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Anions-Directed Metal-Mediated Assemblies of Coordination
Polymers Based on the Bis(4,4'-bis-1,2,4-triazole) LigandYong-Quan Huang, Xiao-Qing Zhao, Wei Shi, Wen-Yong Liu, Zhong-Lei Chen,
Peng Cheng,* Dai-Zheng Liao, and Shi-Ping Yan

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ABSTRACT: Eight coordination polymers, $\{[\text{Cu}(\text{btr})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Cu}_5(\text{btr})_{10}(\text{SCN})_6(\text{BF}_4)_4] \cdot 5\text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Cu}(\text{btr})_2(\text{SCN})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**3**), $\{[\text{Cu}(\text{btr})_2(\text{NO}_3)_2] \cdot \text{H}_2\text{O}\}_n$ (**4**), $\{[\text{Cu}(\text{btr})_3](\text{ClO}_4)_2\}_n$ (**5**), $\{[\text{Cd}(\text{btr})_3](\text{ClO}_4)_2\}_n$ (**6**), $\{[\text{Cd}_3(\text{btr})_8(\text{H}_2\text{O})_2](\text{BF}_4)_6\}_n$ (**7**), and $\{[\text{Cd}_3(\text{btr})_8(\text{N}(\text{CN})_2)_2](\text{BF}_4)_4\}_n$ (**8**), were obtained from the corresponding metal salts with bis(4,4'-bis-1,2,4-triazole) (btr), and their structures were fully characterized. X-ray diffraction analyses revealed that compounds **1** and **2** were analogous, and **2** can be viewed as SCN^- or BF_4^- anions replacing the coordinated water molecules in **1**, exhibiting the two-dimensional (2D) *meso* coordination networks. **2** and **3** were isolated from the same crystallization, and **3** crystallized in a chiral space group $P2_12_12_1$ with one-dimensional (1D) left-handed $[\text{Cu}(\text{btr})]_\infty$ helical chains. When the BF_4^- anions were replaced by NO_3^- and ClO_4^- anions, completely different three-dimensional (3D) coordination polymers **4** and **5** were isolated, respectively; btr exhibited two bridging fashions at the same time in **4**, connecting with the Cu(II) ions to give an unusual 3D network. Compound **4** is the first example of the μ_3 - and μ_2 -btr simultaneity in a single system in triazole-metal complexes. Compound **5** showed the α -polonium-like structure. When the metal center changed, a novel 3D compound **6** was obtained, which had the same coordination numbers for metal centers and the same space group but significantly different topology for coordination networks when compared with **5**. Compounds **7** and **8** were 3D microporous metal-organic frameworks, which had the analogous structural features, including the tetranuclear metallocycles. The variety of dimensionalities based on the tuning of different anions and metal centers were discussed in detail. Variable-temperature magnetic susceptibility studies on the powder samples of **1–5** reveal the overall antiferromagnetic behavior in copper(II) compounds.

Introduction

Crystal engineering based on metal-organic frameworks (MOFs) has attracted great current interest, owing to their versatile framework topologies, as well as their potential applications as functional materials in the fields of molecular magnetism, catalysis, gas adsorption, nonlinear optics, ion-exchange, luminescence, and so on.¹ The main goal in metal-organic crystal engineering is to predict the topology of supramolecular architectures to synthesize extended solid-state materials with desired properties. Although it has been elaborated that rational design and subtle choice of organic building blocks, as well as metal coordination sites, proved significant in controlling the solid structures of the target products, to establish the general and precise principles of constructing desirable framework topologies remains a long-term challenge.

Among the synthetic strategies to achieve these polymeric compounds, one of the most fruitful choices consists in taking advantage of neutral organic groups containing N,N'-bidentate donors that can act as bridging ligands toward transition metal ions. A series of five-membered heterocycles, such as pyrazole, imidazole, triazole, and tetrazole, are good representatives for the small and simple but effective bridging organic ligands. Specifically, 1,2,4-triazole and its derivatives, which represent a hybrid of both pyrazole and imidazole with regard to the arrangement of their three heteroatoms, are very interesting ligands. A large number of one-, two-, and three-dimensional infinite frameworks with 1,2,4-triazole derivatives have been prepared and characterized because of the interest in their unusual magnetic properties and novel topologies.²

Previously, we reported the first example of a three-dimensional (3D) MOF using coordinative interactions constructed via trinuclear triangular Cu(II) secondary building units, in which both Cu(II) ions and 1,2,4-triazole ligands act as three-

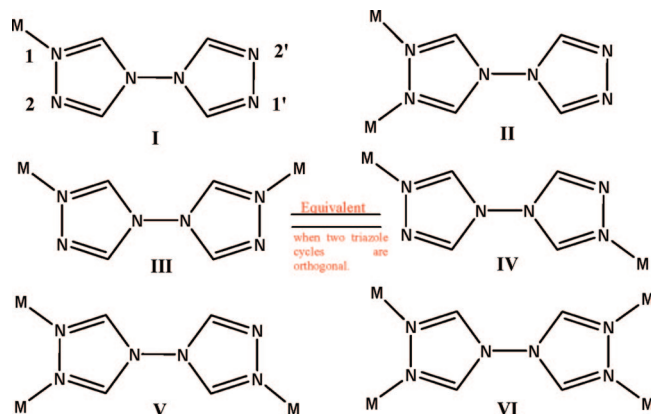
connected nodes to form a $6 \cdot 8^2$ net.³ Recently, we employed the derivative of 1,2,4-triazole (4-(3-pyridinyl)-1,2,4-triazole) with copper(II) ions to form a series of cage-like complexes with different topologies.⁴ We also designed and synthesized a series of 4-substituted⁵ and 3,5-substituted⁶ triazole-cadmium(II) coordination polymers from zero- to three-dimensionalities tuned via different triazole ligands and anions. The first right-helix triazole-metal complex was reported too.⁷

To obtain more information on supramolecular architecture construction and triazole-metal coordinated structures, we designed and synthesized the symmetric triazole-based ligand 4,4'-bis-1,2,4-triazole (btr), which combines the coordination geometry of both 4,4'-bipyridine and 4,4'-bipyrazole more than that most common N1,N2 bidentate fashion in 1,2,4-triazole. Because of its highly cooperative behavior, btr with iron(II) salts has allowed the isolation and investigation of various spin crossover systems that show promising applications in molecular switches and molecular devices. $\text{Fe}(\text{btr})_2(\text{NCS})_2 \cdot \text{H}_2\text{O}$ is one of the most studied spin crossover complexes.⁸ For a long time btr was considered as solely exhibiting a N1,N1' bidentate coordination mode.⁹ As a matter of fact, btr has four potentially coordinated N atoms in a molecule, which may exhibit various bridging modes (Scheme 1.) Thus, btr is quite a versatile ligand, in spite of its apparent simplicity, as recently reported by some chemists.¹⁰ A few crystal structures associated with the btr ligand have been described, while the systematic study of the coordination chemistry of btr in the self-assembly of coordination frameworks is surprisingly quite scarce.

