

Selective Gas Adsorption and Unique Structural Topology of a Highly Stable Guest-Free Zeolite-Type MOF Material with N-rich Chiral Open Channels

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Abstract: A new multifunctional di-topic tetrazolate-based ligand, 2,3-di-1*H*-tetrazol-5-ylpyrazine (H₂dtp) has been designed and synthesized. The solvothermal reaction of this ligand with ZnCl₂ gave a robust guest-free three-dimensional zeolite-like chiral metal-organic framework (MOF) complex, [Zn(dtp)], which crystallized in chiral space group *P*6₁ and possessed chiral open channels with nitrogen-rich

walls and the diameter of approximately 4.1 Å. This framework presents a unique uniform *etd* (8,3) topology, is the first example of its type in MOFs, and exhibits high thermal stability with the decomposition temperature above

Keywords: adsorption • chiral channels • metal-organic framework • microporous materials • selectivity

380 °C and permanent porosity. It is interesting that this material is able to selectively adsorb O₂ and CO₂ over N₂ gas, being a rare example in MOFs. In addition, C₂H₂ and MeOH adsorption results show that although the framework channel holds nitrogen-rich walls that may provide H-bonding sites, no N⋯H H-bond effect between the guest molecules and microporous surface was observed.

Introduction

Microporous metal-organic framework (MOF) materials with zeolite structures have attracted wide attention, owing to their unusual topologies and applicable functions for catalysis, gas separation and storage.^[1] Compared to those of inorganic zeolites, the pore structures of MOFs can be more easily designed and functionally modified to yield the desired shape, size, and surface characteristics.^[2] However, engineering of such MOFs in control of stability, network topology, and functionality is still facing great challenges. In fact, for any practical applications, it is very important that these materials are structurally robust and thermally stable. Unfortunately, thermal instability is a major problem for many MOFs. Guest-free MOFs generally have higher ther-

mal stability, but they are difficult to be constructed, and are also very rare.^[3] In addition, because the pore dimensions of some MOFs typically fall in the range of 4–6 Å, they often exhibit a high adsorption selectivity that is particularly attractive for the separation of small gas molecules.^[4] From the structural point of view, zeolite networks, as the most significant topologies for porous materials, are scarce for porous MOFs. The analysis of such network topology is important in the design and elucidation of crystal structures.^[1c] On the other hand, chirality plays an important role in chemistry and material. It is also challenging to design a crystalline material combining both chirality and porosity.^[5] Recently, it was realized that multi-topic tetrazolate-based organic ligands have great potential for generating MOF materials with novel network topologies and permanent porosity.^[6] Here we report a novel guest-free MOF material, [Zn(dtp)] (**1**) constructed from a new developed di-topic tetrazolate ligand, 2,3-di-1*H*-tetrazol-5-ylpyrazine (H₂dtp) (Figure 1). Remarkably, **1** possesses a unique zeolite-like chiral framework structure with chiral open channels, high thermal stability, and selective gas adsorption ability. We selected H₂dtp as the ligand, in view of its 1) rigidity and non-linearity, which may reduce the probability for interpenetration, 2) nitrogen-rich and multifunctional coordination characteristics, to build complex frameworks with N-donor decorated channels; and 3) potential chirality, to obtain chiral frameworks.

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Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author and contains the full synthesis details for the ligand, FT-IR, CD-UV spectra, TG-DTA, XRPD patterns, additional discussions, and figures.

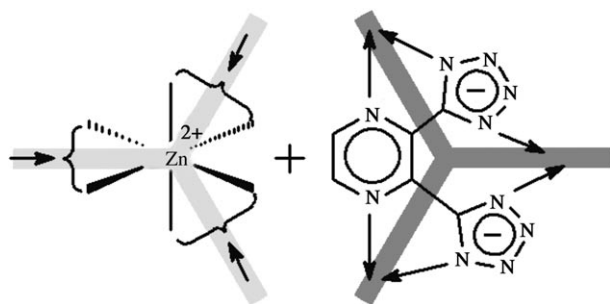


Figure 1. Schematic representation of the construction behaviors of Zn^{II} and the dtp^{2-} ligand in **1**.

