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Isomeric Zinc(II) Triazolate Frameworks with 3-Connected Networks: Syntheses, Structures, and Sorption Properties

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Two pairs of supramolecular isomers based on ternary zinc(II)/triazolate/X (triazolate = 3,5-dimethyl-1,2,4-triazolate (Hdmtz), X = $HCOO^-$, F^-) metal azolate frameworks, namely, [Zn(dmtz)(HCOO)]·H_2O (MAF-X3, **1a**), [Zn(dmtz)(HCOO)]·(1/6Me_2NH)(1/4H_2O) (MAF-X4, **1b**), [Zn(dmtz)F] (MAF-X5, **2a**), and [Zn(dmtz)F] (MAF-X6, **2b**), have been synthesized via variations of the reaction conditions. The 3-connected Zn(dmtz) networks in **1a**, **1b**, **2a**, and **2b** can be described as rarely observed 4.8^2, 4.12^2, (8,3)-*b*, and 8^2.10-*a*, respectively. Besides the μ_3-dmtz, tetrahedral and trigonal-bipyramidal/square-pyramidal coordination of the Zn ions are accomplished by monodentate formate and μ-F, respectively. While **1a** and **2b** are nonporous structures, **1b** and **2a** exhibits 1D nanotubular hydrophilic (*d* 3.2 Å) and hydrophobic (*d* 3.6 Å) channels, respectively. Thermogravimetric analysis shows that the stabilities of **2a** and **2b** are much better than those of **1a** and **1b**, which may be ascribed to different coordination numbers of zinc atoms. Moreover, **1b** and **2a** with different pore properties show selective sorption behavior.

Introduction

Porous coordination polymers (PCPs) have received great attention recently because of their intriguing molecular topologies and potential applications such as gas storage,[1] separation,[2,3] ion change,[4] catalysis,[5] sensor, and magnetism.[6,7] Thus, extensive studies have been carried out for constructing PCPs with novel topologies, and polycarboxylate and polypyridine ligands are the most extensively exploited ligands.[8] More recently, deprotonated polyazahet-

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erocycles such as pyrazoles, imidazoles, triazoles, and tetrazoles have attracted considerable attention as another type of useful ligands, because many metal azolate frameworks (MAFs) have demonstrated low density, high thermal and chemical stabilities, and interesting luminescent, magnetic, and gas-adsorption properties.[9−13] Despite strong coordination capabilities and simple coordination modes for these ligands, interesting examples of supramolecular isomerism have been also found in the low-connected MAFs such as coinage metal imidazolates, pyrazolates, and triazolates, which provided a rich opportunity for the study of crystal engineering and structure−property relationship of coordination polymers.[9a,10a,b,14]

1,2,4-Triazolate and its derivatives are of particular interest in coordination chemistry, since they are effective bridging ligands combining the coordination modes of both imidazoles and pyrazoles. Moreover, μ_3-bridging triazolates are useful for the construction of 3-connected networks that are regarded as the simplest and most important topologies. Although a variety of 3-connected nets were theoretically predicted for a long time,[15] only a very limited number of these nets, mostly 6^3 and 10^3, have been observed in coordination polymers.[16] Some fascinating neutral 3-connected networks have been constructed by 1:1 combination of the monovalent, three-coordinated coinage metal ions and triazolates.[12a,b] To develop novel 3-connected networks, cationic networks can be constructed by an analogous 1:1 combination of divalent metal ions and triazolates. Compared to the trigonal planar coordination modes of coinage metal ions, divalent metal ions can offer different 3-connected configurations. However, another anion is needed to balance the charge request and form the M(II)/triazolate/X (X = F^-, Cl^-, Br^-, I^-, SO_4^{2-}, N_3^-, SCN^-, etc.) system.[17,18]

As an extension of our investigation on the chemistry of MAFs,[12,14d,e] we have studied the role of counteranion and synthetic condition for the construction of various 3-connected zinc 3,5-dimethyl-1,2,4-triazolate (dmtz) networks. Because common building blocks (such as carboxylate groups, counterions, etc.) tend to expose as hydrophilic sites, hydrophobic PCPs can hardly be rationally designed. The ligand dmtz was chosen to construct hydrophobic PCPs, as its methyl groups provide hydrophobic character, and the hydrophilic site can be excluded after coordination to metal ions. Nevertheless, the third component of the M(II)/triazolate/X system, or the counteranion, must be carefully selected to avoid additional hydrophilic functionality. We anticipated that a small anion with strong coordination ability may attach well to a MAF and be shielded by the hydrophobic pendants, resulting in a final hydrophobic PCP, and vice versa. Therefore, formate and fluoride were selected as the hydrophilic and hydrophobic controllers, respectively. Two pairs of supramolecular isomers, namely, [Zn(dmtz)(HCOO)]·H_2O (MAF-X3, **1a**) and [Zn(dmtz)(HCOO)]·(1/6Me_2NH)(1/4H_2O) (MAF-X4, **1b**), as well as [Zn(dmtz)F] (MAF-X5, **2a**) and [Zn(dmtz)F] (MAF-X6, **2b**), have been synthesized and characterized via X-ray diffraction. Moreover, structure−property relationships of these isomers have been also studied by measurements of the thermal abilities and gas sorption properties.

