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Metal–Organic Frameworks

A Zirconium Macrocyclic Metal–Organic Framework with Predesigned Shape-Persistent Apertures

Teng-Hao Chen,*[a] Ilya Popov,[b] and Ognjen Š. Miljanić*[c]

Abstract: A microporous metal–organic framework (MOF) was synthesized from $[Zr_6O_4(OH)_4(C_6H_5COO)_{12}]$ clusters and a triacid ligand based on a shape-persistent arylene ethynylene macrocycle. This framework, dubbed Zr-MCMOF, is held together by metal–ligand coordination and multiple weak interactions: hydrogen bonding, [π···π] stacking, and [C–H···π] interactions. The rigid ligand has a 9 Å-wide central void, which serves as a predesigned aperture for the 1D channels; all of the porosity of Zr-MCMOF comes from the ligand. The resulting framework possesses high hydrolytic and thermal stability and a flexible structure unique among Zr-based MOFs.

Metal–organic frameworks (MOFs) are hybrid porous materials constructed from inorganic metal cluster nodes and organic linkers. Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, MOFs are promising for uses in gas storage and separation, molecular inclusion, environmental remediation, sensing, and catalysis.[1] MOFs with one-dimensional (1D) channels are particularly useful for gas or molecular separations because they can provide uniform pore geometries and accessible metal sites for dynamic trapping and release of the molecules of interest.[2] Introducing macrocyclic motifs into the frameworks is another accessible strategy for selectively sieving and capturing guest molecules.[3] Many soft and rigid macrocyclic molecules possess significant voids available for guest encapsulation and separation.[4] However, while macrocyclic ligands have been used as building blocks for MOF synthesis, their predesigned pores have never served as the exclusive apertures for the resultant 1D channels.[5]

Herein, we present the synthesis and characterization of a Zr-based macrocyclic metal–organic framework (Zr-MCMOF) with 1D channels based on a shape-persistent *m*-phenylene ethynylene macrocyclic triacid ligand **1** (Figure 1a).[6] Remarkably, this is the first example of a MOF in which all the voids are exclusively determined by the organic ligand. We have previously used triacid **1** to construct a flexible mesoporous Zn-based MCMOF in which the organic repeating unit was a pair of [π···π] stacked macrocycles **1**.[7] Similar [π···π] stacking, wherein two molecules of **1** form a unique complex building block, is also observed in the structure of Zr-MCMOF; this stacking distorts the Zr_6 secondary building unit (SBU) in Zr-MCMOF, generating a layered structure rare among Zr-based MOFs.[8] In our previous work, an ester derivative of macrocycle **1** was shown to encapsulate fluoroarenes inside its cavity;[9] thus, the 1D channels in Zr-MCMOF appear to be a unique microenvironment, promising for applications in highly specific separations.

Our initial attempts to prepare Zr-MCMOF involved mixing Zr^{IV} salts and ligand **1** under a variety of solvothermal conditions; however, these attempts invariably produced amorphous materials. The majority of Zr-MOFs are based on Zr_6 carboxylate SBUs.[10] The topological incompatibility of the Zr_6 cluster with the bulky and rigid backbone of ligand **1** might have hampered the in situ formation of the SBU and the resultant framework. Therefore, we decided to pre-synthesize the Zr_6 cluster by first dissolving anhydrous $ZrCl_4$ and a large excess of benzoic acid in *N*,*N*-diethylformamide (DEF), and then heating the solution at 80 °C for one day to obtain the $[Zr_6O_4(OH)_4(C_6H_5COO)_{12}]$ cluster precursor (Figure 1a; for full synthetic details, see the Supporting Information).[11] The solution containing 0.014 mmol of the Zr_6 cluster was added onto 0.014 mmol of solid compound **1**. After sonicating the mixture for 1 h, the macrocycle **1** was slightly dissolved. The resulting mixture was then placed in an oven at 100 °C for 4 d to obtain colorless prismatic crystals of Zr-MCMOF.