Results and Discussion

Heating a mixture of ZnCl_2 and H_2dtp dissolved in *N,N*-dimethylacetamide (DMAC) and MeOH at 120°C for 48 h afforded pure-phase **1** as pale hexaprismatic crystals. The X-ray analysis revealed that **1** crystallizes in the chiral space group $P6_1$ and has a guest-free chiral framework structure with one-dimensional (1D) homochiral open channels. Solid-state CD measurements (Figures 3S, and 4S in the Supporting Information) indicate that a single randomly selected crystal displays dichroic signals corresponding to the absorption of UV spectrum, showing each individual crystal of **1** consists of a single enantiomer, and therefore a chiral crystal in the solid state. It means that each crystal of **1** is spontaneously resolved by chiral crystallization. However, as expected there exists an inverse CD signal when measuring another single crystal, and the mixed bulk crystals do not display dichroic signals. Based on such results, it could be considered that the crystallization of **1** is racemic with equivalent enantiomeric crystals crystallized in $P6_1$ and $P6_5$ space groups, respectively (indeed, the X-ray diffraction for another single crystal in the $P6_5$ has also been performed).

Complex **1** has a three-dimensional (3D) structure, consisting of one type of ligand and one type of Zn^{II} atom. Each ligand coordinates to three Zn^{II} atoms, and each in a bidentate fashion (Figure 1 and 5S in the Supporting Information). It bonds to each of two Zn^{II} atoms through one pyrazine N [$\text{Zn}-\text{N}=2.037(4)$, $2.393(4)$ Å] and one tetrazole N atom [$\text{Zn}-\text{N}=2.627(4)$, $2.023(4)$ Å], and to a third through two tetrazole N donors [$\text{Zn}-\text{N}=2.108(3)$, $2.044(4)$ Å]. In turn, each distorted octahedral Zn^{II} ion is coordinated by three chelating ligands. This results in a zeolite-type 3D framework containing close-packed 1D open channels (Figure 2a,b, and 6S in the Supporting Information). PLATON calculations indicate that **1** contains 40.7% void space that is accessible to the solvent molecules.^[7] It is interesting that the framework is built by three types of single helices (Figure 2c and 7S in the Supporting Information), with 6_1 , 3_1 and 2_1 screw axis, respectively running in parallel along the *c* axis. Each type of helices is homochiral and is achieved by the tetrazolate groups linking Zn^{II} through its 1- and 4-position N atom coordination, which is highlighted in Figure 7S in the Supporting Information. Both 6_1 and 3_1

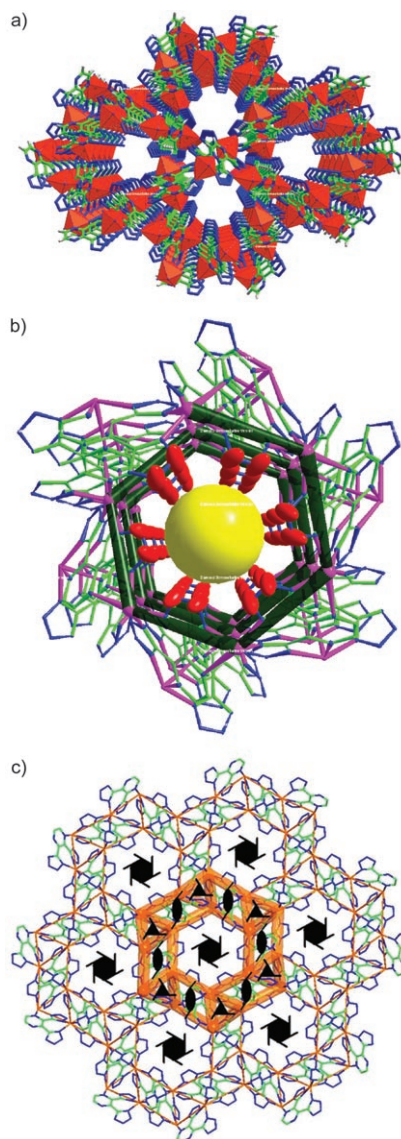


Figure 2. a) Structure of **1** showing open channels along the *c* axis. b) Chiral channels in **1**, N atoms are highlighted by ellipses. c) 2D projection down the *c* axis showing three types of helices.

