Hydrothermal Synthesis and Structural Characterization of Novel Zn−Triazole−Benzenedicarboxylate Frameworks

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Three new metal−organic coordination polymers were synthesized hydrothermally using Zn^{2+} ion, 1,2,4-triazole, and 1,4-benzenedicarboxylic acid (BDC): $Zn_5(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_3 \cdot 3.9H_2O$ (**1**), $Zn_2(C_2H_2N_3)_2(C_2H_3N_3)(C_8H_4O_4) \cdot 2.5H_2O$ (**2**), and $Zn_4(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_2 \cdot 14H_2O$ (**3**). Their crystal structures were determined by single-crystal X-ray diffraction. Their thermal properties were examined by thermogravimetric analysis. Structure **1** crystallizes in the monoclinic $P2_1/n$ space group with $a = 10.192(2)$ Å, $b = 17.764(4)$ Å, $c = 24.437(5)$ Å, $\beta = 91.19(3)°$, and $V = 4423.3(15)$ Å^3. Structure **2** crystallizes in the triclinic $P\bar{1}$ space group with $a = 7.797(2)$ Å, $b = 10.047(2)$ Å, $c = 13.577(3)$ Å, $\alpha = 110.18(3)°$, $\beta = 105.46(3)°$, $\gamma = 93.90(3)°$, and $V = 947.0(3)$ Å^3. Structure **3** crystallizes in monoclinic $P2_1/n$ space group with $a = 13.475(3)$ Å, $b = 26.949(5)$ Å, $c = 13.509(3)$ Å, $\beta = 95.18(3)°$, and $V = 4885.7(17)$ Å^3. In structure **1**, the units of the triazole−Zn polyhedra are linked by BDC in a zigzag fashion to create the stacking of phenyl groups along the *a* axis. In structure **2**, both triazole and BDC bridge Zn polyhedra in the (011) plane, resulting in the eight-membered channels along the *a* axis. In the case of structure **3**, the BDC links the Zn polyhedra along the *b* axis to form a pillared open framework. This structure is the most porous of the compounds presented in this work.

Introduction

The design and synthesis of metal−organic hybrid frameworks (MOFs) have been flourishing in the recent years.[1−6] These materials are coordination polymers, which are built from metal ions and rigid organic bridging ligands. Metal ions can be found as isolated clusters or chains which are connected to each other by the linkers. Organic ligands are often carboxylates or N-donor ligands, such as amines or pyridines, which contain a number of different connection modes. One of the most popular choices of the ligand is 1,4-benzenedicarboxylic acid (BDC) because its dicarboxyl groups manifest various bonding modes and its phenyl ring provides structural rigidity.[7−13] MOFs often contain large pores or channels which can give rise to interesting physical properties. For example, MOFs are investigated for potential applications in gas storage,[8,12−15] ion exchange,[16,17] and catalysis.[18,19] In particular, much attention has been paid to the development of efficient hydrogen sorption materials.[8,15,20−22] Férey and co-workers have recently developed new strategies to design materials with very large pores by combining controlled chemical synthesis and computer simulations.[23−26]

In some cases of MOFs, more than one type of ligand is applied to build a framework to expand the structural diversity as well as to enhance physical properties.[12,13,27,28]

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In the recent work by Kim and co-workers, a number of Zn-based MOFs have been prepared using both aromatic dicarboxylates and diamines as ligands.[13,27] These frameworks have been also studied for their gas sorption properties.

In an effort to discover new materials with interesting three-dimensional topologies and physical properties, we have synthesized new MOFs using Zn^{2+} ion as a metal center and 1,2,4-triazole and BDC as ligands under hydrothermal conditions. In this report, we present the synthesis, thermogravimetric analysis (TGA), and structure determination of three novel Zn−triazole−BDC frameworks, namely, $Zn_5(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_3\cdot 3.9H_2O$, $Zn_2(C_2H_2N_3)_2(C_2H_3N_3)(C_8H_4O_4)\cdot 2H_2O$, and $Zn_4(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_2\cdot 14H_2O$. These materials represent new MOF structure types which are built from isolated metal polyhedra with two different organic linkers.

Experimental Section

Synthesis. All compounds were synthesized under mild hydrothermal conditions using Teflon-lined 23-mL Parr autoclaves. Starting materials include zinc nitrate hexahydrate ($Zn(NO_3)_2\cdot 6H_2O$, 99%, Alfa-Aesar), 1,2,4-triazole ($C_2H_3N_3$, 99%, Alfa-Aesar), BDC (98%, Sigma-Aldrich), triethyleneamine (TEA, 99%, Sigma-Aldrich), 1-butanol (99.9%, Sigma-Aldrich), and deionized water. All reaction mixtures were stirred for 1 h to ensure homogeneity prior to heating. The reactants were heated at 150 °C for 3 days. After reaction, products were filtered, washed with deionized water, and dried in air.