Experiment Section

Materials and Methods. The ligand Hdmtz was synthesized according to the literature method.[19] Other reagents and solvents were commercially available and were used without further purification. IR spectra were obtained from KBr pellets on a Bruker EQUINOX 55 FT IR spectrometer in the 400−4000 cm^{-1} region. Elemental analyses (C, H, N) were performed with a Vario EL elemental analyzer. The phase-purity and crystallinity of each product were checked by powder X-ray diffraction (PXRD) using a Rigaku D/M-2200T automated diffractometer or on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu Kα, 1.5418 Å). The observed and simulated powder XRD patterns of all compounds are displayed in Figures S1−S4, Supporting Information. Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449C instrument. Each sample was heated from room temperature

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to 800 °C with a heating rate of 10.0 °C/min under dinitrogen atmosphere.

Synthesis of [Zn(dmtz)(HCOO)]·H_2O (MAF-X3, 1a). To a mixture of ZnO (49 mg, 0.6 mmol) and Hdmtz (57 mg, 0.6 mmol) in H_2O (4 mL) was slowly added formic acid (1.2 mmol, 88%) with stirring. The resulting solution was stirred at room temperature for 3 h and then filtered. Colorless block crystals of **1a** were obtained by slow evaporation of the resulting solution (yield 105 mg, 78% on the basis of ZnO. Anal. Calcd (%) for $C_5H_9N_3O_3Zn$: C, 26.75; H, 4.04; N, 18.71. Found: C, 26.73; H, 3.98; N, 18.68. IR (cm^{-1}, KBr): 3570(w), 3495(w), 2934(w), 2876(w), 1614(s), 1522(s), 1419(m), 1377(m), 1322(s), 1143(w), 1038(w), 993(w), 779(m), 701(w), 624(w), 572(w), 418(w).

Synthesis of [Zn(dmtz)(HCOO)]·(1/6Me_2NH)(1/4H_2O) (MAF-X4, 1b). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (178 mg, 0.6 mmol), Hdmtz (58 g, 0.6 mmol), and DMF (*N*,*N*-dimethylformamide, 4 mL) was placed in a Teflon lined stainless steel vessel (12 mL) and heated at 90 °C for 72 h and then cooled to room temperature at a rate of 5 °C/h. Colorless, block crystals of **1b** were collected, washed with DMF, and air-dried (yield 96 mg, 75% based on Hdmtz ligand). Anal. Calcd (%) for $C_{5.33}H_{8.67}N_{3.17}O_{2.25}Zn$: C, 29.31; H, 4.00; N, 20.30. Found: C, 29.56; H, 4.12; N, 19.92. IR (cm^{-1}, KBr): 3456(m, br), 2852(w), 1635(vs,), 1508(s), 1424(s), 1378(m), 1338(s), 991(w), 775(m), 625(w).

Synthesis of [Zn(dmtz)F] (MAF-X5, 2a). A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (119 mg, 0.4 mmol), Hdmtz (39 mg, 0.4 mmol), hydrofluoric acid (0.4 mmol, 47%), and DMF (4 mL) was placed in a Teflon lined stainless steel vessel (12 mL) and heated at 90 °C for 72 h and then cooled to room temperature at a rate of 5 °C/h. Colorless, needle-like crystals of **2a** were collected by filtration, washed with DMF and methanol (v/v 4:4), and dried in air to afford 52 mg (72% based on Hdmtz) of product. Anal. Calcd (%) for $C_4H_6FN_3Zn$: C, 26.62; H, 3.35; N, 23.28. Found: C, 26.58; H, 3.38; N, 23.21. IR (cm^{-1}, KBr): 3028(w), 2929(w), 1509(s), 1417(s), 1379(m), 1335(s), 1087(m), 1046(w), 994(w), 764(m), 703(w), 624(w), 489(m), 411(w).

Synthesis of [Zn(dmtz)F] (MAF-X6, 2b). Method A. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (119 mg, 0.4 mmol), Hdmtz (39 mg, 0.4 mmol), hydrofluoric acid (0.8 mmol, 47%), and DMF (4 mL) was placed in a Teflon lined stainless steel vessel (12 mL) and heated at 90 °C for 72 h and then cooled to room temperature at a rate of 5 °C/h. Colorless, block crystals of **2b** were collected by filtration, washed with DMF and methanol (v/v, 4:4), and dried in air to afford 45 mg (62% based on Hdmtz) of product.

Method B. A mixture of **1b** (85 mg, 0.4 mmol), hydrofluoric acid (0.4−0.8 mmol, 47%), and DMF (4 mL) was placed in a Teflon lined stainless steel vessel (12 mL) and heated at 90 °C for 72 h and then cooled to room temperature at a rate of 5 °C/h. Colorless microcrystals of **2b** were collected by filtration, washed with DMF and methanol (v/v = 4:4), and dried in air to afford 30 mg (42% based on **1b**) of product. PXRD and elemental analyses reveal that the microcrystalline sample has the same structure as that of **2b**. Anal. Calcd (%) for $C_4H_6FN_3Zn$: C, 26.62; H, 3.35; N, 23.28. Found: C, 26.58; H, 3.38; N, 23.21. IR (cm^{-1}, KBr): 2985(w), 2936(m), 1607(w), 1514(s), 1414(s), 1332(s), 1127(m), 1038(m), 990(m), 768(m), 698(m), 616(m), 492(m), 431(s).