Single-crystal X-ray analysis of Zr-MCMOF revealed an unprecedented structure with 1D channels, the apertures of which are directly decided by the diameter of macrocycle **1** (Figure 1a). The composition of this framework can be formalized as $[Zr_6O_4(OH)_4(\mathbf{1}\text{-}3H^+)(C_6H_5COO)_9(DEF)_3]$. So far, Zr_6 SBUs with twelve-,[12] ten-,[13] eight-,[14] and six-fold[15] connectivities have been reported. Only five Zr-based MOFs (namely MOF-808,[13] PCN-777,[15a] Zr-BTB,[15b] BUT-12, and BUT-13[15b]) were constructed by tritopic ligands; Zr-MCMOF is the first three-fold connectivity for the Zr_6 SBU. Three benzoate ligands from each pre-prepared $[Zr_6O_4(OH)_4(C_6H_5COO)_{12}]$ SBU are replaced. The two different Zr^{IV} sites coordinated by the carboxylate group of the substituted benzoate are respectively replaced by one DEF

[a] *Prof. T.-H. Chen*
Department of Chemistry, Tamkang University
No.151, Yingzhuan Rd., Tamsui Dist., New Taipei City 25137 (Taiwan)
E-mail: thchen@mail.tku.edu.tw

[b] *Dr. I. Popov*
Chemical Sciences Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)

[c] *Prof. O. Š. Miljanić*
Department of Chemistry, University of Houston
112 Fleming Building, Houston TX 77204-5003 (USA)
E-mail: miljanic@uh.edu

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: http://dx.doi.org/10.1002/chem.201605079.