*Structure **1***. For the synthesis of $Zn_5(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_3\cdot 3.9H_2O$, 0.07 g of triazole, 0.17 g of BDC, 0.60 g of $Zn(NO_3)_2\cdot 6H_2O$, 0.10 g of TEA, and 3.60 g of H_2O were added. The reaction mixture had a molar composition of 2:1:1:1:200 Zn/triazole/BDC/TEA/H_2O. The pH of the reactants was 3.1. The resulting products after heating were colorless, transparent needles (∼0.15 × 0.06 × 0.06 mm).

*Structure **2***. In a typical synthesis, 0.14 g of triazole, 0.17 g of BDC, 0.22 g of $Zn(NO_2)_2\cdot 6H_2O$, 0.10 g of TEA, and 3.60 g of water were sequentially added. The molar composition of the reaction mixture corresponded to 1:2:1:1:200 Zn/triazole/BDC/TEA/H_2O. The pH of the mixture was 4.3. After reaction, the resulting products were thin colorless rhombic plates (∼0.05 × 0.05 × 0.03 mm) and a small amount of white powders.

*Structure **3***. For the synthesis of $Zn_4(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_2\cdot 14H_2O$, 0.14 g of triazole, 0.60 g of $Zn(NO_2)_2\cdot 6H_2O$, 0.17 g of BDC, 1.80 g of water, and 2.22 g of butanol were added, resulting a molar ratio of 2:2:1:100:30 Zn/triazole/BDC/H_2O/BuOH. The pH of the solution was 2.3. After synthesis, the products consisted of small, colorless, transparent prisms (∼0.08 × 0.05 × 0.05 mm) and pale yellow powders.

Crystal Structure Determination. A suitable crystal from each compound was selected using a polarizing optical microscope and was glued to the tip of a glass fiber. The raw intensity data were collected and integrated with software packages SMART[29] and SAINT,[30] and then an empirical absorption correction was applied using SADABS.[31] The crystal structures were solved via direct method and refined assuming anisotropical displacement parameters for all non-hydrogen atoms with SHEXLTL.[32] Zinc atoms were located first, and the remaining atoms (O, C, N) were found from subsequent Fourier difference map synthesis. The hydrogen atoms were added using geometrical constraints (HFIX command). The details of the crystal structures are given in Table 1. Selected bond distances are shown in Tables 2−4.

*Structure **1***. Data collection was performed on a Bruker four-circle P4 single-crystal diffractometer equipped with a 1K charge-coupled device (CCD) detector using Mo Kα radiation. The data were collected at room temperature with an exposure time of 30 s per frame with a detector distance of 5.016 cm. A hemisphere of data were collected with a step width of 0.3° in ϕ and ω. The unit cell constants were calculated and refined from all the intensities $I > 15\sigma(I)$.

*Structures **2** and **3***. The small size of the crystals did not permit the structure characterization using an in-house diffractometer. Data collection and structure determination were carried out at 15-ID ChemMatCARS beamline equipped with a Bruker 6000 CCD detector at Advanced Photon Source, Argonne National Laboratory. The data were collected at 100 K with wavelength of 0.4859 Å, an exposure time of 1 s per frame, and a detector distance of 5.0 cm. A randomly oriented region of reciprocal spaces was examined to a resolution of 0.75 Å. Two major sections of frames were collected with a step size of 0.30° in ω and ϕ. The final unit cell parameters were determined from 1024 strong reflections after integration. For structure **2**, additional symmetry elements were detected when PLATON [33] software was applied to the final refinement results. However, the structure determination based on the suggested $C2/c$ space group was not successful, leading to very poor convergence with high R_{sym} after integration. Large anisotopic displacement parameters (O atoms connecting Zn to the carboxylic groups) were also present in this refinement. It is clear the $P\bar{1}$ structure is derived from distortion of Zn1 atoms.

Thermal Analysis. TGA of each compound was performed using a Netzsch STA 449C instrument. Each sample was heated from room temperature to 750 or 800 °C in air with a heating rate of 5.0 °C/min.

*Structure **1***. The TGA curve in Figure 1a displays two events between 25 and 750 °C. The first event before 200 °C corresponded to the loss of water molecules (observed, 9.8%; calculated, 8.9%). The structure is stable up to 400 °C. The second event occurred at 410−510 °C where the organic linkers got destroyed (observed, 68.2%; calculated, 66.0%). The absence of the peaks from the powder diffraction pattern suggests that the product after heating was amorphous ZnO.