Crystal Structure Determination. Diffraction intensities of the four compounds were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using the multiscan program SADABS.[20] The structures were solved with direct methods and refined with a full-matrix least-squares technique with the SHELXTL program package.[21] Anisotropic thermal parameters were applied to all non-hydrogen atoms. All the hydrogen atoms were generated geometrically except for the hydrogen atoms of solvent molecules in **1b**. Crystal data as well as details of data collection and refinements for the complexes are summarized in Table 1.

Table 1. Summary of the Crystal Data and Structure Refinements for **1a**−**2b**

	compound			
	1a	**1b**	**2a**	**2b**
formula	$C_5H_9N_3O_3Zn$	$C_{5.33}H_{8.67}N_{3.17}O_{2.25}Zn$	$C_4H_6FN_3Zn$	$C_4H_6FN_3Zn$
formula weight	224.52	218.55	180.49	180.49
crystal system	monoclinic	trigonal	trigonal	tetragonal
space group	$C2/c$	$R\bar{3}$	$R\bar{3}c$	$I\bar{4}2d$
a (Å)	18.563(2)	20.2484(16)	18.8698(12)	13.5093(12)
b (Å)	9.1869(11)	20.2484(16)	18.8698(12)	13.5093(12)
c (Å)	9.8073(12)	11.3469(17)	9.7902(13)	6.4195(12)
β (deg)	90.048(2)	90	90	90
V (Å^3)	1672.5(4)	4028.9(8)	3019.0(5)	1171.6(3)
Z	8	18	18	8
D_c (g cm^{-3})	1.783	1.609	1.787	2.047
μ (mm^{-1})	2.908	2.708	3.589	4.111
GOF	1.097	1.110	1.136	0.982
$R_1{}^a$ [$I > 2\sigma(I)$]	0.0415	0.0606	0.0269	0.0323
$wR_2{}^a$ [all data]	0.1109	0.1514	0.0691	0.0788

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

Gas Sorption Measurements. The sorption isotherms for N_2 and CO_2 gas at 77 and 195 K were measured with an automatic volumetric sorption apparatus (BELSORP-max, Bel Japan). Before gas sorption experiments, the as-synthesized samples of **1a** and **1b** were placed in the quartz tubes and dried under high vacuum at 180 °C for 12 h to remove the remnant solvent molecules prior to measurements.

Results and Discussion

Synthesis. As far as we know, the ternary M(II)/triazolate/X frameworks (X = F^-, Cl^-, Br^-, I^-, $SO_4{}^{2-}$, $N_3{}^-$, SCN^-, etc.) were usually synthesized by slow evaporation or under hydrothermal conditions,[16] and only two examples of ternary triazolate framework [Zn(atz)(OAc)] (Hatz = 3-amino-1,2,4-triazole) synthesized by using DMF as the solvent have been reported up to date.[22c,e] In this work, **1b**, **2a**, and **2b** were obtained under solvothermal conditions by using DMF as solvent, and only **1a** was obtained by the conventional evaporation method by using water as solvent. It is noteworthy that the formate anions in **1b** were generated from in situ hydrolysis of DMF. This phenomenon with in situ hydrolysis of DMF is always found in the solvothermal

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conditions.[22e,23] To explain the formation mechanism for isomers **1a** and **1b**, we have tried but failed to synthesize **1b** in aqueous solution by direct reactions of $Zn(NO_3)_2$, Hdmtz ligands, HCOONa (or formic acid), and Me_2NH at the various conditions. These facts indicate that the syntheses of isomers **1a** and **1b** were dependent on not only the solvent but also Me_2NH. Upon addition of HF to the reaction system of **1b** at the same condition, needle-like crystals of **2a** and block-shaped crystals of **2b** can be obtained via precise control of the addition amount of HF with 1 and 2 equiv, respectively. These results indicate that fluoride is of much stronger coordination ability than that of formate, and the concentration of HF greatly influences the formation of isomers **2a** and **2b**, which is a unique case of concentration-induced isomerism. Furthermore, when **1b** was used as the starting material to react with HF in DMF, the single-phase product of **2b** was obtained. This fact further indicates that fluoride ion has stronger coordination ability than formate, leading to the transformation of **1b** into **2b**. In other words, **2b** is a thermodynamic product and is much more stable than **1b**.

Crystal Structures. Single-crystal X-ray structural analysis indicates that all the zinc atoms in **1a** adopt tetrahedral coordination geometry constructed by an oxygen atom from a formate and three nitrogen atoms from three dmtz ligands (Figure S5 in the Supporting Information). The formate only acts as an auxiliary ligand in a monodentate coordination mode (Zn−O 1.919(3) Å), while each dmtz ligand adopts μ_3-bridging mode to connect three zinc(II) ions (Zn−N 1.996(3)−2.032(3) Å), which generates a 2D layered structure (Figure 1a). Although the solvent-accessible volume of **1a** is about 14.4% of the total crystal volume,[24] the aperture is too small for any gas molecule to go through it (1.2 Å). The layered structure of **1a** can be rationalized as a 3-connected 4.8^2 topological network (Figure 1b) when Zn and dmtz are regarded as two kinds of 3-connected nodes. If the dinuclear $[Zn_2(dmtz)_2]$ subunit is further simplified as a square-planar 4-connected node, **1a** has a simple (4, 4) topological network. It should be pointed out that **1a** displays a network similar to those of other reported divalent metal frameworks,[22] as well as those of the 2D layers of Ag(I) and Cu(I) salts of unsubstituted 1,2,4-triazolate.[12b] Although a few M(II)/triazolate/X frameworks have been reported,[16] organic alkyl monocarboxylate anions have been rarely used as the auxiliary ligands.[22b−d] In contrast, dicarboxylate were used as coligands to construct 3D pillared-layer structures of M(II)/triazolate/X frameworks.[25]

