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A New Zeolitic Topology with Sixteen-Membered Ring and Multidimensional Large Pore Channels

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The importance of 4-connected zeolite-type framework is highlighted by many industrial applications of zeolites.[1] It is well known that topological features as well as chemical compositions play vital roles for both established and emerging applications. Therefore, there has been an ever increasing interest in the synthetic design of new crystalline porous materials.

For zeolite scientists, one of the most desirable and intriguing topological features is the 3-ring (i.e., rings with three tetrahedral atoms or T-atoms, not counting bridging oxygen atoms), because it has been proposed that the 3-ring can lead to low framework density and high pore volume.[2] Unfortunately, the 3-ring is uncommon in 4-connected structures because of the inherent strain associated with the small ring size.[3] Thus, one synthetic strategy to create topologies with 3-rings is to lengthen the T–O distance. One specific example is the use of larger T-atoms such as Ge (compared with Al and Si).[4]

Recently, a number of metal organic framework materials have been synthesized by using organic ligands to replace oxygen anions.[5] Of particular interest is the synthesis of metal imidazolate frameworks with 4-connected zeolite-type topologies.[6–10] Intuitively, the large T–L distance in the imidazolate framework should be conducive to the formation of 3-rings. However, few tetrahedral metal imidazolate frameworks were known to have 3-rings prior to this work. It is also worth noting that most known imidazolate structures tend to adopt the same framework topology as those already found in aluminosilicate or phosphate structures.

Because the average ring size in a 4-connected net is assumed to be within a narrow range (around 6),[11] the occurrence of small rings such as 3-rings is likely to be accompanied by the simultaneous occurrence of large or extra-large rings. Our synthetic strategy to create low density framework with large and extra-large ring sizes in the imidazolate system is based on the reasoning that the steric interaction caused by substituents on imidazolate (already observed in some imidazolate frameworks[7]) may lead to large and extra-large rings. With this strategy, 5,6-dimethylbenzimidaozle (H-DMBim) was selected as the building block for fabricating new imidazolate frameworks.

Here, we report two zeolite-like structures (denoted as **TIF-1Zn** and **TIF-1Co**, TIF = tetrahedral imidazolate framework) with a previously unknown topology and highly open microporous framework. This new framework features both 3- and 16-rings (in addition to 4-, 10- and 12-rings), new types of loop configurations, and multidimensional intersecting large pore channels. Prior to this work, the 16-ring is not known in any 4-connected zeolite-type structures.

TIF-1Zn and **TIF-1Co** were synthesized by solverthermal reaction of $Zn(Ac)_2{\cdot}2H_2O$ or $Co(Ac)_2{\cdot}4H_2O$ and 5,6-dimethylbenzimidazole in a mixed solvent (±)-2-amino-1-butanol and benzene at 150 °C. Single crystal $[Zn(DMBim)_2]{\cdot}(G)_x$ (G = guest solvent molecules) and polycrystalline Co^{II} analogue were obtained. The crystal structure of **TIF-1Zn** was determined by single crystal X-ray diffraction while **TIF-1Co** was identified as isostructural to **TIF-1Zn** on the basis of X-ray powder diffraction patterns (Figure S1).

TIF-1Zn crystallizes in a highly symmetrical tetragonal space group $P4_2/mnm$.[12,13] The asymmetric unit (Figure S2) includes four zinc sites, of which only Zn4 is situated on a symmetry site with a 1/4 occupancy. This gives the ratio of 4:4:4:1 for these zinc sites (T_1, T_2, T_3 and T_4). Each unit cell contains 52 T atoms, leading to a very large unit cell volume of 32212 Å[3] (Figure S3). As in zeolites, each T atom is coordinated with four N atoms from four different ligands and each ligand links two T atoms. This unique framework contains three types of loop configurations (Figure 1a–c). The loop configuration of a T-atom is defined by the local coor-

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dination geometry of this T-atom to its adjacent T-atoms and shows the distribution of 3- or 4-rings around this T-atom.

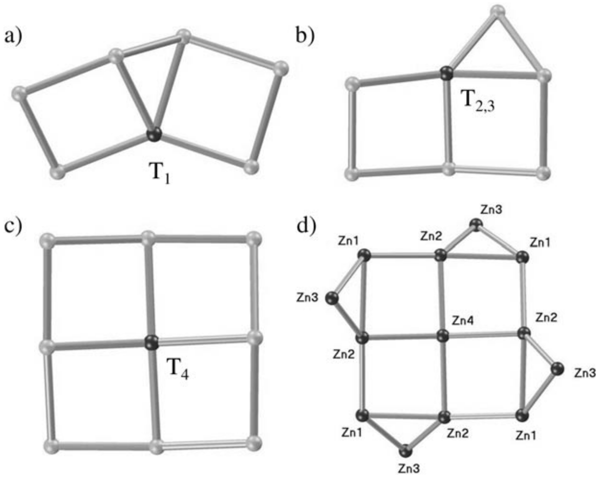

Figure 1. Loop configurations of four kinds of T-atoms (a, b, and c) in secondary building unit (d) in **TIF-1 Zn**.