*Structure **2***. The TGA curve in Figure 1b shows that water molecules were first removed between room temperature and 200 °C (observed, 7.9%; calculated, 6.7%). Unlike the other two structures, once water was removed the framework quickly lost organic components up to 600 °C (observed weight loss, 69.6%; calculated, 69.6%).

*Structure **3***. The TGA curve between 25 and 800 °C is shown in Figure 1c. Water molecules were lost in two steps. About 2.5 mol of water was removed before 120 °C (weight loss, 4.1%), and then the rest of water was lost by 300 °C (observed, 23.7%; calculated, 25.0%). The compound retained its framework up to 380 °C. The organic linkers decomposed progressively between 400 and 600 °C, leaving amorphous ZnO as a final product (observed, 72.5%; calculated, 71.7%).

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Table 1. Crystallographic Data and Structure Refinement Results

	structure **1**	structure **2**	structure **3**
empirical formula	$C_{32}H_{31.8}N_{12}O_{17.9}Zn_5$	$C_{14}H_{15}N_6O_6Zn_2$	$C_{24}H_{48}N_{12}O_{24}Zn_4$
formula weight	1179.79	536.12	1150.34
collection temp (K)	298(2)	100(2)	100(2)
wavelength (Å)	0.710 73	0.485 95	0.485 95
space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
unit cell dimensions (Å, deg)	$a = 10.192(2)$ $b = 17.764(4)$ $c = 24.437(5)$ $\beta = 91.19(3)$	$a = 7.797(2)$ $b = 10.047(2)$ $c = 13.577(3)$ $\alpha = 110.18(3)$ $\beta = 105.46(3)$ $\gamma = 93.90(3)$	$a = 13.475(3)$ $b = 26.949(5)$ $c = 13.509(3)$ $\beta = 95.18(3)$
volume (Å^3)	4423.3(15)	946.9(3)	4885.7(17)
Z, calcd density (g/cm^3)	4, 1.829	2, 1.880	4, 1.502
absorption coefficient (mm^{-1})	2.764	1.366	0.695
$F(000)$	2408	540	2224
crystal size	0.15 × 0.08 × 0.05	0.05 × 0.05 × 0.03	0.08 × 0.04 × 0.04
θ range for data collection (deg)	1.42−27.10	1.15−17.68	1.04−18.90
index ranges	$-13 \le h \le 11$ $-22 \le k \le 22$ $-31 \le l \le 31$	$-9 \le h \le 9$ $-12 \le k \le 12$ $-16 \le l \le 16$	$-17 \le h \le 17$ $-35 \le k \le 35$ $-15 \le l \le 17$
total reflections	30 402	13 576	58 522
independent reflections	9652 [R(int) = 0.0446]	3870 [R(int) = 0.0297]	11 818 [R(int) = 0.0582]
completeness to θ (%)	98.9	99.8	97.6
absorption correction	SADABS	SADABS	SADABS
max, min transmission	0.867, 0.647	0.921, 0.827	0.973, 0.946
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	9652/0/623	3870/0/283	11 818/0/578
goodness of fit	1.053	1.146	1.036
final R [$I > 2\sigma(I)$]	R1 = 0.0496 wR2 = 0.1309	R1 = 0.0345 wR2 = 0.0926	R1 = 0.0575 wR2 = 0.1483
R (all data)	R1 = 0.0754 wR2 = 0.1562	R1 = 0.0361 wR2 = 0.0934	R1 = 0.0633 wR2 = 0.1524
largest difference peak and hole (e·Å^{-3})	2.391 and −0.799	1.353 and −0.877	1.88 and −1.42

Results and Discussion

All three compounds were synthesized hydrothermally in the form of single crystals. In each reaction, TEA was added as a mineralizer. Structures **1** and **2** were prepared with pure water while structure **3** was obtained using a mixture of water and 1-butanol. Attempts to synthesize structure **3** using pure water were not successful; light gray powders and a small amount of poor quality crystals were obtained when only water was used as a solvent. Small changes in molar ratio of zinc to organic linkers in the reactants led to different topologies of the frameworks and stoichiometry of the final products. For example, structure **2**, synthesized from a Zn-to-ligands ratio of 1:3, shows the highest density with a Zn/ligand ratio of 1:2. Structures **1** and **3** contain less organic components with Zn-to-ligand ratios of 1:1.4 and 1:1.5, respectively.