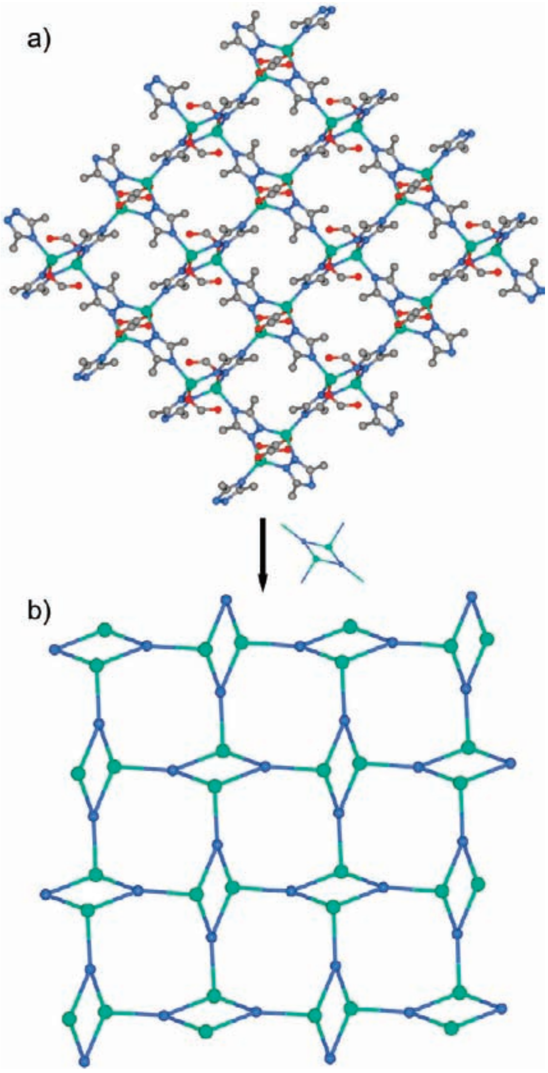

Figure 1. Two-dimensional network (a) and its 4.8^2 topological net (b) of **1a**. All hydrogen atoms are omitted for clarity.

Being similar to **1a**, the zinc atoms in **1b** also adopt tetrahedral coordination environments that are surrounded by three nitrogen atoms from three dmtz ligands (Zn−N 2.012(4)−2.035(4) Å) and one oxygen atom from the disordered, monodentate formate (Zn−O 1.92(2)−1.94(2) Å) (Figure 2a). As shown in Figure 2b, each dmtz ligand also adopts μ_3-bridging mode but propagates the structure into a 3D framework with 1D channels. The disordered formate ligand protrudes into these channels, reducing the effective pore diameter to 3.2 Å (after considering van der Waals radii) with hydrophilic pore surfaces (Figure 2c). The cavity volume is estimated to be approximately 20.9% of the total crystal volume.[24] When both Zn and dmtz are regarded as 3-connected nodes, the 3D structure of **1b** can be rationalized as a 3-connected 4.12^2 topological network (Figure 2d). By further denoting dinuclear $[Zn_2(dmtz)_2]$ subunits as a square-

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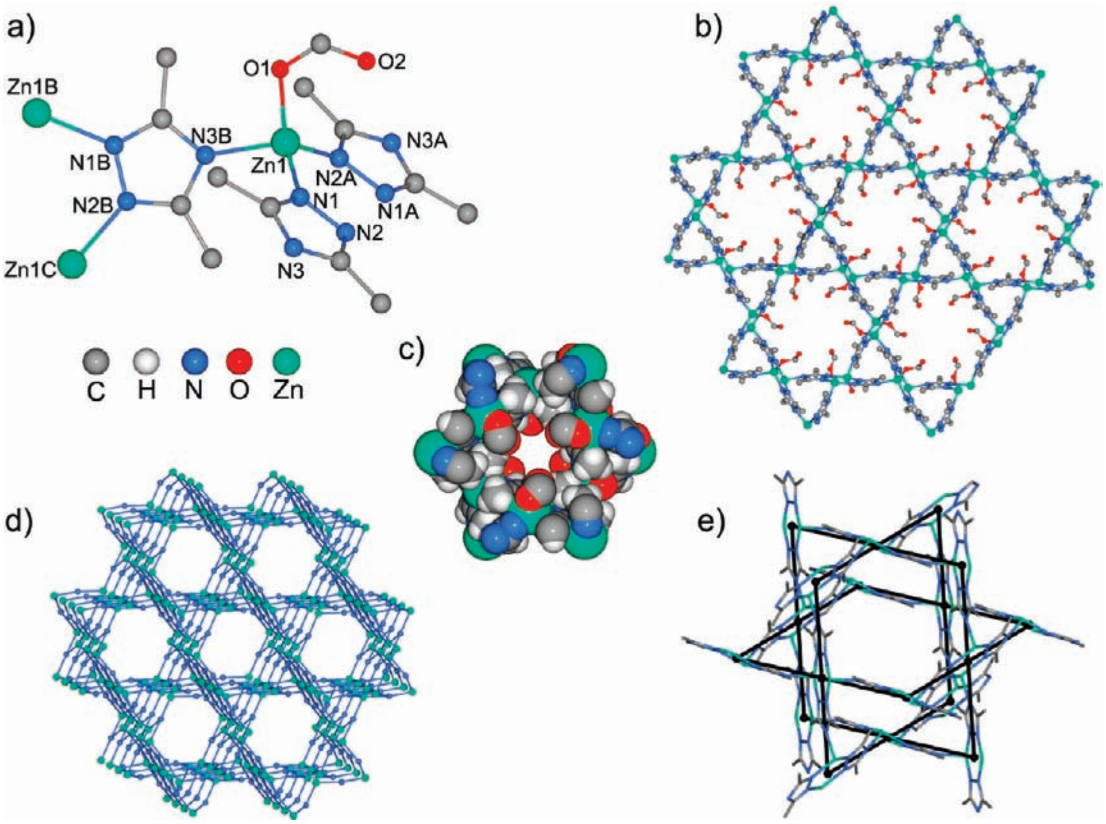