helices are right-handed, but those of 2_1 are opposite with equal numbers to those of 3_1 . Thus, the framework presents chirality being made for such 6_1 helices, thereby **1** crystallized in $P6_1$ space group. Such 6_1 helical chains generate the chiral channels with the diameter of approximately 4.1 Å, and are so small that they are highly stable without guest molecules incorporated. Another interesting feature is that the channels have a nitrogen-rich (or N-donor functional) wall with helical arrangements of 2- and 3-position N atoms of tetrazolate groups (Figure 2b and 6S in the Supporting Information). These N atoms may act as basic adsorption site to interact with guest molecules, especially by providing H-bonding sites in some cases.^[2d]

Control of chirality in MOFs is a great challenge, in which one of the most successful approaches is based on using a chiral organic ligand to link the metal atom (or cluster) in

the framework.^[5c] And yet, there is also the possibility of forming chiral solids from achiral building blocks by a *topological framework construction* strategy. In **1**, the ligands dtp^{2-} is chiral similar to 1,1'-binaphthyl derivatives,^[5c] based on such a fact: two tetrazolate groups are not parallel with a dihedral angle of 33.5° , and have different degree of torsion with respect to the pyrazine plane (the dihedral angles are 12.4 and 25.7° , respectively). However, the 3-connected 3D net offers an alternative mechanism for rendering the chirality because the topology of such frameworks is often chiral due to the presence of helices, such as the (10,3)-*a* net.^[8] Herein, the origin of chirality in **1** should be best ascribed to the 3-connected topological construction of ligands and metal ions, probably also has close relationship with the ligand chirality. The simplification of the 3D framework of **1** by regarding each Zn^{II} atom and each dtp^{2-} ligand as 3-connecting nodes to generate a uniform (8,3) net with the vertex symbol of $8.8.8_2$ and the Schläfli symbol of 8^3 (Figure 3), containing topological 4_1 , 6_1 and 12_1 helices

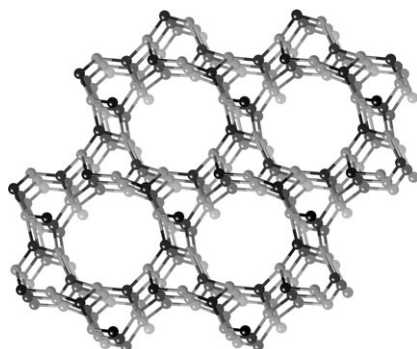


Figure 3. The underlying 3-connected (8,3) *etd* topology of **1**, ligands are represented as black spheres, Zn^{II} as grey.

(chemical 2_1 , 3_1 and 6_1 helices as described above) arrayed along the crystallographic *c* direction. Topologically, a feature of this net is the 4_1 helices running in the *c* direction, which are all of the same handedness, and of different handedness to all the 6_1 and 12_1 helices arranging in the same direction. This results in the overall 3D framework chirality. Indeed, fifteen uniform (8,3) nets sub-divided from *-a* to *-o* were elucidated by Wells in his classic monographs on networks.^[8] Some of them containing (8,3)-*a*, *b*, and *c* were now known to be displayed by real crystal structures,^[9] however (8,3) nets are still rare comparing with (10,3) ones. The net of **1** is clearly different from those reported, considering the linkage configurations and symmetry. On the other hand, this net can also be assigned as the *etd* abbreviation according to O'Keeffe's categorization,^[10] which is closely related to other plane 3-connected (8,3) nets of *eta*, *etb*, *etc* [that is, (8,3)-*c*], *etf* and *noj*, but topologically different, as compared in Table 1. Owing to the existence of two chemically or crystallographically different 3-connected nodes (two kinds of vertex), Zn^{II} and ligand, the space group $P6_122$ of the most symmetrical configuration of the *etd* net is lowered to $P6_1$ in