*Description of Structure **1***. The crystal structure of $Zn_5(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_3\cdot 3.9H_2O$ is described in Figures 2−4. Zn polyhedra and organic linkers are connected through corners to form a dense, complex three-dimensional framework. There are five crystallographically independent Zn atoms which are bonded to N atoms from triazole and O atoms from BDC as well as water. They lie in tetrahedral and octahedral coordination environments. The Zn−O and Zn−N bond distances are consistent with the previously reported values,[10,27] ranging from 1.94 to 2.18 Å and from 1.99 to 2.20 Å for Zn−O and Zn−N, respectively (see Table 2). The bond valence sums[34] around Zn atoms are consistent with the oxidation state of Zn^{2+}, ranging from 1.95 to 2.10. The structure is built on the clusters of isolated Zn polyhedra, which are linked by triazoles (Figure 3). Each cluster contains two zigzag chains made up of Zn tetrahedra and triazoles along the (100) direction. The chains are further connected to one another through triazole and Zn3 octahedra, effectively forming eight-membered rings of 7.2 × 4.0 Å^2 in free dimension, based on the distances between Zn atoms. Two neighboring moieties are linked by BDC anions in the *bc* plane. Along the *c* axis, each BDC ligand acts as a tridentate ligand by linking a Zn tetrahedron from one moiety to Zn octahedron and tetrahedron from the other group. However, the BDC along the *b* axis behaves as a bis-monodentate ligand because only one O atom from each CO_2 group is bonded to Zn. Along the *a* axis, the phenyl rings are stacked within a distance of 3.8 Å, which induces a significant $\pi-\pi$ interaction.[35] As seen in Figure 4, because the moieties of Zn polyhedra occur in a zigzag fashion, the porosity is greatly reduced, resulting in a relatively dense structure. Sites partially occupied by water molecules are located in the cavities between two Zn polyhedra moieties and near the carboxylates. Hydrogen bonding interactions are present between water and uncoordinated oxygens from carboxyl groups. ($O_w\cdots O-C = 2.8$ Å).

*Description of Structure **2***. The crystal structure of $Zn_2(C_2H_2N_3)_2(C_2H_3N_3)(C_8H_4O_4)\cdot 2H_2O$ is shown in Figure 5. The structure is based on three crystallographically unique Zn atoms, which are linked by triazole and BDC ligands. The Zn1 atom displays a five-coordianted trigonal bipyramidal geometry by bonding to two N atoms from two triazoles

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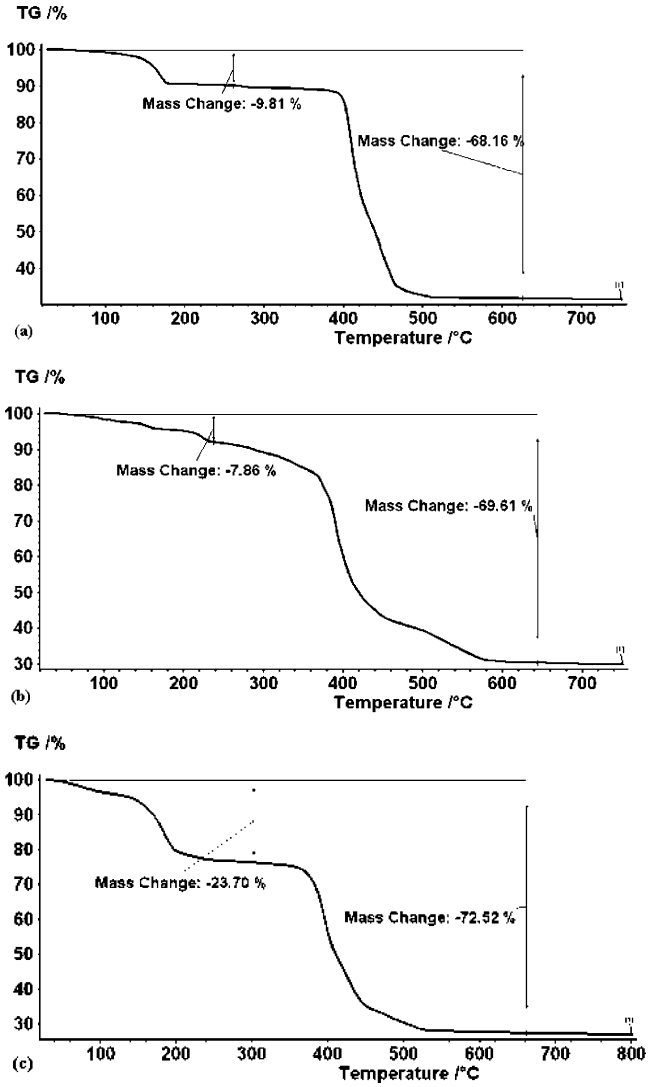

Figure 1. TGA plots of (a) structure **1**, (b) structure **2**, and (c) structure **3**.

and three O atoms from two BDC ligands. The Zn1−O2 bond is significantly longer than other Zn−O bonds (2.37 vs 2.02−2.07 Å), because Zn1 is bonded to both O atoms from the same carboxylate group, resulting in the strong distortion of the polyhedron. Both Zn2 and Zn3 atoms lie in octahedral coordinations by coordinating to N atoms from triazoles. The Zn−N bond distances, ranging from 2.12 to 2.25 Å, are slightly longer than the Zn−O distances (refer to Table 3). The bond valence sums around Zn atoms ranged from 1.97 to 2.08, suggesting that all the ligands to Zn are properly assigned.