An unusual feature is the occurrence of a unique type of secondary building unit (SBU) composed of 13 T atoms (Figure 1d). Each SBU is bonded to four adjacent SBUs by $T_1T_1T_3T_3$ 4-rings to form a 2D layer (Figure S6a). Two adjacent layers, related by 4_2 symmetry operation, are joined together in the ABAB sequence by $T_3T_3T_3T_3$ 4-rings (Figure S6b) to generate a 3-D framework (Figure 2a).

One of the most striking features here is the co-existence of 3- and 16-membered rings, which helps to produce a framework with very low framework density and multidimensional channels. The presence of 16-rings is confirmed by vertex symbols of T-atoms ($3.12_5.4.4.12_2.16$ for T_1; $3.4.4.12_3.10.12_2$ for T_2; $3.4.4.10.12_2.16$ for T_3; and $4.4.4.4.10.10$ for T_4) (Figure S4). It is of interest to note that rings of five different sizes co-exist here. Two of these ring sizes (i.e., 3- and 16-rings) are quite rare for metal imidazolate frameworks (Figure S5). The largest 16-ring has a window size of 28.5 Å × 22.6 Å as measured using the interatomic distances.

As expected from the presence of both small (3-rings) and extra-large rings (16-rings), **TIF-1 Zn** has a very low framework density. The framework density (FD) is defined as the number of T-atoms per 1000 Å,[3] which is traditionally used to characterize the openness of zeolite frameworks. Because of the large size of imidazolate ligand, the framework density of this topology is much lower than that of aluminosilicate zeolites or phosphates. The framework density of TIF-1Zn (1.61) is comparable to other metal imidazolate frameworks (e.g., SOD 2.50; RHO 2.01; LTA 2.04; GME 2.09).

Also of interest is the multidimensional large pore channel system with the ring size of 12, 12, 12, 10, and 10, respectively, for channels along various crystallographic directions (Figure S7). The channels along the [110] and [0$\bar{1}$0] directions are very unusual because they are defined by alternating 16- and 12-rings. Figure 2b shows the cross-sectional view of multidirectional channels.

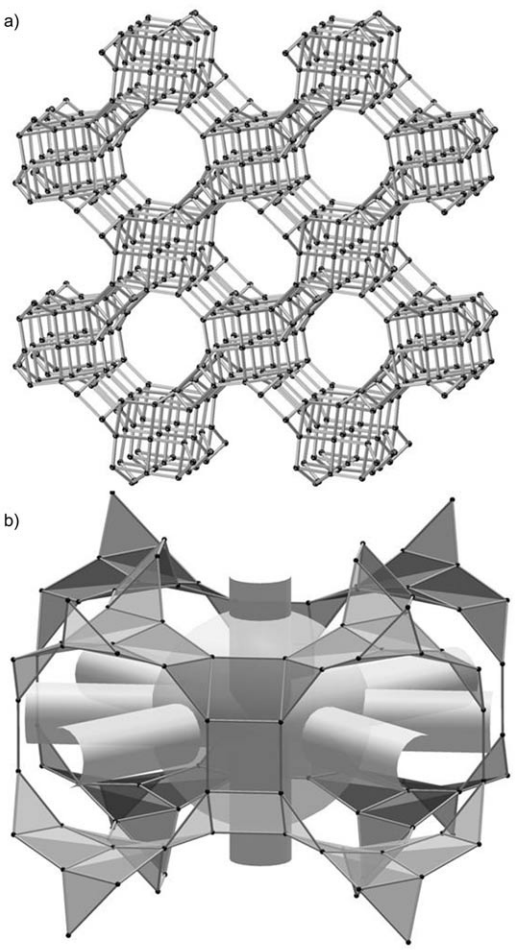

Figure 2. a) The topological network of **TIF-1 Zn** viewed along [001]. b) Cross-sectional view of multidimensional channels.

Despite the highly open framework topology and multidimensional large pore system, **TIF-1 Zn** exhibits high thermal stability. Thermal gravimetric analysis (TGA) under the N_2 atmosphere performed on **TIF-1 Zn** (washed with ethanol and dried in air) shows a gradual weight loss of 0.93 % between 30–140 °C, likely due to the loss of residual solvent molecules. A long plateau in the temperature range between 150 and 440 °C was observed (Figure S8). Such thermal stability up to about 440 °C is rather high for a framework structure containing organic building blocks.