Table 1. A topological comparison for some close relative uniform 3-connected (8,3) nets.^[10]

Symbol	Space group ^[a]	Kinds of vertex	Kinds of edge	Vertex symbol	Net feature
<i>etd</i>	$P6_122$	1	3	$8.8.8_2$	chiral uniform
<i>eta</i>	$P6_222$	1	2	$8.8.8_2$	chiral uniform
<i>etb</i>	$R\bar{3}m$	1	2	$8.8.8_2$	uniform
<i>etf</i>	$R\bar{3}c$	1	3	$8.8.8_2$	uniform
<i>etc</i>	$P6_3/mmc$	2	2	$8_2.8_2.8_2$	uniform
<i>noj</i>	$P4_122$	2	3	$8_2.8_2.8_2$ $8.8.8_3$ $8.8.8$	chiral uniform

[a] On the most symmetrical configuration.

1. Furthermore, in the topologically simplified net of **1**, three links around each node are not of equivalent distance, with the sizes of ~ 3.2 , 3.9 and 4.2 Å, respectively, and the three angles around each node are also not equal. In addition, the 2D projection down the hexagonal axis (i.e. the *c* direction), with 4-, 6- and 12-membered rings, is reminiscent of a number of well-known zeolite frameworks, such as the AFI, ATO, GME, and OFF zeotypes (Figure 8S in the Supporting Information).^[11] However, it should be noted that many of the zeolite nets are based on a 4-connected node, but the net in **1** is 3-connected. Such an example is very rare in zeolite-like MOFs.

TG-DTA analysis (Figure 4) indicates that **1** is thermally stable until near 380°C . Thus, it provides an opportunity for probing gas adsorption properties. To our surprise, attempts

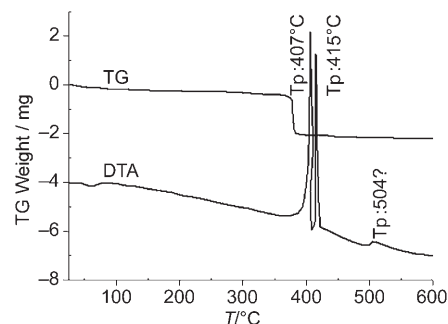


Figure 4. TG-DTA diagram of **1**.

to measure an N_2 adsorption isotherm for **1** at 77 K revealed almost no N_2 uptake (Figure 5). In contrast, it was found that a significant amount of O_2 (77 K) and CO_2 (195 K) are adsorbed, and both present typical Type-I adsorption curve as defined by the IUPAC. The uptake amounts at 1.0 atm are 79.3 and 98.8 cm^3g^{-1} for O_2 and CO_2 , respectively. Fitting the Langmuir equation to the isotherm of O_2 and CO_2 gave an estimated surface area of ~ 279 and ~ 390 m^2g^{-1} , and to the BET equation give ~ 246 and ~ 313 m^2g^{-1} , respectively. Using the D-R equation, the micropore volume of **1** is estimated to be ~ 0.16 cm^3g^{-1} from the CO_2 adsorption isotherm, which is smaller than that of 0.29 cm^3g^{-1} calculated from the

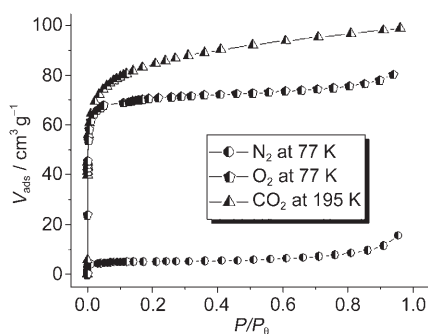


Figure 5. Adsorption isotherms of N₂, O₂ and CO₂ for **1**.

crystal structure. This discrepancy can be attributed to the gas molecules being unable to fill the void space efficiently. Notably, the monolayer coverage predicted by fitting the Langmuir and BET equations to the O₂ and CO₂ isotherms were also different, suggesting that there probably exist different number of binding sites being accessible in each case.