The structure is based on isolated Zn octahedra along the (100) direction, which are bridged by triazole molecules (Figure 5a). Two adjacent octahedra are brought together by bonding to N atoms in the 1,2 positions of a triazole, which further links the Zn1 trigonal bipyramid with the N atom in the 4 positon. As a result, clusters containing eight-membered rings are created along the (010) direction. These rings share similarities in size and shape with the ones in structure **1**, which are also formed by Zn polyhedra and triazoles. Two clusters on the edges of the unit cell are joined to one another via the linkage between Zn1 polyhedra and BDC anions which run diagonally in the *bc* plane (Figure 5b).

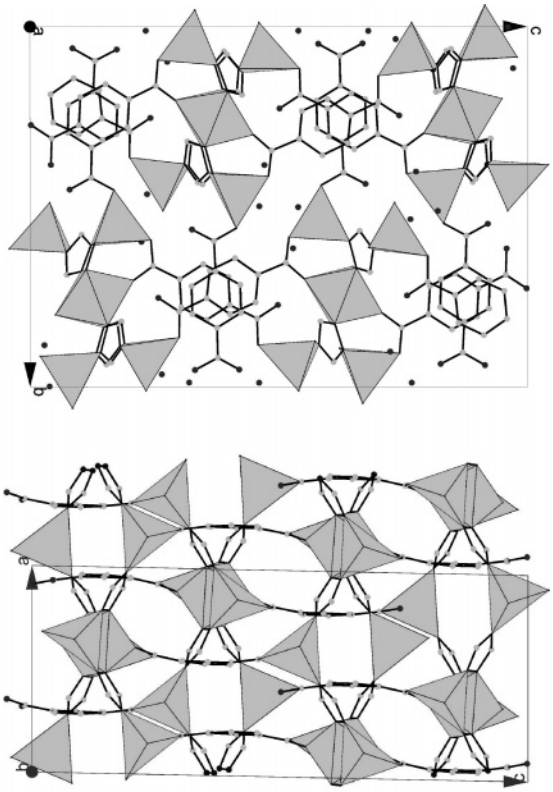

Figure 2. Crystal structure of **1** viewed along the *a* axis (above) and along the *b* axis (below). Zn octahedra and tetrahedra are linked by BDC and triazole ligands. Water molecules (in dark gray circles) occupy the cavities in the structure.

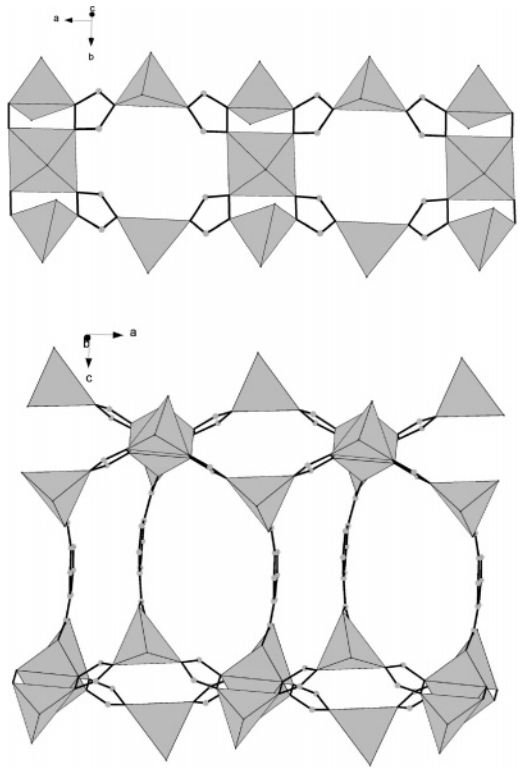

Figure 3. Details of structure **1** depicting the linkage of Zn polyhedra by triazole and BDC ligands.

Water molecules are located in the cavities in the structure. These sites are close to carboxylic groups (O_w···O−C distance of 2.9 Å), suggesting hydrogen bonding interactions. Because the triazole rings are very close to the phenyl groups

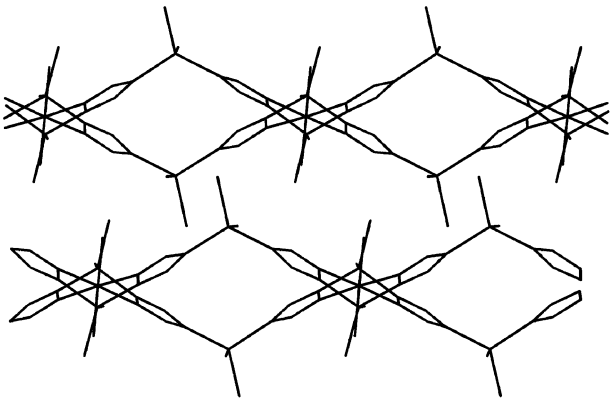

Figure 4. Wire representation of structure **1** viewed along the (010) direction. Two adjacent clusters of Zn polyhedra−triazole are oriented to form an interpenetrated framework. BDC molecules are omitted for clarity.

