazolate-, or tetrazolate-based ligands and represents the second highest among the 1,2,3-triazolate-based MOFs.[10] The pore-size distribution analysis based on the Ar adsorption data at 87 K revealed that the pore size of MTAF-1 is predominantly around 10 Å, which is close to the channel sizes observed crystallographically.

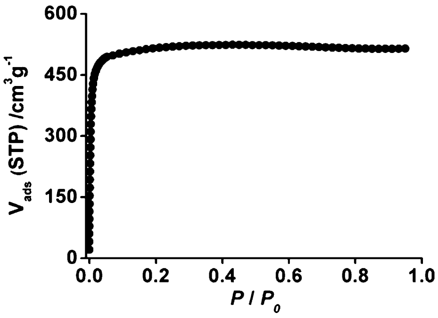
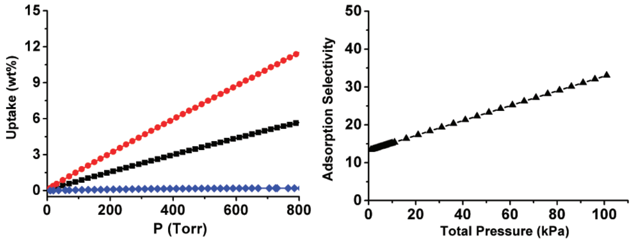


Figure 3. N_2 adsorption isotherm of MTAF-1 at 77 K.

We investigated the CO_2 uptake performances of MTAF-1. As shown in Figure 4a, MTAF-1 can uptake substantial amounts of CO_2 with the uptake capacities of 11.1 wt % at 273 K and 5.6 wt % at 298 K under 1 atm of pressure. These values are moderate compared to some porous MOFs with open metal sites or amine functional groups[16,17] and can be tentatively attributed to the relatively modest heats of adsorption of 20–25 kJ/mol (22 kJ/mol at zero coverage) over the CO_2 loading range (Figure S5 in the SI), as is commonly observed in porous MOFs without open metal sites.[16]



(a) (b)

Figure 4. (a) Gas adsorption isotherms of MTAF-1 (red, CO_2 at 273 K; black, CO_2 at 298 K; blue, N_2 at 273K). (b) IAST-predicted adsorption selectivity of the mixture of CO_2 and N_2 for MTAF-1 at 273 K.

We also evaluated MTAF-1 for the selective uptake of CO_2 over N_2, which is related to postcombustion CO_2 capture application. The N_2 adsorption isotherm at 273 K indicates that MTAF-1 can adsorb a very small amount of N_2 (0.19 wt % at 1 bar; Figure 4a), meaning a selective uptake capacity of 40 for CO_2/N_2 at 273 K and 1 bar. Given that our attempts to measure the low-pressure N_2 adsorption isotherms at 298 K could not generate meaningful data points because of the extremely low N_2 uptake capacity, we decided to utilize the adsorption isotherms at 273 K to assess the potential of MTAF-1 for possible postcombustion CO_2 capture application. We employed the ideal adsorption solution theory (IAST),[18] which has been shown to be valid for calculating the gas selectivity of MOFs,[19] to estimate the adsorption selectivity of MMPF-4 for CO_2/N_2 in postcombustion flue-gas streams, typically composed of 15% CO_2 and 85% N_2. The selectivity $S_{A/B}$ in a binary mixture of components A and B is defined as $(x_A/y_A)/(x_B/y_B)$, where x_i and y_i are the mole fractions of component *i*

(i = A, B) in the adsorbed and bulk phases, respectively. As shown in Figure 4b, MTAF-1 is calculated to exhibit an adsorption selectivity of 35 for CO_2 over N_2 at 273 K and 1 bar. To the best of our knowledge, both the selective uptake capacity observed experimentally and the adsorption selectivity estimated from IAST of MTAF-1 for CO_2 over N_2 are the highest yet reported for azolate-based MOFs[9,16] and are also among the highest for porous MOFs without open metal sites.[16b] The high selective uptake of CO_2 over N_2 for MTAF-1 could be mainly attributed to the large quadrupole moment of CO_2 compared to N_2, and the exposed N atoms of the 1,2,3-triazolate groups could also afford stronger interactions with CO_2 compared to N_2, as illustrated in recent studies.[20]