Figure 2. (a) View of the coordination environment of the zinc atoms in **1b**. Symmetric codes: A, $-x + 1$, $-y + 1$, $-z$; B, $2/3 - x + y$, $4/3 - x$, $1/3 + z$; C, $2/3 + x - y$, $1/3 + x$, $1/3 - z$. (b) View of the 3D network of **1b** along the *c*-axis. (c) Space filling diagram of a single tube in **1b**. (d) The 4.12^2 net. (e) Each NbO cage in **1b**. The formate anions are omitted in (e), and the hydrogen atoms are omitted for clarity in (a−c).

planar 4-connected node, this framework can be simplified into a NbO ($6^4.8^2$) net (Figure 2e). **1b** also represents rare examples of the microporous triazolate frameworks.[12b−e] Furthermore, solvent-dependent isomers **1a** and **1b** show extremely rare examples of (4,4)-grid and NbO-net isomers.[26]

As shown in Figure 3a, the zinc atom of **2a** shows a distorted trigonal-bipyramidal geometry (trigonality index $\tau = 0.89$),[27] being coordinated by three nitrogen atoms from three different dmtz ligands (Zn−N 2.035(3)−2.100(2) Å) and two μ-F$^-$ anions (Zn−F 1.9992(9) Å). The framework of **2a** is propagated by the μ_3-dmtz ligands and μ-F$^-$ anions into a 3D framework containing large hexagonal channels with an effective pore diameter of 3.6 Å (Figure 3b). As shown in Figure 3c, the methyl groups protrude into these channels, reducing their effective diameter and making hydrophobic pore surfaces. Moreover, the fluorides are shielded by two adjacent methyl groups with C−H···F hydrogen bonds (C···F 2.98 Å, H···F 2.20 Å, C−H···F 137.1°), ensuring the totally hydrophobic pore surfaces. The solvent-accessible volume is approximately 17.0% of the total crystal volume.[24] The crystal structure of **2a** is isostructural to the previously reported, hydrophilic Zn/triazolate/fluoride structures[28] constructed by simple 1,2,4-triazolate. While hydrophilic adsorbents are relatively common, the hydrophobic channels of **2a** are more interesting for potential separation applications. For example, Li et al. reported the hydrophobic framework [Zn(tbip)] (H_2tbip = 5-*tert*-butyl isophthalic acid) with guest-free channels and high thermal stability showing a unique capability for separation of dimethyl ether from methanol.[29] As an indication, no guest molecule is found in the small channel of **2a**. From the topological point of view, the Zn(dmtz) network can be defined as a 3-connected (8,3)-*b* net (long Schläfli symbol $8.8.8_2$) (Figures 3e,f). To the best of our knowledge, 3D 3-connected uniform 8^3 nets are still rarely documented compared to other uniform 3-connected nets such as 6^3 and various 10^3,[30] and only three coordination polymers has been reported to feature the (8,3)-*b* net.[30a−c]

2b is a genuine supramolecular isomer of **2a**, because both compounds have the same molecular formulas but different

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(27) The trigonallity index τ ($\tau = 0$ denotes ideal square pyramidal; $\tau = 1$ denotes ideal trigonal bipyramidal) was calculated according to the literature. See Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