Table 2. Selected Bond Lengths and Valences for Structure 1

bond	length (Å)	valence	bond	Length (Å)	valence
Zn1−O5	2.008(4)	0.44	Zn2−O1	2.002(4)	0.45
Zn1−O13	2.038(4)	0.41	Zn2−O3	1.941(3)	0.53
Zn1−N3	1.991(4)	0.55	Zn2−N1	1.997(4)	0.54
Zn1−N5	1.991(4)	0.55	Zn2−N4	2.001(4)	0.53
		$\sum_s = 1.95$			$\sum_s = 2.05$
Zn3−O2	2.176(4)	0.28	Zn4−O9	1.962(4)	0.50
Zn3−O4	2.060(4)	0.38	Zn4−O14	2.019(4)	0.43
Zn3−N6	2.207(4)	0.30	Zn4−N2	1.996(4)	0.54
Zn3−N8	2.090(4)	0.42	Zn4−N5	1.993(4)	0.55
Zn3−N10	2.199(4)	0.31			$\sum_s = 2.02$
Zn3−N12	2.099(4)	0.41			
		$\sum_s = 2.10$	Zn5−O7	1.979(4)	0.47
			Zn5−O8	1.958(4)	0.50
			Zn5−N9	2.010(4)	0.52
			Zn5−N11	2.033(4)	0.49
					$\sum_s = 1.98$

within a distance of 4.0 Å, a strong $\pi-\pi$ interaction may be present between two ligand molecules.[30] Unlike structures **1** and **3**, structure **2** is unstable upon heating as the framework quickly collapses once water molecules are removed (Figure 1b). This may be attributed to the presence of the protonated N atom from one of the triazole molecules, which was not observed in the two other structures in this work. Because this N atom is not coordinated to any Zn atom, the triazole linker may be more susceptible to decomposition upon heating.

Description of Structure 3. The crystal structure of $Zn_4(H_2O)_2(C_2H_2N_3)_4(C_8H_4O_4)_2 \cdot 14H_2O$ is depicted in Figures 6−8. The asymmetric unit consists of four crystallographically independent Zn sites. There are three different coordination environments for Zn atoms. Tetrahedrally coordinated Zn1 and Zn2 atoms are bonded to three N atoms from triazole molecules and one O atom from dicarboxylates. Octahedrally coordinated Zn3 is bonded to three N atoms, two O atoms from the dicarboxylate, and one water molecule. Zn4 displays a trigonal bipyramidal geometry by bonding to three N atoms, one O atom from dicarboxylate, and one water molecule. The Zn−O and Zn−N bond lengths are similar to those of structures **1** and **2,** ranging from 1.96 to 2.26 Å and 1.98 to 2.12 Å, respectively (Table 4). The bond valence sum around each Zn atom is close to 2, as expected. Although there are no deviations in bond distances, the Zn polyhedra exhibit distortion. In particular for the Zn3