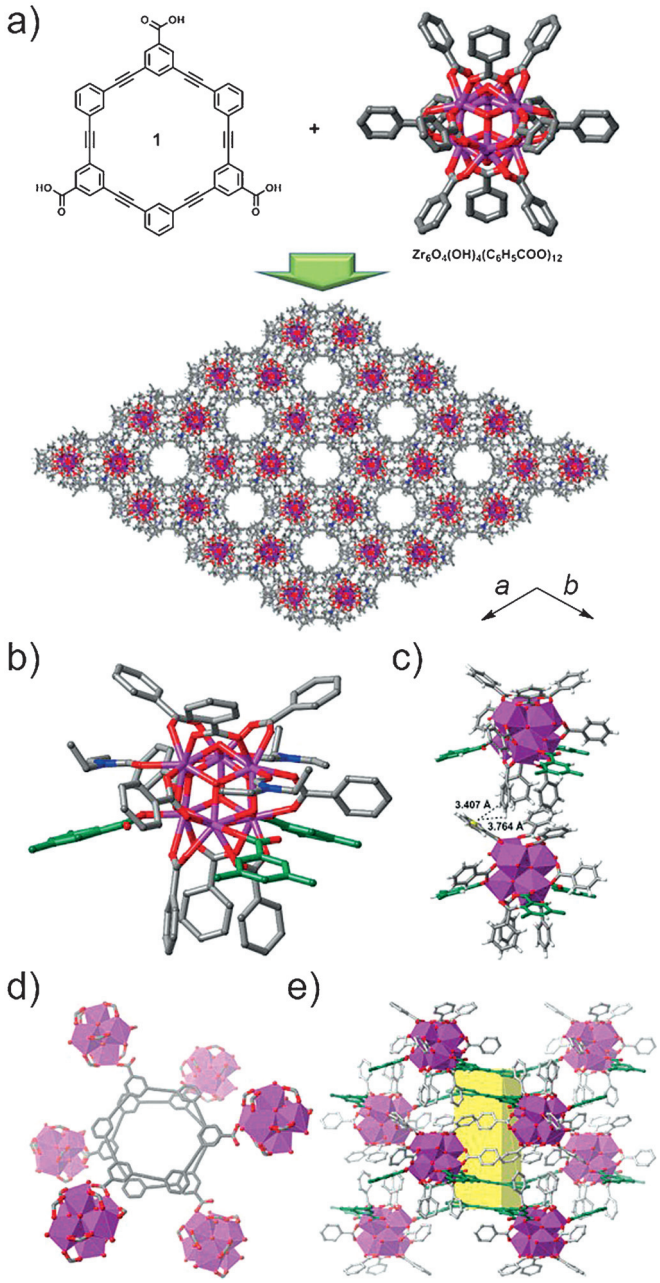

Figure 1. Synthesis and single-crystal X-ray structure of Zr-MCMOF. a) Reaction of macrocycle **1** and pre-prepared $[Zr_6O_4(OH)_4(C_6H_5COO)_{12}]$ cluster precursor gives rise to Zr-MCMOF with 1D channels along the crystallographic *c*-axis. b) Zr_6 SBU of Zr-MCMOF; the segments of **1**-3 H^+ are highlighted in green. c) The one-dimensional packing of SBUs through [C–H···π] interactions. d) The [π···π] stacked macrocyclic complex of ligand **1**. e) The hexagonal 1D channel (highlighted yellow) formed by two pairs of [π···π] stacked macrocyclic complexes. C gray, Zr purple, O red, N blue, H white. In (b), (d), and (e), hydrogen atoms are omitted for clarity. In (c), (d), and (e), Zr–O connections are presented as polyhedra for clarity.

molecule and one **1**-3H^+, the segments of which are highlighted in green (Figure 1b). Notably, only one oxygen from each carboxylate group of the macrocyle coordinates to Zr^{IV}, while the other oxygen forms a hydrogen bond with the adjacent μ^3-OH, with the measured [O···H] distance of 1.77 Å.[16] The crystallographic C_{3v} symmetry of $[Zr_6O_4(OH)_4(C_6H_5COO)_{12}]$ cluster[17] is forced to transform into a C_3 symmetry of $[Zr_6O_4(OH)_4$(**1**-3 H^+)$(C_6H_5COO)_9(DEF)_3]$ due to the coordinating DEF molecules and macrocycles **1**, which tend to stay coplanar. As a result, orthogonal to the plane of macrocycles, three benzoates on each end of the cluster form one small and one large angle concaves, respectively. The three-benzoate-concave with larger angle allows the insertion of the smaller angle one from the adjacent SBU (Figure 1c). There is an edge-to-face [C–H···π] interaction between the two hydrogen atoms on the edge of benzoate of the smaller concave and the centroid (highlighted in yellow in Figure 1c) of benzene ring of the larger concave (distances are 3.41 Å and 3.76 Å).[18] Therefore, the SBUs are aligned one-dimensionally via weak noncovalent interactions. The SBUs are bridged by **1**-3 H^+ horizontally, and a two-dimensional infinite network is formed through metal–ligand bonding. Remarkably, the macrocycles still prefer to [π···π] stack in pairs (Figure 1d, centroid–centroid distance of two adjacent macrocycles is 3.45 Å), and that slightly distorts the backbones of these molecules.[19] As can be seen in Figure 1e, one 2D layer is attached to another upside-down 2D layer and thus forms a 2D double-layer sheet by [π···π] stacking. The pairs of macrocycles are packing in a staggered orientation, with their connected SBUs interdigitating each other. The 2D double-layer sheets then pack on the top (or bottom) of another one via the edge-to-face [C–H···π] interactions mentioned above, constructing a 3D framework with 1D hexagonal channels (highlighted in yellow in Figure 1e). Two pairs of [π···π] stacked macrocycles form accessible small cages for guest molecules. The distance between the centroid of the two inner macrocycles of the cage is 11.61 Å.[19] Overall, Zr-MCMOF is the first Zr-based supramolecular framework constructed by four different interactions: metal–ligand coordination, hydrogen bonding, [C–H···π], and [π···π] interactions.