Several factors, such as the coordination nature of the metal ions, ligand structures, and number of coordination sites provided by organic ligands, counteranions, and metal–ligand ratio, which may be the key for the rational design of crystalline materials, remarkably influence the structural topologies of the resultant coordination frameworks. In particular, the role of the anions and the metal centers in the self-assembly processes has emerged as an increasingly active theme in recent studies.¹¹ The

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Scheme 1. Six Connection Modes of btr



anions can have two key effects upon the structure of the final product.¹² First, the coordinative ability of the anions can clearly influence the coordination sphere of the metal ions used and hence framework connectivity. Second, the anions can play a crucial role in stabilizing the coordination frameworks because of the supramolecular interactions such as hydrogen bonds between anions and host coordination networks or lattice water molecules. Thus, when designing coordination architectures, the roles of the metal center, the anion, and the ligand all need to be considered.

In this context, we describe the successful syntheses of eight btr and M(II) ($M = \text{Cu}$ and Cd) coordination polymers with a variety of one- to three- dimensional frameworks, which are remarkably manipulated by the anions and the metal centers. The eight complexes, namely, $\{[\text{Cu}(\text{btr})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}\}_n$ (**1**), $\{[\text{Cu}_5(\text{btr})_{10}(\text{SCN})_6(\text{BF}_4)_4] \cdot 5\text{H}_2\text{O}\}_n$ (**2**), $\{[\text{Cu}(\text{btr})_2(\text{SCN})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**3**), $\{[\text{Cu}(\text{btr})_2(\text{NO}_3)_2] \cdot \text{H}_2\text{O}\}_n$ (**4**), $\{[\text{Cu}(\text{btr})_3](\text{ClO}_4)_2\}_n$ (**5**), $\{[\text{Cd}(\text{btr})_3](\text{ClO}_4)_2\}_n$ (**6**), $\{[\text{Cd}_3(\text{btr})_8(\text{H}_2\text{O})_2](\text{BF}_4)_6\}_n$ (**7**), and $\{[\text{Cd}_3(\text{btr})_8(\text{N}(\text{CN})_2)_2](\text{BF}_4)_4\}_n$ (**8**), were revealed by single-crystal X-ray diffraction analyses. The interesting bridging modes of btr in the eight complexes were described and discussed in detail. The effects of anion functionality and metal center control were investigated within the $M(\text{II})$ –btr system. IR spectra of the complexes have been characterized, and variable-temperature magnetic susceptibility studies on the powder samples of **1**–**5** reveal the overall antiferromagnetic behavior in copper(II) compounds.

Experimental Section

Materials. The triazole ligand btr was synthesized according to the literature method.¹³ All other reagents were commercially available and used without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bio-Rad FTS 135 spectrometer. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer.

Syntheses. $\{[\text{Cu}(\text{btr})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot 2\text{H}_2\text{O}\}_n$ (**1**). btr (1.0 mmol, 0.36 g) and $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.173 g) were heated under reflux in H_2O for 2 h and then the resulting solution was filtered. Sky blue single-crystals suitable for X-ray diffraction were obtained by slow evaporation in glass vial within several days. Yield: 60%. Elemental analysis (%) calculated for **1**: C 16.88, H 3.12, N 29.23; found: C 16.52, H 2.77, N 28.91. IR (KBr pellets, λ , cm^{-1}): 3447.1m, 3111.8m, 1646.9w, 1576.1w, 1517.0w, 1490.1m, 1394.9m, 1121.5s, 1084.3s, 1044.6s, 744.5w, 617.3m.

A mixture of btr (1.0 mmol, 0.36 g) and $[\text{Cu}_5(\text{btr})_{10}(\text{SCN})_6(\text{BF}_4)_4] \cdot 5\text{H}_2\text{O}$ (2**). A mixture of btr (1.0 mmol, 0.36 g) and $\{[\text{Cu}(\text{btr})_2(\text{SCN})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**3**). A mixture of btr (1.0 mmol, 0.36 g) and NH_4SCN (0.5 mmol, 0.039 g) in 20 mL of boiling**

H_2O was added into a 20 mL $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.173 g) boiling aqueous solution. The mixed solution stayed at room temperature for a day and was filtered. The crystal products were collected from the filtration after two weeks. The colored crystal products, dark blue for **2** and green for **3**, were found in the relative ratio of 70:30. Elemental analysis (%) calculated for **2**: C 22.71, H 2.33, N 37.97; found: C 22.45, H 2.05, N 37.54. Elemental analysis (%) calculated for **3**: C 24.76, H 2.32, N 40.72; found: C 24.61, H 2.48, N 40.19. IR (KBr pellets, λ , cm^{-1}): for **2**: 3446.8s, 3120.4m, 3046.1w, 2055.3m, 1652.5m, 1511.5mw, 1494.9w, 1341.5m, 1300.0w, 1208.8w, 1124.1m, 1083.9s, 1034.9m, 964.1w, 876.9w, 617.2s; IR (KBr pellets, λ , cm^{-1}): for **3**: 3459.5s, 3402.8m, 3138.4s, 3122.5m, 2097.2s, 2075.3s, 1656.7w, 1615.2w, 1519.8m, 1494.9w, 1333.2w, 1333.0w, 1212.9w, 1196.3w, 1084.9s, 1025.9s, 980.7w, 972.4w, 964.1w, 852.1w, 606.4s.

$\{[\text{Cu}(\text{btr})_2(\text{NO}_3)_2] \cdot \text{H}_2\text{O}\}_n$ (**4**). btr (1.0 mmol, 0.36 g) in 20 mL of boiling H_2O was added into a 20 mL $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.5 mmol, 0.121 g) boiling aqueous solution. The mixed solution stayed at room temperature for a day. The blue crystal products were obtained after several days. Yield: 55%. Elemental analysis (%) calculated for **4**: C 20.11, H 2.11, N 41.04; found: C 19.61, H 2.18, N 40.41. IR (KBr pellets, λ , cm^{-1}): 3445.6s, 3104.2m, 1635.7m, 1524.2m, 1384.7s, 1200.2w, 1084.5w, 1034.4m, 613.2m.

$\{[\text{Cu}(\text{btr})_3](\text{ClO}_4)_2\}_n$ (**5**). The mixture of btr (1.5 mmol, 0.54 g) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mmol, 0.173 g) was heated under reflux in 20 mL of H_2O for 2 h and then the resulting solution was filtered. Blue single-crystals suitable for X-ray diffraction were obtained by slow evaporation in a glass vial within several days. Yield: 65%. Elemental analysis (%) calculated for **5**: C 21.49, H 1.80, N 37.59; found: C 21.40, H 1.78, N 37.05. IR (KBr pellets, λ , cm^{-1}): 3443.7s, 3099.2m, 1635.4m, 1507.9w, 1121.1m, 619.2m.

$\{[\text{Cd}(\text{btr})_3](\text{ClO}_4)_2\}_n$ (**6**). This complex was obtained following the method described above for **5** but replacing $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Yield: 67%. Elemental analysis (%) calculated for **6**: C 20.03, H 1.68, N 35.03; found: C 20.40, H 1.86, N 35.67. IR (KBr pellets, λ , cm^{-1}): 3425.0s, 3126.1s, 1620.64w, 1518.1m, 1298.7w, 1084.1s, 1011.3m, 933.4w, 859.4m, 616.1s.