In summary, a double-walled porous MOF, MTAF-1, has been constructed based upon the custom-designed tab ligand featuring 1,2,3-triazolate and carboxylate donor groups and the in situ generated pentanuclear zinc cluster SBU. MTAF-1 possesses a Langmuir surface area of 2300 m^2/g and demonstrates interesting selective uptake of CO_2 over N_2. The strategy of employing a bifunctional linker with both the azolate and carboxylate groups as donor groups represents a promising way to construct highly porous azolate-based MOFs for various applications, particularly gas storage and CO_2 capture. Ongoing work in our laboratories includes the custom design of new variants of 1,2,3-triazolate-based ligands for the construction of functional MTAF materials and exploration of their use for applications in sensor, catalysis, and CO_2 capture.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental procedures for synthesis of the tab ligand and MTAF-1, PXRD patterns, Ar adsorption isotherm at 87 K, TGA plots, heats of adsorption of CO_2, IR spectra, and crystal data of MTAF-1. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sqma@usf.edu (S.M.), xiaodong.shi@mail.wvu.edu (X.S.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors acknowledge the University of South Florida for financial support of this work. This work was also supported, in part, by the University of South Florida Internal Awards Program under Grant 18325. X.S. thanks the NSF for financial support (Grant CHE-0844602).

■ REFERENCES

(1) (a) Long, J. R.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1213. (b) Zhou, H.-C.; Long, J. R.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 673.

(2) (a) Murray, L. J.; Dinca, M.; Long, J. R. *Chem. Soc. Rev.* **2009**, *38*, 1294. (b) Ma, S.; Zhou, H.-C. *Chem. Commun.* **2010**, *46*, 44. (c) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. *Chem. Rev.* **2012**, *112*, 782. (d) Wu, H.; Gong, Q.; Olson, D. H.; Li, J. *Chem. Rev.* **2012**, *112*, 836.

(3) (a) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. *Chem. Soc. Rev.* **2009**, *38*, 1477. (b) Ma, S. *Pure Appl. Chem.* **2009**, *81*, 2235. (c) Li, J.-R.; Sculley, J.; Zhou, H.-C. *Chem. Rev.* **2012**, *112*, 869.

(4) (a) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. *Chem. Soc. Rev.* **2009**, *38*, 1450. (b) Corma, A.; Garcıa, H.; Llabrees i Xamena, F. X. *Chem. Rev.* **2010**, *110*, 4606. (c) Lykourinou, V.; Chen, Y.; Wang, X.-S.; Meng, L.; Hoang, T.; Ming, L.-J.; Musselman, R. L.; Ma, S. *J. Am. Chem. Soc.* **2011**, *133*, 10382. (d) Yoon, M.; Srirambalaji, R.; Kim, K. *Chem. Rev.* **2012**, *112*, 1196.

(5) (a) Chen, B.; Xiang, S. C.; Qian, G. D. *Acc. Chem. Res.* **2010**, *43*, 1115. (b) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Duyne, R. P. V.; Hupp, J. T. *Chem. Rev.* **2012**, *112*, 1105. (c) Cui, Y.; Yue, Y.; Qian, G.; Chen, B. *Chem. Rev.* **2012**, *112*, 1126.

(6) (a) Ma, S.; Meng, L. *Pure Appl. Chem.* **2011**, *83*, 167. (b) Wang, X.-S.; Meng, L.; Cheng, Q.; Kim, C.; Wojtas, L.; Chrzanowski, M.; Chen, Y.-S.; Zhang, X. P.; Ma, S. *J. Am. Chem. Soc.* **2011**, *133*, 16322. (c) Wang, C.; Zhang, T.; Lin, W. *Chem. Rev.* **2012**, *112*, 1084. (d) Zhang, W.; Xiong, R. *Chem. Rev.* **2012**, *112*, 1163. (e) Cohen, S. M. *Chem. Rev.* **2012**, *112*, 970. (f) Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Ferey, G.; Morris, R. E.; Serre, C. *Chem. Rev.* **2012**, *112*, 1232. (g) Betard, A.; Fischer, R. A. *Chem. Rev.* **2012**, *112*, 1055.

(7) (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) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (c) Ockwig, N. W.; Delgado-Friedrichs, O.; O'Keeffe, M.; Yaghi, O. M. *Acc. Chem. Res.* **2005**, *38*, 176.

(8) (a) Qiu, S.; Zhu, G. *Coord. Chem. Rev.* **2009**, *253*, 2891. (b) Tranchemontagne, D. J.; Mendoza-Cortes, J. L.; O'Keeffe, M.; Yaghi, O. M. *Chem. Soc. Rev.* **2009**, *38*, 1257. (c) Perry, J. J.; Perman, J. A.; Zaworotko, M. J. *Chem. Soc. Rev.* **2009**, *38*, 1400. (d) O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2012**, *112*, 675.