Powder X-ray diffraction (PXRD) analysis was performed to study the phase purity of bulk materials (Figure 2). Noticeably, the peak at $2\theta = 7.2^\circ$ splits in the PXRD pattern of as-synthesized Zr-MCMOF (Figure 2b). This phenomenon was studied when the pores of MOFs were occupied by organic and inorganic species.[20] The large discrepancy between the PXRD patterns of the as-synthesized and activated samples implied the transformation of framework.[21] As reported, many porous materials constructed by weak interactions such as hydrogen boding and [π···π] stacking exhibit flexible structures.[22] After soaking Zr-MCMOF in various solvents at 25 °C for 24 h, the PXRD patterns displayed obvious shifting of peaks (Supporting Information, Figure S3), which is rare for Zr-based MOFs.[23] Despite its 2D layered structure, we did not observe delamination (using optical microscopy) while soaking Zr-MCMOF in these solvents.[24] Zr-based MOFs are hydrolytically robust and chemically stable compared to other MOFs.[25] Zr-MCMOF was treated with water for 24 h and large shifting of peaks on the PXRD pattern was observed as well (Figure 2d). We then resoaked the crystals into DEF at 25 °C for another 24 h, and the PXRD pattern showed the recovery of the major peaks of the as-synthesized sample (Figure 2e). This behavior implies the re-occupation of DEF molecules in the pores of Zr-MCMOF. The PXRD pattern was not completely reversed to that of the as-synthe-

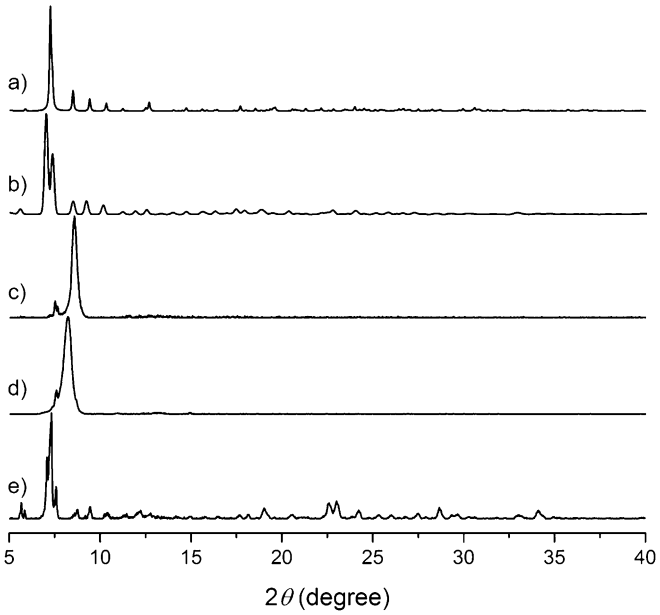

Figure 2. PXRD patterns of a) simulated Zr-MCMOF from the single-crystal X-ray structure, b) as-synthesized Zr-MCMOF, c) Zr-MCMOF after activation at 120 °C for 15 h, d) Zr-MCMOF after water treatment at 25 °C for 24 h, and e) Zr-MCMOF after soaking water-treated sample into DEF at 25 °C for 24 h.