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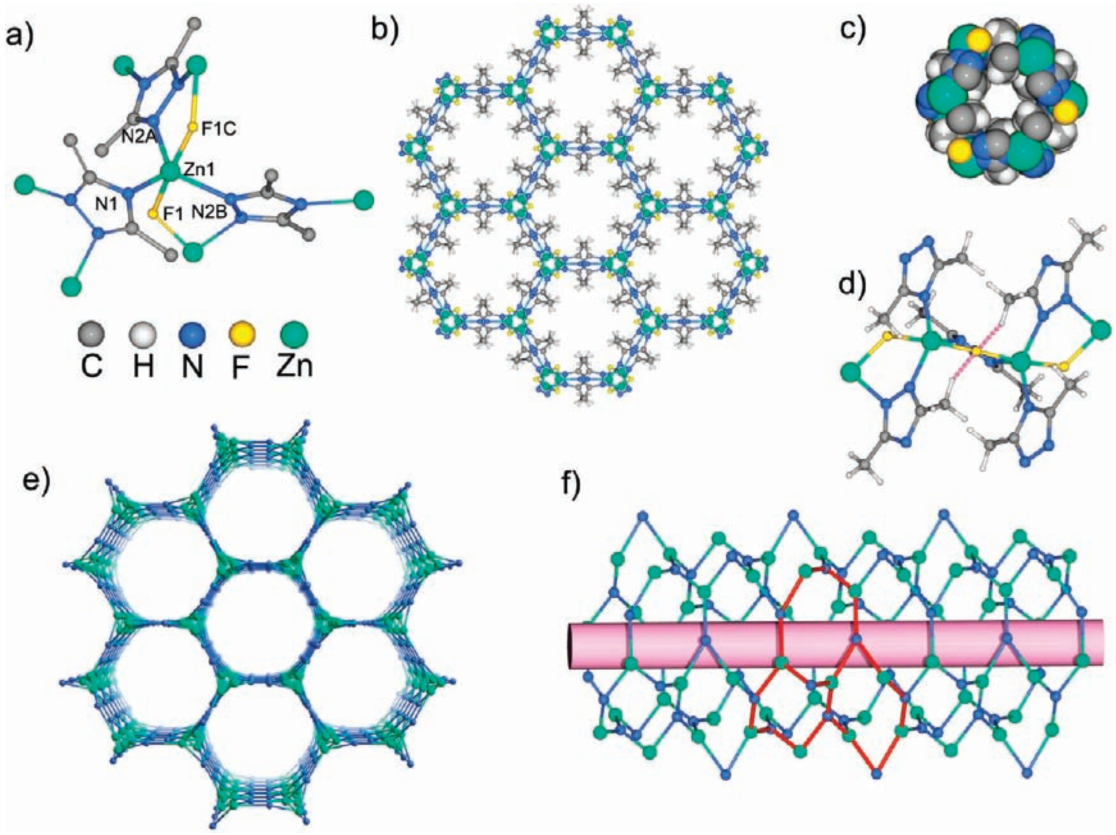

Figure 3. (a) Coordination environment of the zinc atoms in **2a**. Symmetric codes: A, $-x-y+1$, $y+1$, $-z$; B, $1/3+x$, $5/3+x-y$, $1/6+z$; C, $4/3-y$, $7/6+x-y$, $z-5/6$. (b) View of the 3D network of **2a** along the *c*-axis. (c) Space filling view along the hexagonal windows in **2a**. (d) Illustration of the C−H···F hydrogen bonds. (e) The 8^3-*b* topological network. (f) The sideview of topology with each tube showing the shortest circuits of 8-gons. The hydrogen atoms are omitted for clarity in (a) and (c).

structures. As shown in Figure 4a, the zinc atom in **2b** is also five coordinated, but in a highly distorted square-pyramidal geometry (trigonality index $\tau = 0.38$) constructed by three nitrogen atoms from μ_3-dmtz ligands (Zn−N 2.040(4)−2.122(3) Å) and two μ-F$^-$ atoms (Zn−F 1.9672(14) Å). Each pyramidal base is defined by two μ-F$^-$ atoms (F1 and F1C) and two nitrogen atoms (N2A, N2B) from μ_3-dmtz ligands, and the apical site is occupied by one nitrogen atom (N1) from a dmtz ligand. Similar to **2a**, each fluoride is shielded by two adjacent methyl groups with weak C−H···F hydrogen bonds (C···F 3.17 Å, H···F 2.39 Å, C−H···F 137.5°). **2b** also exhibits a 3D framework bridged by μ_3-dmtz ligands and μ-F$^-$ atoms (Figure 4b), and the methyl groups protrude into the small channels constructed by $Zn_4(dmtz)_4$ units, making **2b** a dense structure. The Zn(dmtz) network of **2b** can be simplified as a 3-connected $8^2.10$-*a* net (long Schläfli symbol $8.8.10_3$) (Figure 4c). Although a lot of supramolecular isomers have been reported, porous **2a** and nonporous **2b** represent a rare example of genuine 3D supramolecular isomers.[9a,31] Furthermore, they also represent rare examples of 3-connected networks different from other 3-connected nets such as planar 6^3 nets and various 10^3 nets.[30]

Thermal Stability. Isomers of **1** possess different thermal stabilities from those of **2**, respectively. TGA (Figure 5) of **1a** shows a steady weight loss of water molecules below 150 °C (observed, 7.9%; calculated, 8.0%) and no further weight loss below 220 °C until decomposition. However, the desolvated **1a** shows a totally different PXRD pattern, and most peaks are significantly shifted to higher 2θ angles, indicating the formation of a dense structure. TGA of **1b** shows a weight loss of 3.4% from 30 to 140 °C. There is no further weight loss below 220 °C until decomposition. The variable temperature PXRD analysis reveals that the diffraction pattern was virtually unchanged to 240 °C, indicating that the framework of **1b** is retained below 240 °C (Figure S9 in the Supporting Information). Both **2a** and **2b** are stable up to 400 °C and thus are much more stable than **1a** and **1b**. The variable temperature PXRD analysis also reveals that porous **2a** can be retained up to 400 °C. Furthermore, TGA of the porous framework of **2a** shows no weight loss between 25 to 400 °C, suggesting no solvent guest in **2a**, which is consistent with the single-crystal X-ray diffraction analysis. The distinctly different thermal stabilities between **1** and **2** might be explained by the coordination difference of the zinc atoms, in which five-coordination and strongly coordinated fluoride ions enhance the framework stabilities of **2**.