The selective sorption of O₂ and CO₂ over N₂ may be attributed to the restricted size of the channels in **1**, which distinguishes these gases with small kinetic diameters (O₂, 3.46 Å; CO₂, 3.3 Å) from those with larger ones (N₂, 3.64 Å) (having different diffusion rates).^[12] This behavior is analogous to the molecular sieve effect observed in zeolite 4 Å.^[13] To our knowledge, only a few known MOF materials have the similar effect, including Mn-formate,^[4a] Mg-2,6-naphthalenedicarboxylate,^[4b] CUK-1^[4c] and PCN-13.^[4d] The selective adsorption behavior may be useful in achieving certain gas separations. Therefore, this material may find applications, such as utility for the separation of O₂, CO₂ and N₂ from air.

It is interesting that the channels in **1** have a nitrogen-rich surface, which may form H-bond interactions with some guest molecules such as C₂H₂ and MeOH. Therefore, it may have different adsorption ability for C₂H₂ or MeOH from that for CO₂, as observed in [Cu₂(pzdc)₂(pyz)] (pzdc²⁻ = pyrazine-2,3-dicarboxylate, pyz = pyrazine),^[2d] in which the specific sorption for C₂H₂ is ascribed to the formation of H-bonds between acetylene molecule and the basic oxygen atom sites in the microporous surface. To test this hypothesis, the adsorption isotherms of C₂H₂ (at 197 K) and MeOH (at 298 K) were carried out. As shown in Figure 6, the adsorptions show also a similar type-I isotherm for both gases, the uptake amounts are about 90.0 cm³ g⁻¹ at 1.0 atm, and are similar to that of CO₂. Thus, it is in contrast to the adsorption behavior of [Cu₂(pzdc)₂(pyz)],^[2d] probably, because the N atoms of the dtp²⁻ tetrazol rings are weaker H-bond acceptors than the O atoms of pzdc. The adsorption behavior of **1** is also different from those of magnesium and manganese formats reported recently by Kim et al.,^[14] which have adsorption selectivity for C₂H₂ over CO₂. This selective adsorption was “presumably due to the slightly larger size of C₂H₂ relative to CO₂, which provides the former with more-effective van der Waals interactions with the framework walls”.^[14] On the other hand, the adsorptions (and desorp-

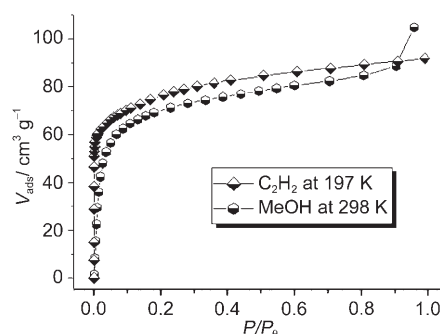


Figure 6. Adsorption isotherms of C₂H₂ and MeOH for **1**.

tions) for C₂H₂ and MeOH in **1** are reversible, similar to those for O₂ and CO₂. These results indicate that the incoming guest molecules can move freely into the channels, without forming H-bonding interaction with the pore surface. In addition, in the isotherm curve of MeOH the second increase above $P/P_0=0.8$ may be attributed to the adsorption on the external crystallite surface.^[15]

Conclusion

A new tetrazolate-based ligand has been synthesized, and used to react with Zn^{II} in solvothermal conditions to give a robust guest-free zeotype MOF material that contains chiral channels. This framework material has a unique *etd* (8,3) topology, the first example in MOFs, high thermal stability and permanent porosity. It exhibits rare gas-adsorption selectivity for O₂ and CO₂ over N₂ gas, and could be useful in the separation of air. In addition, C₂H₂ and MeOH adsorptions show that although the framework channels have nitrogen-rich walls that may provide H-bonding sites, no N⋯H H-bond interaction effect was observed, and thus also no discrimination of CO₂ and C₂H₂, as expected. The channels in **1** might also be useful for polymerization reactions (such as C₂H₂) and hydrogen uptake, both of which are now under investigation.