sized sample, even after further solvent exchange with DEF. This was probably due to the encapsulated and unexchanged solvent molecules in the structure. The transformable structures induced by solvent molecules are well-studied in supramolecular porous frameworks.[26] However, the exact nature of the solvent-transformed structures of Zr-MCMOF could not be revealed by PXRD and single-crystal X-ray analysis. The chemical stability of Zr-MCMOF was investigated by soaking crystals into 1 M $HCl_{(aq)}$ and $NaOH_{(aq)}$ solution for 24 h. The PXRD analysis revealed that Zr-MCMOF remained crystalline in acidic solution but decomposed under basic conditions (Supporting Information, Figure S3). The lowered chemical stability of Zr-MCMOF relative to other Zr-based MOFs could be a consequence of the fact that only one oxygen atom from each carboxylate of **1** coordinated to the Zr_6 SBU.[25] Interestingly, the major PXRD peaks of Zr-MCMOF were recovered by resoaking the 1 M $HCl_{(aq)}$-treated sample into DEF and heating it at 100 °C for 24 h (Supporting Information, Figure S4). This result implies that the framework is flexible and stable under acidic conditions. In summary, Zr-MCMOF possesses the highest hydrolytical and chemical stability among all MOFs constructed by weak interactions.[27]

Thermal stability of Zr-MCMOF was studied using thermogravimetric analysis (TGA) under N_2 with 2 °C min^{-1} heating rate. The weight loss before 450 °C was about 19 wt%, which is consistent with the loss of both free and coordinated DEF molecules (18.3 wt%) from the crystal structure (Figure 3). This is the first example that the Zr SBU of MOF is coordinated by DEF molecules and thus the TGA trace looks quite different from other Zr-based MOFs. We speculated that, due to the coordinating DEF molecules being trapped inside the spaces between Zr_6 SBUs, the temperature needed to remove them was much higher than the boiling point of DEF (176 °C).[8a] Steeper weight loss, which suggests decomposition, begins around 450 °C, which is more in tune with the decomposition temperature of other Zr-based MOFs.[25]

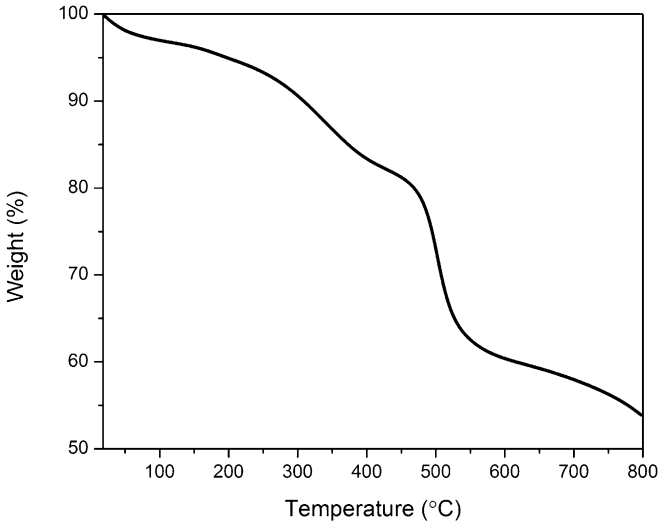

Figure 3. TGA trace of as-synthesized Zr-MCMOF.

Transannular distances in **1** (defined as the distances between the internal hydrogen atoms positioned furthest away from each other across the macrocycle) are 9.06 Å.[28] Nitrogen adsorption–desorption (77 K) measurements were performed to study the porosity of Zr-MCMOF (Figure 4). About 100 mg of Zr-MCMOF crystals were soaked in MeOH for 3 d and the solvent was exchanged with fresh MeOH every day. Before the adsorption analysis, the material was activated by heating in a vacuum oven at 120 °C for 15 h. A type I adsorption isotherm for microporous structure was obtained and the Brunauer–Emmett–Teller (BET) surface area was 317 $m^2 g^{-1}$. The NLDFT pore size distribution shows a range of micropore diameters mainly from 8.0 to 10.5 Å (Figure 4, inset), which is close to the