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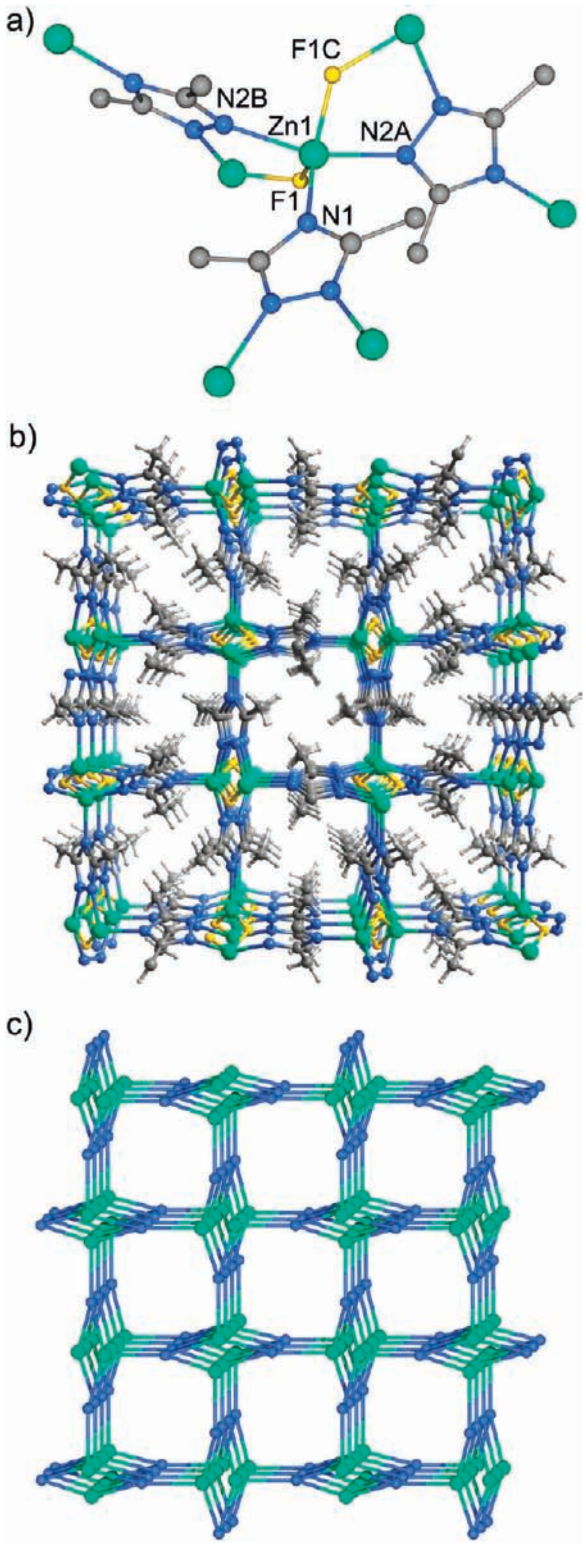

Figure 4. (a) Coordination environment of the zinc atoms in **2b**. The hydrogen atoms are omitted for clarity. Symmetric codes: A: 1/2 − *y*, *x* − 1/2, 1/2 − *z*; B: 1/2 − *y*, −*x* + 1, *z* − 1/4; C: 1/2 − *x*, 1/2 − *y*, 1/2 + *z*. (b) 3D network of **2b** view along the *c*-axis. (c) $(8^2.10)$-*a* net of **2b**. Color codes: Zn, green; N, blue; C, gray; F, yellow.

Sorption Properties. The separation and purification of small gas molecules such as H_2/N_2, H_2/CO, and CO_2/CH_4 using microporous coordination polymers have attracted considerable attention,[32] since such separation is more economical, and shows a technical innovation toward the breakthrough of traditional industrial technique. Up to now, most reported PCPs with the small pores usually feature selective capture of CO_2 over N_2.[32b−f,33] Besides the size-exclusive effects,[32b,c] the polarizabilities of gas molecules or the polarities of frameworks also affect the amount of adsorption, especially for CO_2,[34] since it is also known that CO_2 has a significant quadrupole moment that induced specific interactions with adsorbents.[34b,c] Such reasons seem to make PCPs with small pores always show special capture of CO_2 over N_2.

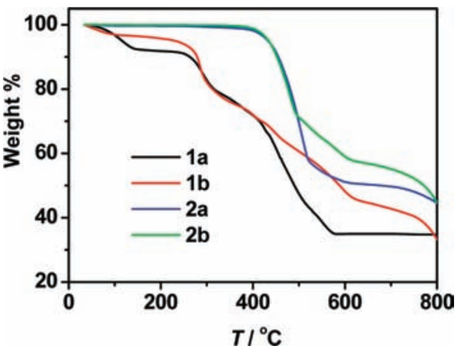

Figure 5. TG curves of the isomers **1** and **2** in N_2.

To confirm the structure-dependent porous properties, gas sorption experiments were carried out for CO_2 and N_2. Preliminary sorption studies showed that activated **1a** and **2b** do not exhibit porosity, confirming their nonporous structures. Although **1b** possesses a very small effective channel diameter (3.2 Å), the desolvated **1b** can absorb CO_2 instead of N_2 at their corresponding boiling points (Figure 6). The adsorption isotherm of CO_2 at 195 K displays a steep rise at the low relative pressure region, and the isotherm can be categorized as type I, indicating a typical physisorption process of a microporous material. The Langmuir and BET surface areas estimated from the CO_2 sorption isotherm are 440 and 280 $m^2\ g^{-1}$, respectively. The adsorption amount at 1 atm (80 mL/g) corresponds to 0.74 CO_2 molecules per formula unit, or 4.4 CO_2 molecules per NbO pore. To explain the CO_2 and N_2 sorption behaviors, PXRD patterns of as-synthesized and desolvated **1b** are compared. Most peaks of desolvated **1b** are slightly shifted to higher 2θ angles (Figure S12 in the Supporting Information), implying that the structure was slightly shrunk after removal of the guests.