$\{[\text{Cd}_3(\text{btr})_8(\text{H}_2\text{O})_2](\text{BF}_4)_6\}_n$ (**7**). The mixture of btr (2.0 mmol, 0.72 g) and $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.394 g) was heated under reflux in 20 mL of H_2O for 2 h and then the resulting solution was filtered. Colorless single-crystals suitable for X-ray diffraction were obtained by slow evaporation in a glass vial within several days. Yield: 50%. Elemental analysis (%) calculated for **7**: C 23.36, H 2.20, N 40.84; found: C 22.96, H 1.98, N 40.51. IR (KBr pellets, λ , cm^{-1}): 3444.5m, 3134.8m, 1636.2w, 1508.5m, 1299.7m, 1084.6s, 862.2m, 614.0s, 521.8m.

$\{[\text{Cd}_3(\text{btr})_8(\text{N}(\text{CN})_2)_2](\text{BF}_4)_4\}_n$ (**8**). A mixture of btr (2.0 mmol, 0.72 g) and NH_4SCN (0.8 mmol, 0.061 g) in 20 mL of boiling H_2O was added into a 20 mL $\text{Cd}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.0 mmol, 0.394 g) boiling aqueous solution. The mixed solution stayed at room temperature for a day and was filtered. The crystal products were collected from the filtration after 2 weeks. Yield: 61%. Elemental analysis (%) calculated for **8**: C 22.69, H 1.69, N 39.69; found: C 22.28, H 2.05, N 39.26. IR (KBr pellets, λ , cm^{-1}): 3445.2s, 3118.2s, 2147.4s, 1636.1m, 1507.0m, 1297.3m, 1083.5s, 935.4w, 861.2m, 614.1s, 521.4m.

Crystal Structure Determination. Diffraction intensities for seven complexes were collected on a computer-controlled Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated $\text{Mo K}\alpha$ radiation with a radiation wavelength 0.71073 Å by using the ω - φ scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs.¹⁴ Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The hydrogen atoms of the organic ligands were generated geometrically; the hydrogen atoms of the water molecules were located from difference Fourier maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystallographic data and structure refinements for **1**–**8** are summarized in Tables 1 and 2.

Results and Discussion

Synthetic Route for 1–8. Triazole and its derivatives have been demonstrated to provide a wealth of coordination polymers

Table 1. Crystal Data and Structure Refinements for Complexes 1–4

complexes	1	2	3	4
empirical formula	CuC ₈ H ₁₆ B ₂ F ₈ N ₁₂ O ₄	CuC _{9.2} H ₁₀ B _{0.8} F _{3.2} N _{13.2} OS _{1.2}	CuC ₁₀ H ₁₂ N ₁₄ O ₂ S ₂	Cu ₂ C ₁₆ H ₂₀ N ₂₈ O ₁₄
formula weight	581.49	492.94	488.00	955.68
temperature (K)	294 (2)	113(2)	113(2)	294 (2)
crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	7.9693(18)	10.964(3)	6.8459(6)	10.6466(16)
<i>b</i> (Å)	12.977(3)	12.672(3)	12.4795(11)	12.0502(18)
<i>c</i> (Å)	10.267(2)	182.837(3)	21.686(2)	12.7926(19)
α (deg)	90	90	90	90
β (deg)	90.221(4)	91.011(5)	90	92.320(3)
γ (deg)	90	90	90	90
<i>V</i> (Å ³)	1061.8(4)	1783.3(7)	1852.7(3)	1639.9(4)
<i>Z</i>	2	4	4	2
<i>F</i> (000)	582	986	988	964
ρ_{calc} (Mg/m ³)	1.819	1.835	1.750	1.935
μ (mm ^{−1})	1.144	1.434	1.448	1.410
refl. collected	5278	8170	16418	8939
independent refl.	1879	2106	4405	3285
GOF	1.159	1.114	0.987	1.022
final <i>R</i> indices(<i>I</i> = 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0506, <i>wR</i> ₂ = 0.1356	<i>R</i> ₁ = 0.0345, <i>wR</i> ₂ = 0.0989	<i>R</i> ₁ = 0.0207, <i>wR</i> ₂ = 0.0454	<i>R</i> ₁ = 0.0375, <i>wR</i> ₂ = 0.0905
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0664, <i>wR</i> ₂ = 0.1496	<i>R</i> ₁ = 0.0430, <i>wR</i> ₂ = 0.1029	<i>R</i> ₁ = 0.0251, <i>wR</i> ₂ = 0.0461	<i>R</i> ₁ = 0.0567, <i>wR</i> ₂ = 0.1006

Table 2. Crystal Data and Structure Refinements for Complexes 5–8

complexes	5	6	7	8
empirical formula	CuC ₁₂ H ₁₂ N ₁₈ O ₈	CdC ₁₂ H ₁₂ Cl ₂ N ₁₈ O ₈	CdC _{10.67} H ₁₂ N ₁₆ O _{0.67} B ₂	Cd ₃ C ₃₆ H ₃₂ N ₅₄ B ₄ F ₁₆
formula weight	670.84	719.70	661.05	1905.60
temperature (K)	293 (2)	293(2)	293(2)	294 (2)
crystal system	rhombohedral	rhombohedral	tetragonal	tetragonal
space group	<i>R</i> $\bar{3}c$	<i>R</i> $\bar{3}c$	$\bar{4}$	$\bar{4}$
<i>a</i> (Å)	10.9709(11)	11.1514(9)	12.7471(15)	12.691(2)
<i>b</i> (Å)	10.9709(11)	11.1514(9)	12.7471(15)	12.691(2)
<i>c</i> (Å)	35.314(6)	102.578(11)	22.545(3)	23.216(8)
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	120	120	90	90
<i>V</i> (Å ³)	3681.0(8)	11047.0(18)	3663.3(8)	3739.4(16)
<i>Z</i>	>6	18	6	2
<i>F</i> (000)	2022	6408	1940	1868
ρ_{calc} (Mg/m ³)	1.816	1.947	1.798	1.692
μ (mm ^{−1})	1.189	1.189	0.994	0.956
refl. collected	6098	19245	10436	10146
independent refl.	729	2523	3745	3305
GOF	1.086	1.017	1.043	1.113
final <i>R</i> indices(<i>I</i> = 2 σ (<i>I</i>))	<i>R</i> ₁ = 0.0571, <i>wR</i> ₂ = 0.1614	<i>R</i> ₁ = 0.0394, <i>wR</i> ₂ = 0.1000	<i>R</i> ₁ = 0.0290, <i>wR</i> ₂ = 0.0818	<i>R</i> ₁ = 0.0440, <i>wR</i> ₂ = 0.1454
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0606, <i>wR</i> ₂ = 0.1657	<i>R</i> ₁ = 0.0569, <i>wR</i> ₂ = 0.1098	<i>R</i> ₁ = 0.0337, <i>wR</i> ₂ = 0.0851	<i>R</i> ₁ = 0.0450, <i>wR</i> ₂ = 0.1463

with unusual architectures and a range of physical properties. As anticipated, the reactions of btr with M(II) are characterized by an unusually varied structural chemistry. The synthetic route for **1–8** is shown in Scheme 2. First of all, only BF₄[−] was chosen as the counteranion when btr reacted with Cu(II) ion, obtaining compound **1**. When the short bridge NCS[−] was added as another co-counteranion with BF₄[−], compounds **2** and **3** were isolated from the same crystallization. Changing the BF₄[−] to the NO₃[−] anion had led to the formation of **4**. While the ClO₄[−] anion was used, compound **5** could be obtained. With regard to the MOFs **6–8**, they were all Cd(II) center coordination polymers with the anions of ClO₄[−], BF₄[−] and N(CN)₂[−], respectively. Coordination polymers **1–8** are air stable with the maintenance of their crystallinity for at least several weeks and are insoluble in common organic solvents and water, being consistent with their polymeric and neutral nature.