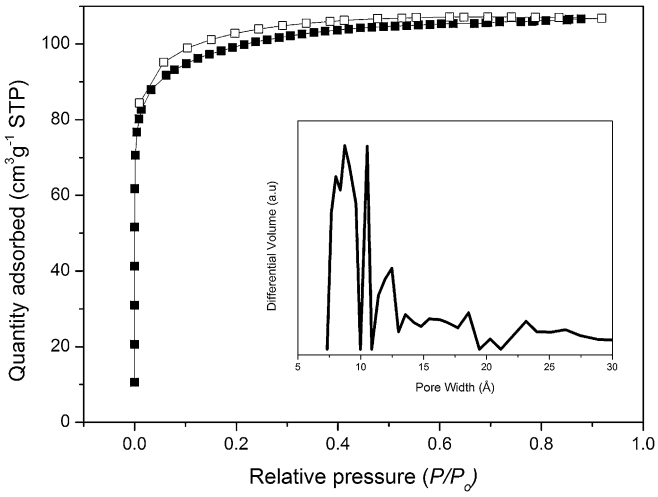

Figure 4. Nitrogen (77 K) adsorption–desorption isotherm and NLDFT pore size distribution (inset) of activated Zr-MCMOF. ■ adsorption, □ desorption.

pore size of macrocyclic ligand **1**. However, the pore size distribution is broad, which is probably due to the structural change of activated sample as shown from its PXRD pattern (Figure 2c); we speculate that macrocycles **1** may no longer line up to form regular 1D channels after activation. However, as structure of Zr-MCMOF can be recovered after resoaking the activated sample into DEF at 100 °C for 24 h (Supporting Information, Figure S4), the regular 1D channels appear to be reestablished as well. To the best of our knowledge, Zr-MCMOF is the first Zr-based MOF possessing 1D channels with uniform and exclusive apertures. Looking along the 1D channels formed by the rigid macrocycle **1**, the internal hydrogen atoms of the ligand macrocycles are pointing towards the pore centers, which is unlike the pores of most MOFs pores built from linkers with rotatable benzene rings. These features provide a potentially unique platform for host–guest chemistry and guest molecule separations.[29]

In summary, we have synthesized Zr-MCMOF, which possesses a novel architecture characterized by 1D channels with uniform apertures, hydrolytic and thermal stability, and a flexible structure. This material is held together by an array of interactions: metal–ligand coordination, hydrogen bonding, [π···π] stacking, and [C–H···π] interactions. Importantly, the rigid macrocycle guarantees the minimum pore size of the resultant MOF by its own interior pores, which can be synthetically engineered. Site-specific substitution with functional groups can be accomplished on both the interior and exterior of macrocycles as well.[30] The coordinating DEF molecules on SBUs could also be replaced by various motifs to perform chemical reactions inside the channels.[11,31] Taking all the structural features into account, Zr-MCMOF is promising for displaying special host–guest interactions, which could be useful in separations of structural isomers. As shape-persistent arylene ethynylene macrocycles can be fashioned in a variety of sizes and shapes, we are currently exploring whether those relatives of **1** can also be reticulated into MOFs, and what their structural influence on the overall framework topology will be studied. Studying guest encapsulation in these unusual pores will be the next step.

Experimental Section

Crystallographic information for Zr-MCMOF: formula $C_{140.75}H_{132}N_{5.50}O_{37.50}Zr_6$, $M_r = 3047.84\ g\,mol^{-1}$; trigonal crystal system; space group $P\bar{3}c1$; unit-cell dimensions: $a = 24.0688(3)$ Å, $b = 24.0688(3)$ Å, $c = 30.1366(5)$ Å, $\alpha = \beta = 90.0°$, $\gamma = 120.0°$, $V = 15\,119.4(4)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.34\ Mg\,m^{-3}$; $\mu = 3.886\ mm^{-1}$; radiation wavelength 1.5418 Å; $T = 113(2)$ K; $\theta_{max} = 66.63°$; 103 552 measured reflections (out of which 9606 independent); $R_{int} = 0.0263$; $R_1 = 0.0386$; $wR_2 = 0.1230$; largest diff. peak and hole: 1.089 and −0.611 e Å^{-3}. CCDC 1481581 contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Additional experimental data can be found in the Supporting Information.

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