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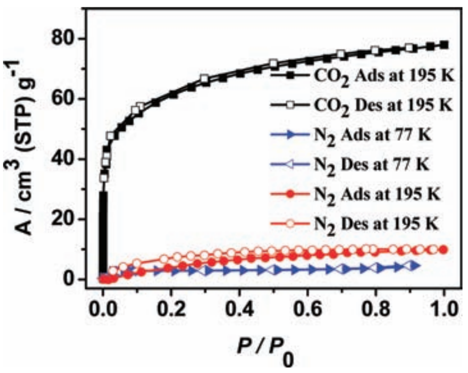

Figure 6. Gas sorption isotherms of desolvated **1b**.

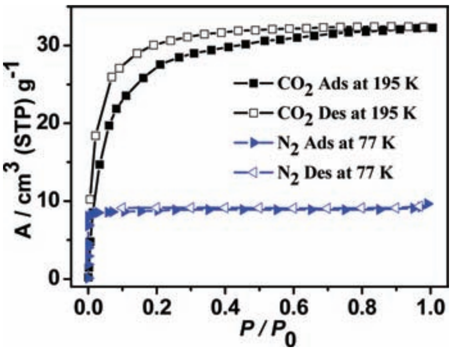

Figure 7. Gas sorption isotherms of **2a**.

Such structural contraction may reduce the effective pore opening of desolvated **1b**. Since the effective pore diameter of as-synthesized **1b** (3.2 Å) is very close to the kinetic diameter of CO_2 (3.3 Å) and significantly smaller than that of N_2 (3.64 Å), the selective adsorption behaviors of CO_2 over N_2 are ascribed to the size-controlled effect. Besides, the larger polarizability and quadrupole moment of CO_2 interact better with the hydrophilic pore surface, making a further contribution to the potential energy of adsorption. It is worth mentioning that the aperture size is controlled by the flexible (disordered), monodentate formate groups. The N_2 adsorption at 195 K (Langmuir surface area: 67 $m^2\ g^{-1}$) is significantly higher than that observed at 77 K (Langmuir surface area: 13 $m^2\ g^{-1}$), confirming the flexibility of the apertures. Such a phenomenon with adjustable aperture size brought by flexible pendant groups has been rarely reported.[12e]

The CO_2 sorption of **2a** (Figure 7) also revealed a type I behavior typical for microporous materials with a small hysteresis between sorption/desorption curves. The Langmuir and BET surface areas of **2a** are calculated to be 195 and 155 $m^2\ g^{-1}$, respectively. At a pressure of 1 atm, approximately 0.26 CO_2 molecules per formula unit or 1.56 CO_2 molecules per unit pore were adsorbed. As the length of a unit pore (9.79 Å) is shorter than twice that of a CO_2 molecule (2 × 5.4 Å), the adsorption amount indicates a nonstoichiometric pore-filling mechanism. Being different from hydrophilic **1b**, the hydrophobic **2a** can adsorb a small amount of N_2 at 77 K. The adsorption amount at 1 atm corresponds to 0.08 N_2 molecules per formula unit or 0.48 N_2 molecules per unit pore. While the CO_2 uptake at 195 K near $P/P_0 = 1$ is close to saturation, N_2 uptake at 77 K near $P/P_0 = 1$ is much less than expected since the N_2 isotherm is obvious microporous adsorption rather than particle surface adsorption. Theoretically, the saturation uptakes of N_2 and CO_2 should be comparable since their molecular dimensions are similar (N_2 3.1 × 3.0 × 4.0 Å^3, CO_2 3.3 × 3.2 × 5.4 Å^3),[35] and the framework of **2a** only shows one type of uniform pore. Such special sorption phenomena have been scarcely reported to date.[33b] The unconventional sorption behaviors may be ascribed to the formation of different guest-dependent sorption states or temperature-dependent adsorbent structures instead of simple pore filling. To corroborate these hypotheses, structural studies of the sorption complexes should be carried out.

Conclusions

In summary, isomeric triazolate frameworks with the formula Zn/triazolate/X (X = $HCOO^-$ (**1**), F^- (**2**)) have been constructed by using 3-connected divalent zinc ions and dmtz ligands, as well as formate or fluoride anions as the auxiliary ligands. The topologies of isomers **1** and **2** can be described as a serial of uniform 3-connected nets including 4.8^2 (**1a**), 4.12^2 (**1b**), 8^3-*b* (**2a**), and $(8^2.10)$-*a* (**2b**). Moreover, the isomers of **1a** and **1b** can be further simplified as 4-connected 4^4 and NbO topologies, respectively. Thermoanalysis reveals that tetrahedrally coordinated zinc atoms with formate anion as the auxiliary ligands have lower thermal stabilities than five-coordinated zinc atoms with fluoride atoms as the apical or auxiliary ligands. Gas sorption studies show that the porous frameworks of **1b** and **2a** display selective adsorption of CO_2 over N_2. Such selective gas sorption behaviors are mainly based on size-selective effects.

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Supporting Information Available: The TGA curves, PXRD, and additional structural plot, as well as X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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