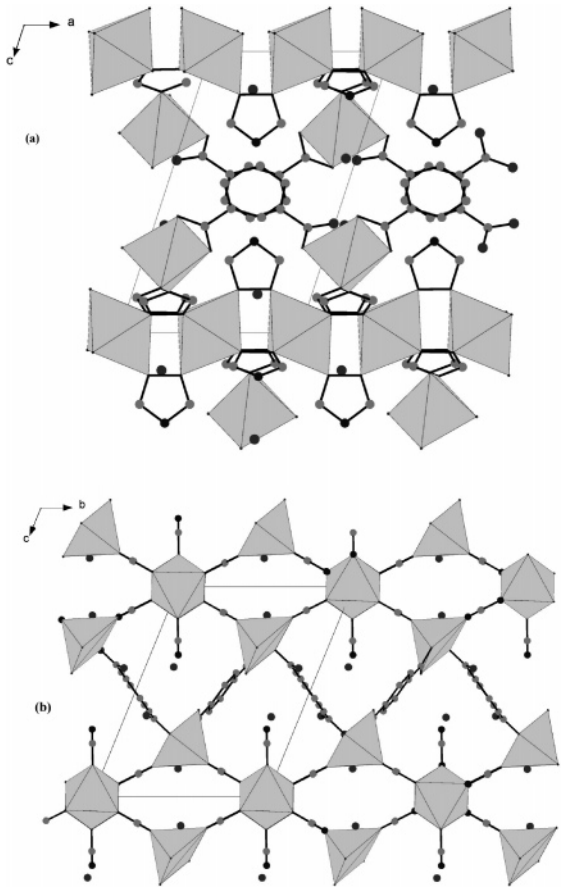

Figure 5. Crystal structure of **2** viewed along the (010) (above) and (100) (below) directions. Zn octahedra and trigonal bipyramids are connected by triazole and BDC. Water molecules (in dark gray circles) are located near the uncoordinated N and O atoms from the ligands.

Table 3. Selected Bond Lengths and Valences for Structure 2

bond	length (Å)	valence	bond	length (Å)	valence
Zn1−O1	2.067(2)	0.37	Zn2−N1 × 2	2.235(3)	0.28
Zn1−O2	2.374(3)	0.16	Zn2−N4 × 2	2.123(3)	0.39
Zn1−O3	2.016(2)	0.43	Zn2−N7 × 2	2.134(3)	0.37
Zn1−N8	2.029(3)	0.50			$\sum_s = 2.08$
Zn1−N9	2.019(3)	0.51			
		$\sum_s = 1.97$	Zn3−N2 × 2	2.247(3)	0.27
			Zn3−N5 × 2	2.142(3)	0.36
			Zn3−N8 × 2	2.128(3)	0.38
					$\sum_s = 2.02$

octahedra, the N4−Zn3−N5 and O4−Zn3−O5 angles deviate from the expected angle of 90°, displaying 103.4 and 59.8°, respectively. This distortion results from the fact that Zn3 is coordinated to both oxygen atoms from one carboxylate group, resulting in the compression of one equatorial octahedral edge.

The structure **3** displays a three-dimensional open framework. Along the *b* axis, four dimeric units of Zn polyhedra linked by triazole molecules form eight-membered rings (Figure 7). The dimers of Zn polyhedra are formed by sharing a common triazole molecule; that is, Zn1 and Zn3 are bonded to two N atoms in the 1,2 positions of the same triazole. Zn2 and Zn4 are also bonded to another triazole in the same manner. The dimensions of the rings, approximately 3.1 × 3.1 Å^2, are smaller than those from structures **1** and **2**. Adjacent layers of Zn polyhedra and triazole are then pillared by BDC ligands through Zn−O bonds, resulting in the channels along the *c* axis.

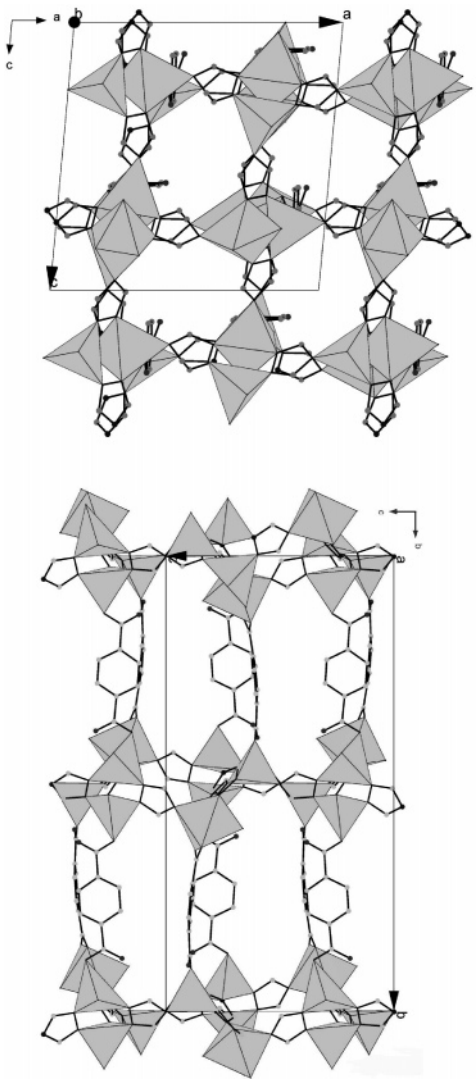

Figure 6. Crystal structure of **3** viewed along the (010) (above) and (100) (below) directions. Zn−triazole clusters are pillared by BDC ligands. Water molecules are omitted for clarity.

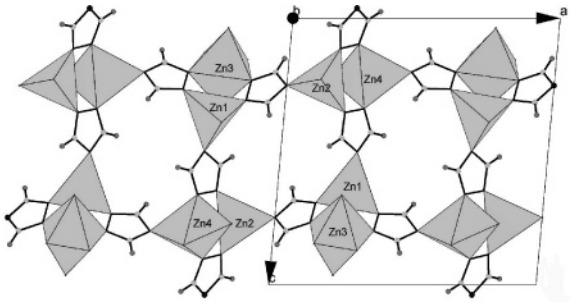

Figure 7. Details of Zn polyhedra−triazole clusters forming eight-membered rings in structure **3**.