The permanent porosity of **TIF-1 Zn** was confirmed by gas adsorption measurements performed on Micromeritics ASAP 2010 surface area and pore size analyzer. The sample for surface area analysis was treated by immersing as-synthesized **TIF-1 Zn** with methanol, and then dichloromethane, followed by evacuation at room temperature. The treated sample was characterized by XRD to confirm that it has the same structure with as-synthesized sample (Figure S9). The sample was degassed at 150 °C prior to the measurement. A Type I isotherm was observed, indicating

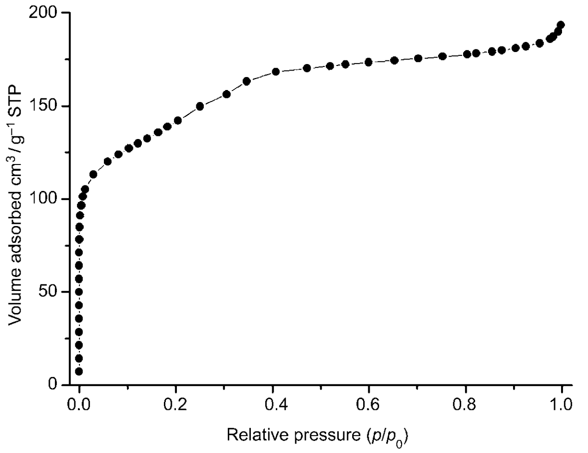

Figure 3. Nitrogen gas adsorption isotherm at 77 K for **TIF-1Zn**. p/p_0 is the ratio of gas pressure (p) to saturation pressure (p_0), with p_0= 740 Torr.

that **TIF-1Zn** is microporous (Figure 3). The Langmuir surface area of 667.5 m^{2}g^{-1}and the pore size of 11.7 Å were calculated using the data in the range of p/p_0=0.059–0.205. A single data point at relative pressure 0.250 gives a micropore volume of 0.231 cm^{3}g^{-1}by Horvath–Kawazoe equation.

In conclusion, two new 4-connected metal imidazolates with unprecedented 4-connected topology have been synthesized and structurally characterized. TIF-1Zn exhibits permanent microporosity and has high thermal stability. It features unusual topological features such as 3-, and 16-rings and multidimensional large pore channels and underlines the rich synthetic and structural chemistry of imidazolate based porous frameworks that are yet to be explored.

Experimental Section

Typical synthesis of TIF-1Zn: $Zn(Ac)_2\cdot 2H_2O$ (118.8 mg), 5,6-dimethylbenzimidazole (157.6 mg), (±)-2-amino-1-butanol (4.0 mL) and benzene-(3.2 mL) are mixed in a Teflon-lined autoclave and stirred for 30 min. The autoclave was then sealed and heated at 150°C for 5 d, followed by cooling to room temperature. A large amount of colorless crystals were obtained with a yield of 43.2% (76.6 mg; based on zinc salt). The crystals were washed using ethanol three times and dried in air for other measurements. IR data for as-synthesized **TIF-1Zn** (KBr): $\tilde{\nu}$ = 1475s, 1337 m, 1203 m, 1167w,1093w, 1021w, 848 m, 813w, 648w cm^{-1}. The synthesis of **TIF-1Co** was similar with that of **TIF-1Zn**, except for the replacement of the $Zn(Ac)_2\cdot 2H_2O$ by $Co(Ac)_2\cdot 4H_2O$. A large amount of violet powder was obtained with a yield of 39.2% (68.2 mg).

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Keywords: adsorption · metal imidazolate frameworks · nitrogen · zeolites

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[12] Crystallographic data of **TIF-1Zn**: $[Zn(DMBim)_2]\cdot(G)_x$, tetragonal, $P4_2/mnm$, $a=b=30.8800(8)$ Å, $c=33.781(2)$ Å, $V=32213(2)$ Å^3, $Z=52$, $2\theta_{max}=41.7$ $(-25\leq h\leq 29,\ -28\leq k\leq 28,\ -31\leq l\leq 33)$, $T=$ 150 K, 81886 measured reflections, $R_1=0.1179$ for 8551 reflections $[I>2\sigma(I)]$, GOF=1.163. Single-crystal X-ray analysis was performed on a Bruker Smart APEX II CCD area diffractometer with nitrogen-flow temperature controller using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å), operating in the ω and ϕ scan mode. The SADABS program was used for absorption correction. The structure was solved by direct methods and the structure refinements were based on $|F^2|$. Most of non-hydrogen atoms were refined with anisotropic displacement parameters, except the atoms of disordered fragments, which were refined isotropically. No hydrogen atoms were placed in calculated positions. All crystallographic calculations were conducted with the SHELXTL software suites. The high $R(F)$ is caused by the disorder of partial ligands and solvent. CCDC 682400 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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