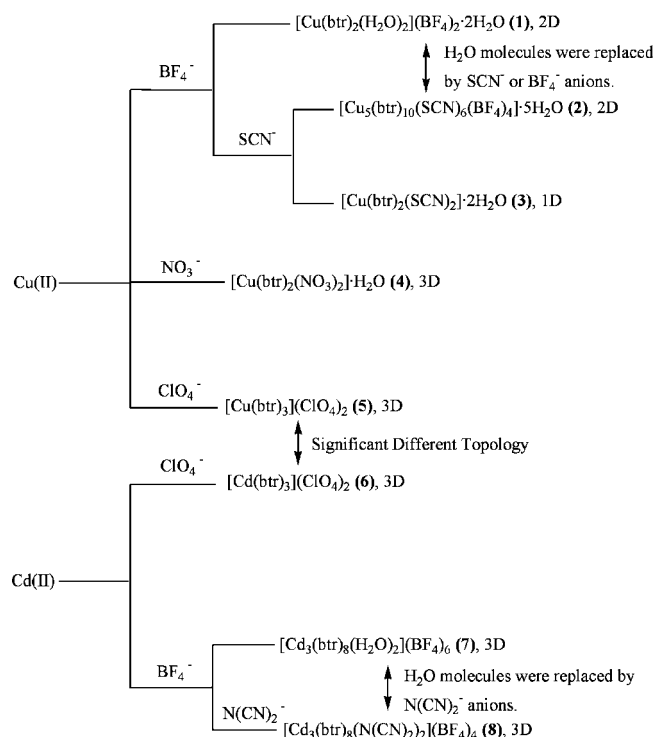
Structural Description. Two-Dimensional (2D) Grids (1 and 2) and One-Dimensional (1D) Left-handed Helical Chain (3). As shown in Figure 1, the coordination geometry around the Cu(II) ion in **1** and **2** is centrosymmetric and can be described as a regular elongated octahedron, where the bridged triazole ligands occupy the square plane and the terminal ligands, such as water molecules or SCN[−] anions, weakly coordinate in the two axial positions because of the Jahn–Teller effect. X-ray diffraction studies reveal that compounds **1** and **2** are

analogous, and **2** can be viewed as SCN[−] or BF₄[−] anions replacing the coordinated water molecules in **1** (Figure 1b). **1** contains a 2D infinite network, which contains an equal amount of right- and left-handed [Cu(btr)]_∞ helices along the *a* and *b* directions (Figure 2.) The average bond length associated with the Cu atom in **1** (2.141 Å) is slightly longer than that in **2** (2.128 Å). From the packing structures of **1** and **2**, hydrogen bonds play an important role in the crystal packing and the stability of them (see Supporting Information).

Compounds **2** and **3** were isolated from the same crystallization. With repeat preparations, we isolated the different color crystals by hand. The IR spectra show different absorption peaks, one peak (2055 cm^{−1}) and two peaks (2097 and 2075 cm^{−1}) in the region 2000–2200 cm^{−1} (characteristic of the stretching C=N bond of thiocyanate) for different color crystals, respectively, indicating the presence of different crystal products in the reaction system.

In **3**, the coordination environment of Cu(II) ion is a square-pyramidal geometry (Figure 3,) where the pyramid base-plane is formed by two SCN[−] anions and two btr ligands in a *trans* mode, while a btr molecule occupies the axial site with relative longer Cu–N bond length (2.248 Å). It is noted that the coordination modes of two SCN[−] anions in **3** are different,

Scheme 2. Synthetic route for 1–8



whereas all SCN^- anions in **2** in the same coordination mode. The structural feature is consistent with IR results.

Very recently, an identical copper complex with **3** was reported in a short communication and the complex was described as a zigzag chain.¹⁵ Furthermore, **3** crystallizes in a chiral space group $P2_12_12_1$, and linked by btr ligands. Cu(II) ions are arranged in a single left-handed helical 2_1 chain in **3** (Figure 4.) The width of the helix is calculated to be 6.6 Å, and the pitch is 12.5 Å, containing two Cu(II) ions per turn. The driving force in the formation of helical chains is likely $\text{O} \cdots \text{N}$ hydrogen-bonding interactions, with the distances ranging from 2.976 to 2.914 Å. It is well-known that bulk water contains various discrete water clusters, which are capable of guiding the self-assembly processes in chemical systems.¹⁶ In this case, dimeric water clusters induce the special configuration and prevent the coordination of N atoms in btr ligands. Therefore, the inorganic supramolecular $[\text{Cu}(\text{btr})]_\infty$ *meso* helix was isolated based on dimeric water clusters, which represents a particularly unusual example among triazole-based coordination compounds. It is of interest to note that all helices in **3** are of the same chirality and are packed in a parallel manner, leading to a noncentrosymmetric and chiral solid, as shown in Figure 5.

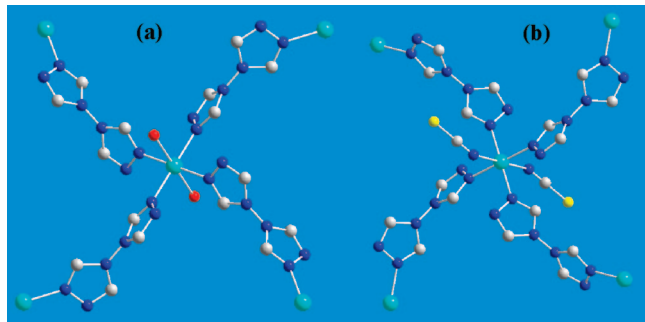


Figure 1. Coordination environment of Cu(II) in **1** and **2** for (a) and (b), respectively. Cyan, Cu; red, O; gray, C; blue, N; yellow, S; brown, B; green, F; H atoms are omitted.

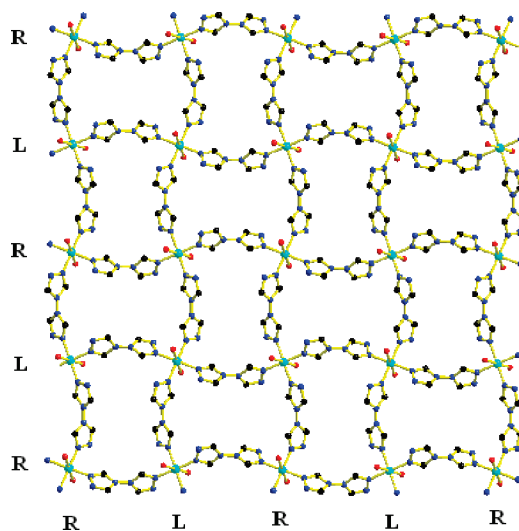


Figure 2. 2D coordination network of **1** constructed via alternatively right (R) and left (L) helix chains along *ab* plane. Cyan, Cu; red, O; gray, C; blue, N.