It is interesting to note that the BDC ligands are not straight, creating a sinusoidal wave along the *b* axis (Figure 8). This kind of aromatic ligand bending has been observed in the materials containing BDC ligands, including $Zn_2(DABCO)(BDC)_2 \cdot 4DMF \cdot 1/2H_2O$[27] where dimeric Zn units are bridged by BDC. There are two types of BDC units in the structure, where one acts as a tridentate by chelating to Zn1 and Zn3 atoms while the other is a bis-monodentate by connecting Zn2 and Zn4 atoms. These two BDC anions are nearly perpendicular to each other as they are oriented along

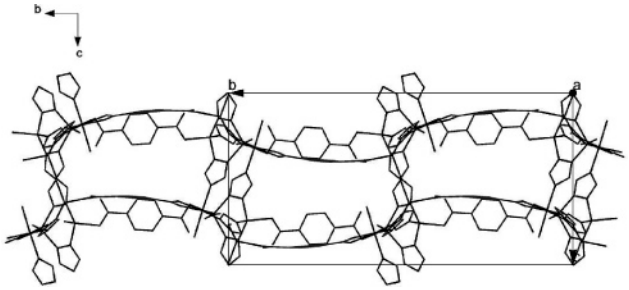

Figure 8. Wire representation of structure **3**. BDC ligands are bent such that sinusoidal waves are formed along the *b* axis.

Table 4. Selected Bond Lengths and Valences for Structure 3

bond	length (Å)	valence	bond	length (Å)	valence
Zn1−O2	2.044(7)	0.40	Zn2−O3	1.958(4)	0.50
Zn1−N2	1.983(4)	0.56	Zn2−N1	1.990(4)	0.55
Zn1−N7	2.008(5)	0.52	Zn2−N6	1.988(4)	0.55
Zn1−N12	1.981(5)	0.56	Zn2−N8	1.991(5)	0.55
		$\sum_s = 2.04$			$\sum_s = 2.15$
Zn3−O1	2.158(4)	0.29	Zn4−O6	2.182(4)	0.27
Zn3−O4	2.161(4)	0.29	Zn4−O7	2.041(4)	0.40
Zn3−O5	2.261(5)	0.22	Zn4−N9	2.075(4)	0.44
Zn3−N3	2.108(4)	0.40	Zn4−N10	2.116(5)	0.39
Zn3−N4	2.072(4)	0.44	Zn4−N11	2.046(4)	0.47
Zn3−N5	2.068(4)	0.45			$\sum_s = 1.97$
		$\sum_s = 2.09$			

(010) and (001) directions. Because the phenyl rings are not stacked, there is no significant $\pi-\pi$ interaction (phenyl−phenyl distance = 6.9−9.3 Å).

The size of pillared channels is approximately 5.7 × 8.1 Å^2, and they are occupied by disordered water molecules. Uncoordinated O atoms from the carboxylates and water interact with each other via hydrogen bonding ($O_w \cdots O-C$ distances = ∼2.9 Å). With channels running along both the *a* and the *b* axes, structure **3** displays the most porosity among the three compounds discussed in this work. It may possess interesting sorption or exchange characteristics when it is calcined.

Conclusion

We have synthesized three new three-dimensional MOFs based on the Zn^{2+} ion, 1,2,4-triazole, and BDC under hydrothermal conditions. All three structures are based on the isolated Zn polyhedra linked by triazole and BDC, with structure **1** containing tetrahedra and octahedra, while structures **2** and **3** show an additional five-coordinated trigonal bipyramidal geometry. All structures contain eight-membered rings built from Zn polyhedra and triazole. These rings are subsequently connected by BDC.

It is not simple to predict the geometry of the resulting frameworks prior to reaction. There have been some discussions regarding the prevention of interpenetrated frameworks to maximize the porosity of the structure, such as the reactions with nonaqueous solvents.[12,36,37] This report demonstrated how different phases can be produced from the same reactants by simply varying the ratio of reactants and solvent. By applying different metals and ligands in different

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(37) Livage, C.; Guillou, N.; Marrot, J.; Férey, G. *Chem. Mater*. **2001**, *13*, 4387.

reaction conditions (pH, temperature, solvents, etc.), a variety of new MOFs with large pores could be designed and synthesized.

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Supporting Information Available: Crystallographic information files (CIF) for structures **1**−**3**. This material is free of charge via the Internet at http://pubs.acs.org.

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