(9) Zhang, J.-P.; Zhang, Y.-B.; Lin, J.-B.; Chen, X.-M. *Chem. Rev.* **2012**, *112*, 1001.

(10) (a) Denysenko, D.; Grzywa, M.; Tonigold, M.; Streppel, B.; Krkljus, I.; Hirscher, M.; Mugnaioli, E.; Kolb, U.; Hanss, J.; Volkmer, D. *Chem.—Eur. J.* **2011**, *17*, 1837. (b) Biswas, S.; Grzywa, M.; Nayek, H. P.; Dehnen, S.; Senkovska, I.; Kaskel, S.; Volkmer, D. *Dalton Trans.* **2009**, 6487. (c) Demessence, A.; D'Alessandro, D. M.; Foo, M. L.; Long, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 8784. (d) Demessence, A.; Long, J. R. *Chem.—Eur. J.* **2010**, *16*, 5902. (e) Zhang, Z.; Xiang, S.; Chen, Y.-S.; Ma, S.; Lee, Y.; Phely-Bobin, T.; Chen, B. *Inorg. Chem.* **2010**, *49*, 8444. (f) McDonald, T. M.; D'Alessandro, D. M.; Krishna, R.; Long, J. R. *Chem. Sci.* **2011**, *2*, 2022. (g) Wang, X.-L.; Qin, C.; Wu, S.-X.; Shao, K.-Z.; Lan, Y.-Q.; Wang, S.; Zhu, D.-X.; Su, Z.-M.; Wang, E.-B. *Angew. Chem., Int. Ed.* **2009**, *48*, 5291.

(11) Catalan, J.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1869.

(12) (a) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596. (b) Juríček, M.; Kouwer, P. H. J.; Rowan, A. E. *Chem. Commun.* **2011**, *47*, 8740.

(13) X-ray crystal data for MTAF-1: $C_{45}H_{25}N_{15}O_{12}Zn_5$, fw = 1294.65, tetragonal, $I4cm$, $a = 28.368(3)$ Å, $b = 28.368(3)$ Å, $c = 33.958(4)$ Å, $V = 27328(5)$ Å^3, $Z = 8$, $T = 100$ K, $\rho_{calcd} = 0.629$ g/cm^3, R1 $[I > 2\sigma(I)] = 0.0534$, wR2 (all data) = 0.1502.

(14) Zeng, M.-H.; Wang, Q.-X.; Tan, Y.-X.; Hu, S.; Zhao, H.-X.; Long, L.-S.; Kurmoo, M. *J. Am. Chem. Soc.* **2010**, *132*, 2561.

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

(16) (a) Li, J.-R.; Ma, Y.; McCarthy, M. C.; Sculley, J.; Yu, J.; Jeong, H.-K.; Balbuena, P. B.; Zhou, H.-C. *Coord. Chem. Rev.* **2011**, *255*, 1791. (b) 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.

(17) (a) An, J.; Fiorella, R. P.; Geib, S. J.; Rosi, N. L. *J. Am. Chem. Soc.* **2009**, *131*, 8401. (b) Vaidhyanathan, R.; Iremonger, S. S.; Shimizu, G. K. H.; Boyd, P. G.; Alavi, S.; Woo, T. K. *Science* **2010**, *330*, 650. (c) Burd, S. D.; Ma, S.; Perman, J. A.; Sikora, B. J.; Snurr, R. Q.; Thallapally, P. K.; Tian, J.; Wojtas, L.; Zaworotko, M. J. *J. Am. Chem. Soc.* **2012**, *134*, 3363.

(18) Myers, A. L.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121.

(19) (a) Bae, Y.-S.; Mulfort, K. L.; Frost, H.; Ryan, P.; Punnathanam, S.; Broadbelt, L. J.; Hupp, J. T.; Snurr, R. Q. *Langmuir* **2008**, *24*, 8592. (b) Mason, J. A.; Sumida, K.; Herm, Z. R.; Krishna, R.; Long, J. R. *Energy Environ. Sci.* **2011**, *4*, 3030.

(20) Lin, Q.; Wu, T.; Zheng, S.-T.; Bu, X.; Feng, P. *J. Am. Chem. Soc.* **2012**, *134*, 784.