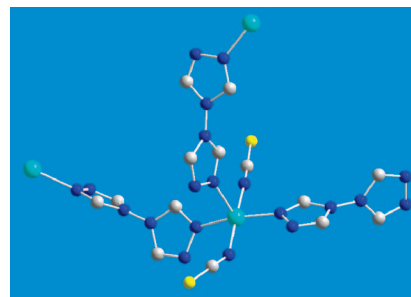


Figure 3. Coordination environment of Cu(II) in **3**. Cyan, Cu; red, O; gray, C; blue, N; H atoms are omitted.

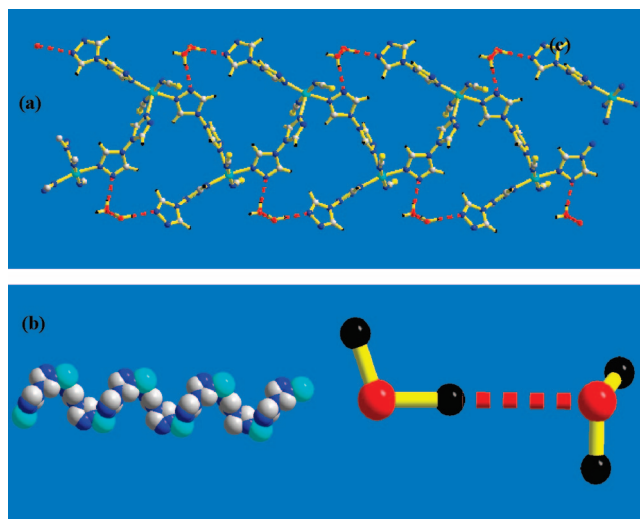


Figure 4. 1D supramolecular chain in **3** (a), space-filling of $[\text{Cu}(\text{btr})]_\infty$ left-handed helical chain (b), and dimeric water clusters (c). Blue, N; cyan, Cu; gray, C; black, H; red, O; yellow, S; red dot line, hydrogen bond.

Generally, right- and left-handed helices are obtained in equal amounts as a *meso* compound when achiral building blocks are used. A *meso* compound **2** contains an equal amount of right- and left-handed helices in a single crystal, which is achiral and crystallizes in a central symmetrical space group. In **3**, however,

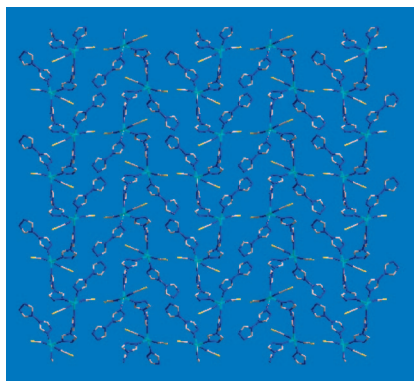


Figure 5. Packing structure of **3** showing all helical chains in left-handed motif. Gray, C; blue, N; cyan, Cu; yellow, S.

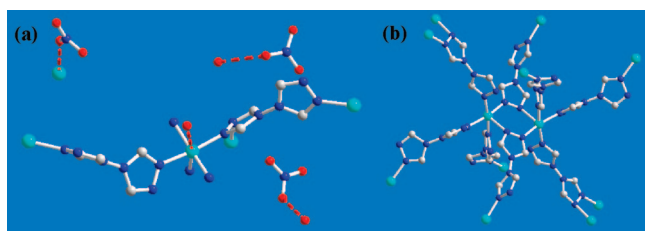


Figure 6. Coordination environment of Cu(II) in **4** (a), and the dinuclear coordination unit of **4** (b). Gray, C; blue, N; cyan, Cu; red, O.

spontaneous resolution occurs during the crystallization, where the coordination polymer is noncentrosymmetric and chiral even if it contains no chiral molecular unit. We impose the self-assemble process as follow: upon the addition of the anions SCN^- , the coordination water molecules were induced to break away from the Cu(II) center in **1**, being replaced by the anions SCN^- and **2** produced consequently. As the increasing of the lattice discrete water molecule, a fire-new compound **3** was isolated based on the dimeric water clusters.

3D MOF of 4. Compound **4** displays a novel 3D framework. As depicted in Figure 6(a), the coordination environment of Cu(II) ion is a square-pyramidal geometry, where the pyramid base-plane is formed by four N atoms from different btr ligands, while a $\mu_{1,2}$ -bridged btr molecule occupies the axial site. The axial Cu–N bond length (2.310 Å) is longer than the average one at the base plane (2.005 Å). It is noted that one O atom of NO_3^- weakly coordinated with Cu(II) center in the axial position with Cu...O distance 2.747 Å. The dinuclear coordination unit of **4** is shown in Figure 6(b). Two N1,N2-bridged btr ligands link two Cu(II) ions to form secondary building units with Cu...Cu distance of 4.084 Å, which are further connected by btr ligands to construct a 3D coordination polymer with unique topology.

As shown in Figures 7 and 8, there are two kinds of btr ligands in the structure with μ_3 - and μ_2 -coordination modes. The μ_3 -btr ligands connect Cu(II) ions to form a 2D 48^2 topology (Figure 7 (b)), which is further linked via μ_2 -btr ligands to give an unusual 3D topology. The Cu(II) ion and μ_3 -btr ligand can be considered as five- and three-connected nodes, having the Schläfli symbol 46^58^4 and 48^2 , respectively, thus the network can be described with two kinds of nonequivalent points: $(46^58^4)(48^2)$ (Figure 8b). Figure 9 exhibits the overall topology corresponding to binding direction provided by bicopper secondary building blocks is in the form of “body-centered cubic net” with the Schläfli symbol 4^246^4 and a CsCl-like net. The structures show that NO_3^- anions and water molecules exist in

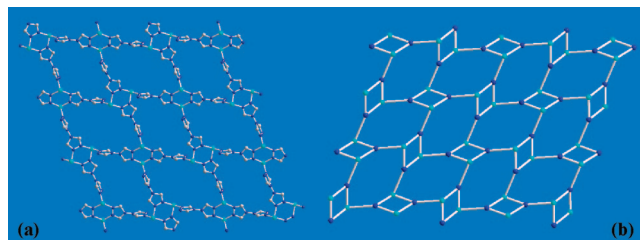


Figure 7. 2D grid layer in **4** connected by μ_3 -btr ligands (a), gray, C; blue, N; cyan, Cu; the 2D $4 \cdot 8^2$ topology (b), cyan, Cu; blue, μ_3 -btr ligands.