Experimental Section

The ligand 2,3-di-1*H*-tetrazol-5-ylpyrazine (H₂dtp) was synthesized by replicating a literature procedure developed by Sharpless et al.^[16] (see the Supporting Information for details). [Zn(dtp)] (**1**) was prepared by the solvothermal reaction: a mixture of H₂dtp (43 mg, 0.2 mmol) and ZnCl₂ (55 mg, 0.4 mmol) in 8 mL of DMAC-MeOH (1:1, DMAC = *N,N*-dimethylacetamide) mixture solvent was sealed in a Teflon-lined stainless autoclave and heated at 120 °C under autogenous pressure for 48 h, and then cooled to room temperature. Pale hexaprismatic crystals were collected and washed by DMAC, methanol and ether. Yield: 50% based on H₂dtp. Element analysis (%): Calcd. for C₆H₂N₁₀Zn (Mr: 279.53): C 25.78, H 0.72, N 50.11; found: C 25.64, H 0.85, N 50.32. For FT-IR (KBr, cm⁻¹), see Figure 1S in the Supporting Information. The phase purity was confirmed by comparison of experimental XRPD pattern with that simulated from the single-crystal data (Figure 2S in the Supporting Information). This material is almost insoluble in common solvents, even in

DMF, DMAC and DMSO. It has high thermal stability as shown in Figure 4, in which a little of the weight loss in 25–100 °C may be attributed to the dampness of the measured sample. In addition, after heated at 100 °C for 20 min, the crystals are still transparent and XRPD pattern is intact (Figure 2S in the Supporting Information).

Caution! Although we have met no problems in handling Zn-azides and Zn-tetrazolate during this work, it should be treated with great caution, owing to their potential explosive nature.

X-ray single crystal diffraction measurement for **1** was carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. The determinations of unit cell parameters and data collections were performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) and unit cell dimensions were obtained with least-squares refinements. The program SAINT^[17] was used for integration of the diffraction profiles. The structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.^[18] Zn^{II} atoms were found from *E*-maps and other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on *F*². The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factor. Crystal data: C₆H₂N₁₀Zn, Mr = 279.55; hexagonal; space group *P6*₃; *a* = 14.163(2), *c* = 11.568(2) Å; *V* = 2009.3(6) Å³; *Z* = 6; $\rho_{\text{calc}} = 1.386 \text{ g cm}^{-3}$; *T* = 293(2) K; collected/unique = 11658/3092; *R*₁ = 0.0363, *wR*₂ = 0.1041 (for *I* > 2 θ (*I*)); *R*₁ = 0.0465, *wR*₂ = 0.1077 (for all data) and GOF = 1.050; flack parameter = 0.07(2). CCDC 642658 (**1**) 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.

Thermal analyses were carried out in the temperature range of 25–600 °C by means of a Rigaku standard TG-DTA analyzer in N₂ with an increasing temperature rate of 10 °C/min. An empty Al₂O₃ crucible was used as reference.

Measurements for the gas adsorption isotherms of N₂ (77 K), O₂ (77 K), CO₂ (195 K), C₂H₂ (197 K) and MeOH (298 K) were performed in the gaseous state by using BELSORP18-Plus volumetric adsorption equipment from BEL Japan. Gases are highly pure and a 41.3 mg crystal sample of **1** was used for all the five measurements, time and again.

Acknowledgements

The authors thank Dr. S.R. Batten of Monash University for very helpful discussion on the topological type, and the financial support from NSF of China (nos. 5067304 and 20531040), the 973 Program of China (2007CB815305), and NSF of Tianjin, China (07 J CZDJ C00500).

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Received: September 13, 2007
Published online: January 28, 2008