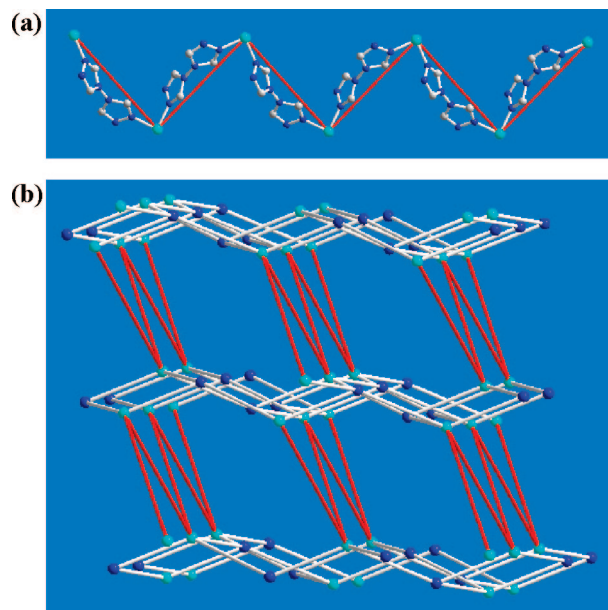


Figure 8. (a) 1D zigzag-chain in **4** linked by μ_2 -btr ligands, gray, C; blue, N; cyan, Cu; (b) the 3D $(46^58^4)(48^2)$ topology of **4**, cyan, Cu; blue, μ_3 -btr ligand; red line, μ_2 -btr ligand.

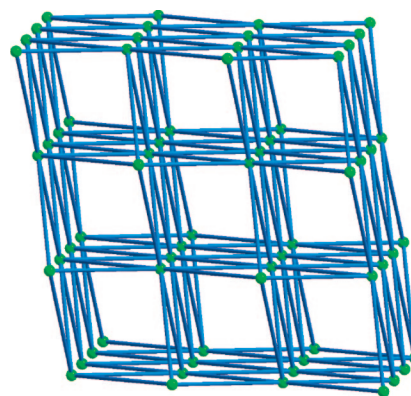


Figure 9. CsCl-like 8-connected topology based on bicopper units, green, bicopper units.

the microporous MOF constructed via $\text{Cu}(\text{btr})_2$, where the hydrogen bonds between H_2O and NO_3^- and weak coordination interactions between Cu(II) and NO_3^- help to stabilize them (see Supporting Information).

α -Polonium-Like Structure of 5. The structure studies of the famous spin-crossover $\text{Fe}(\text{II})$ –btr complex¹⁷ encourage us to consider that the self-assembly of $\text{M}(\text{ClO}_4)_2$ and btr in the ratio of 1:3 should give 3D coordination polymers with btr as double bridged ligands.

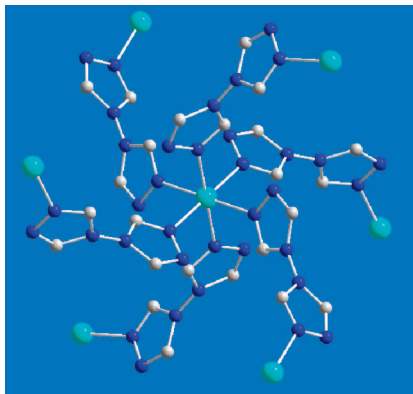


Figure 10. Coordination environment of Cu(II) in **5**.

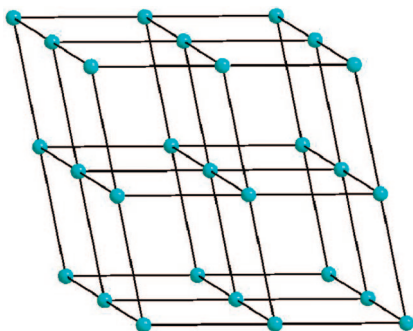


Figure 11. α -Polonium-like topology of **5**. Cyan, Cu; gray, C; blue, N; cyan, Cu.

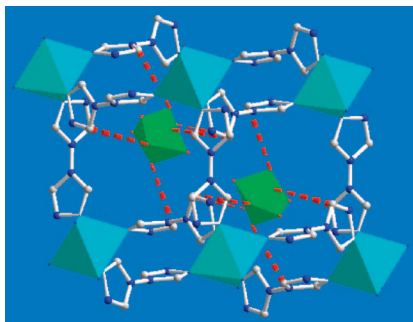


Figure 12. Perchlorate anions located in the pores of **5**. Gray, C; blue, N; cyan polyhedra, CuN_6 ; green polyhedra, ClO_4^- .

Single-crystal X-ray diffraction analysis shows that compound **5** is a 3D coordination polymer. As depicted in Figure 10, all Cu(II) centers have the same coordination environment with an octahedral geometry. Six btr ligands coordinate to a Cu(II) ion with Cu–N bond length of 2.107 Å, all btr ligands act as bridges to link two metal centers, and the adjacent Cu...Cu distance is 8.646 Å. The overall coordination network is 3D with the α -polonium like topology (the Schläfli symbol $4^{12}6^3$) (Figure 11). There are two crystallographically independent perchlorate anions located in the void of the 3D architecture, as shown in Figure 12. These anions show several hydrogen contacts with the carbon atoms of the 1,2,4-triazole rings, which may be helpful to retain perchlorate anions in the void.

3D MOF of 6. The reaction of $\text{Cd}(\text{ClO}_4)_2$ and btr produced a 3D coordination polymer **6**. The structure reveals two crystallographically independent Cd(II) sites, as shown in Figure 13. Each site is surrounded by six N atoms from six different btr ligands. One kind of Cd(II) ions form dinuclear SBUs, which

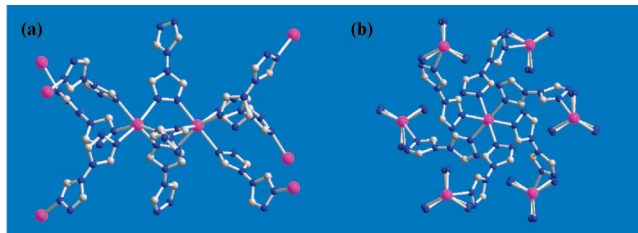


Figure 13. Coordination environment of two kinds of Cd(II) in **6**, blue, N; gray, C; purple, Cd.

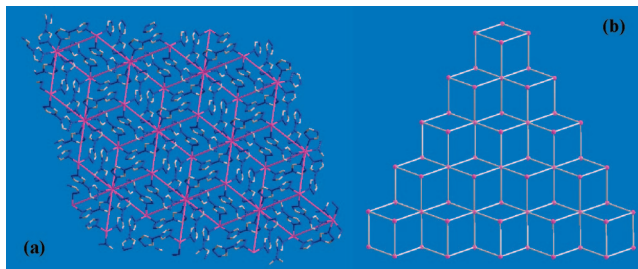


Figure 14. 2D layer structure (a) and the $4^3 4^6$ topology (b) constructed by $\mu_{1,1'}$ -bridged btr in **6**, blue, N; gray, C; purple, Cd.

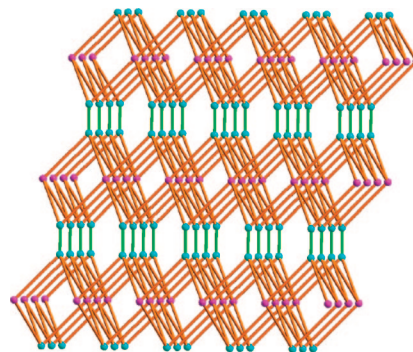


Figure 15. Schematic drawing of the $(4^3 6^3)(4^6 6^6 8^3)$ topology for the 3D coordination network in **6**. Purple, six-connected Cd; cyan, four-connected Cd; yellow line, $\mu_{1,1'}$ -bridged btr; green line, $\mu_{1,2}$ -bridged btr.

are link via three N1,N2-bridged btr ligands (Figure 13a). Another kind of Cd(II) ions locate in the 3-fold axis to connect six dinuclear SBUs (Figure 13(b)). Though all btr in **6** are bidentate, there are two coordination modes $\mu_{1,1'}$ and $\mu_{1,2}$. If we only consider the $\mu_{1,1'}$ -bridged btr in the coordination network, a 2D layer with $4^3 4^6$ topology is found (Figure 14.) On use of three $\mu_{1,2}$ -bridged btr ligands in a dinuclear SBU as linkers, a schematic drawing of topology for the 3D coordination network is presented in Figure 15. In the framework, there exist two kinds of nodes, namely, four- and six-connected, and the network can be symbolized as a $(4^3 6^3)(4^6 6^6 8^3)$ net.

Compared with **5** and **6**, they had the same coordination numbers for metal centers but significantly different topology for coordination networks. Another fact we should specially note is that both **5** and **6** have the same rhombohedral crystal system and space group $R\bar{3}c$, and moreover, both single crystals of **5** and **6** are hexagonal. As shown in Figure 16, the 3D packing structures along the c direction show significant similarity for both compounds. For dinuclear SBUs in **6**, they connect six Cd(II) ions and locate in the 3-fold axis, which act as similar functionality as that of the six-node Cd(II) ions. If we consider

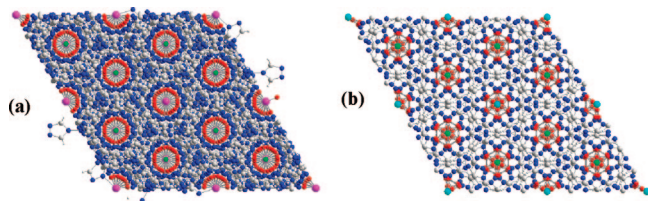


Figure 16. 3D packing structures of **5** (a) and **6** (b) along the *c* direction. Blue, N; gray, C; purple, Cu; cyan, Cd; green, Cl.

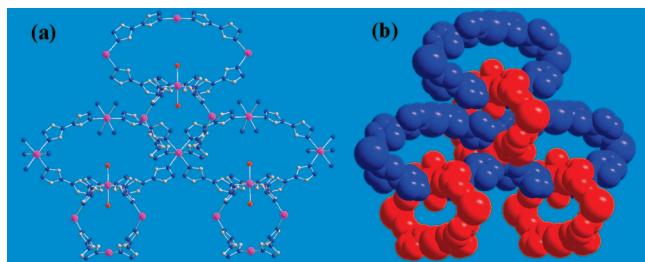


Figure 17. (a) Tetranuclear metallocycles showing the coordination environment of two different Cd(II) ions in **7**, blue, N; gray, C; purple, Cd; (b) the space-filling view.

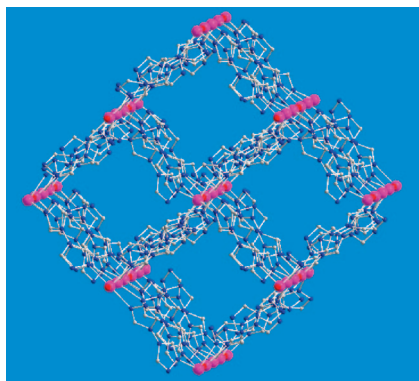


Figure 18. 3D microporous MOFs with 1D channels along the *c* direction in **7**.

the dinuclear SBUs as six nodes, the overall topology of **6** is the same as **5**. As a result, both **5** and **6** have similarity in the bulk.

3D Microporous Framework of 7 and 8. The structure reveals that there are two kinds of Cd(II) ions in the molecular structure of **7**, as shown in Figure 17. All Cd(II) centers are octahedral, where the Cd1 ion coordinates four N atoms of different btr ligands and two water molecules while the Cd2 ion has six N atoms of different btr ligands. All btr ligands adopt $\mu_{1,2}$ -bridged modes, connecting with one Cd1 ion and with three Cd2 ions to form a tetranuclear metallocycle. These cycles link with each other perpendicularly, constructing 3D microporous MOFs with 1D channels along the *c* direction (Figure 18.). As shown in Figure 18, the N1,N1' bridge of the 4,4'-bitriazole provided for large holes in which the BF_4^- anions and the coordination water molecules were stored, where the BF_4^- anions had the weak interactions with the btr ligands and water molecules (Figure 19.). A PLATON program analysis suggests that there is approximately 36.3% of the crystal volume accessible to solvents.¹⁸ If we consider btr's as linkers and metal centers as nodes, the 3D MOF of **7** can be represented as Figure 20. For the four- and six-connected nodes (Cd1 and Cd2), the network can be symbolized as a $(4^26^4)(4^76^88^2)$ net. While the

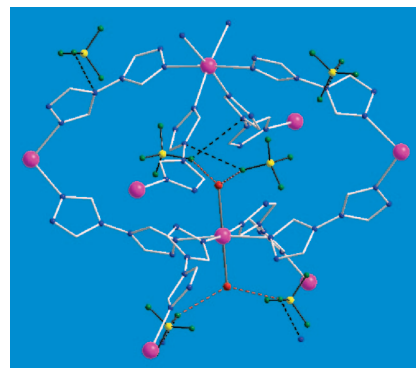


Figure 19. Structure showing the interactions between BF_4^- anions and the coordinated water molecules in **7**. Blue, N; gray, C; purple, Cd; yellow, B; olive, F.

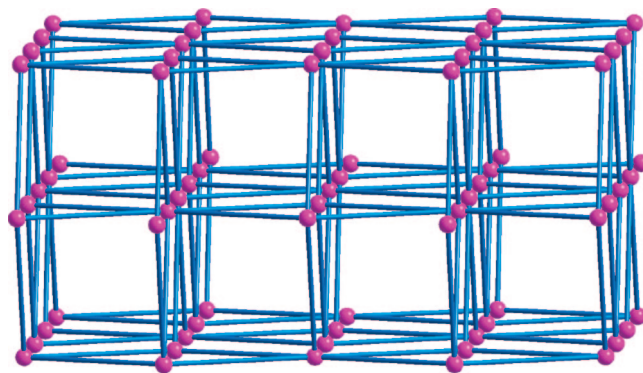


Figure 20. 3D $(4^26^4)(4^76^88^2)$ topology of **7**. Purple, Cd.

$\text{N}(\text{CN})_2^-$ anions exist in the self-assembly of $\text{Cd}(\text{BF}_4)_2$ and btr in **7**, an analogous compound **8** was obtained. The X-ray crystal diffraction reveals that with $\text{N}(\text{CN})_2^-$ instead of coordination water molecules the coordination network remains in the same topology (see Supporting Information).

Role of Anions and Metal Centers in the Construction of the Molecular Architecture. It is noteworthy that a variety of framework structures can be achieved on the basis of the btr ligand with four potentially coordinated N atoms as building blocks and the M(II) ($\text{M} = \text{Cu}$ and Cd) transition metal ion centers. From these results, the choice of anions and metal centers are clearly critical in determining the binding fashions of the btr ligand, as well as the resultant extended networks of MOFs. For example, when we use the Cu(II) as the metal center, and the short bridge SCN^- was added as another co-counter-anion with BF_4^- , a 2D grid compound **2** and a 1D left-handed helical chain compound **3** were isolated from the same crystallization. Just as in compound **1**, the btr acted as a common bidentate $\mu_{1,1}$ -bridged ligand (mode IV) in **2**, which had the isostructure with **1**. The dihedral angles of the two triazole cycles in **1** and **2** are equal to 80.8 and 86.0°; thus, the coordination modes III and IV are different. However, btr ligands adopted not only the N1,N1' bridging fashion but also the solely N1 coordination mode (mode I) in **3**; as a result, a 1D helical chain was isolated, which was unexpected. The isolation of compounds **2** and **3** stressed the significant influence that small changes in anions can have upon the network architectures in the Cu(II) system. Changing the BF_4^- anion to NO_3^- had led to the discovery of a unique 3D compound **4**, where the btr exhibited the very unusual N1,N1',N2 bridging mode (mode V) and the N1,N1' bridging fashion at the same time. To our best knowledge, this is an unprecedented example of μ_3 - and

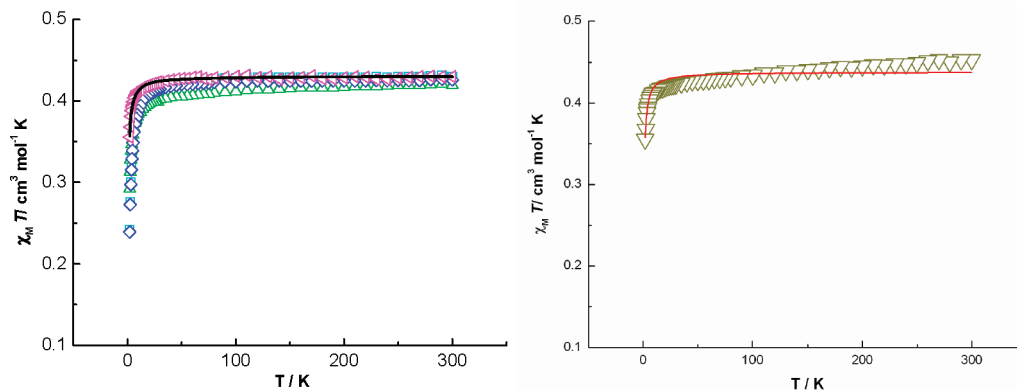


Figure 21. Thermal dependence of the $\chi_M T$ curves for **1** (green), **2** (blue), **3** (purple), **4** (yellow), and **5** (cyan); black and red lines represent the best fitting for **3** and **4**, respectively.

μ_2 -btr simultaneity in a single system in triazole-metal complexes. Not surprisingly, a completely different 3D compound **5** was obtained when the ClO_4^- anion was used instead of the NO_3^- . Only bidentate $\mu_{1,1'}$ -bridged btr ligands could be found in **5**, which shows the α -polonium-like structures.

To further our understanding of the controlled assembly of metallosupramolecules, we changed the metal center from Cu(II) to Cd(II). Upon addition of the anion ClO_4^- , **6** had the same coordination numbers for metal centers and the same space group but significantly different topology for the coordination networks when compared with **5**. As a matter of fact, two types of btr participation were observed in **6** ($\mu_{1,1'}$ -bridging and $\mu_{1,2}$ -bridging (mode II)) whereas only the $\mu_{1,1'}$ -bridging mode in **5**. This may be due to the different coordination nature of the metal centers. In contrast to the anion ClO_4^- , the reaction of BF_4^- with btr formed a 3D microporous MOF **7**, where btr adopted only the N1,N1' bridging fashion. It is easy for us to understand that the coordination polymer networks of **7** remarkably differ from the 2D compound **1** because of the different metal center. While $\text{N}(\text{CN})_2^-$ anions exist in the self-assembly of $\text{Cd}(\text{BF}_4)_2$ and btr in **7**, an isotopological compound **8** was obtained. However, in this Cd(II) system, no other new complex was obtained that can alter the coordination mode of btr and give a distinct topology, just as the phenomena observed in the Cu(II) system (such as compound **3**). This may be also attributed to the different coordination properties of the metal centers, acting as the different mediators in the self-assembly process of the coordination frameworks.

The anions adopt very specific stacking in the heteroaromatic frame, which exhibit anion- π interactions. In the structure of **2**, the $\text{O} \cdots \text{centroid}$ of triazole cycle distance is 3.241 Å and the angle of the $\text{O}-\text{H} \cdots \text{centroid}$ is 123.62°, which show weak hydrogen bonding interactions between H_2O and triazole. In the structure of **4**, **6**, **7**, and **8**, the weak anion- π interactions are observed. The $\text{O} \cdots \text{centroid}$ distances in the structure of **4** and **6** are 3.025 and 3.148 Å, while the $\text{F} \cdots \text{centroid}$ distances in the structure of **7** and **8** are 3.139 and 3.162 Å, respectively. There exists $\text{CN} \cdots \pi$ interaction in **8**, and the $\text{CN} \cdots \text{centroid}$ distance is 3.157 Å. Those types of interactions also justify that the bitriazole is a versatile ligand.

The foregoing facts undoubtedly exhibit that the anions and the metal centers play a controlling role in the molecular tectonics of the MOFs. The results suggest that the rational choice of the anions and the metal centers would be an effective way to construct novel metal-triazolate coordination polymers. This clearly has wider implications for research in coordination networks.

Magnetic Properties. Informative magnetic susceptibility measurements of **1–5** have been performed on a Quantum Design MPMS-5S SQUID magnetometer in the 2–300 K temperature range (Figure 21). The diamagnetic correction was evaluated by using Pascal's constants. The $\chi_M T$ values are in the range of 0.416–0.453 $\text{cm}^3 \text{K mol}^{-1}$ for **1–5** at room temperature, which are expected spin-only values for an isolated Cu(II) ion. The $\chi_M T$ values of the five compounds decreased at low temperatures, showing that antiferromagnetic exchange interactions occur in these compounds. The linear fit via $\chi_M = C/(T - \theta)$ reveals a Curie–Weiss behavior over 2–300 K with $C = 0.42, 0.43, 0.43, 0.45, 0.43 \text{ cm}^3 \text{mol}^{-1} \text{K}$ and $\theta = -1.4, -1.1, -0.37, -1.96, -1.01 \text{ cm}^{-1}$ for **1–5**, respectively (see Supporting Information). The negative θ values further confirm that compounds **1–5** are weakly antiferromagnetic.

Compound **3** has an isolated linear structure, and the magnetic susceptibilities of **3** may be treated by a uniform $S = 1/2$ infinite chain model that takes into account the possible chain breaking [the Hamiltonian being $\hat{H} = -2J\sum(S_i \cdot S_{i+1})$] derived by Bonner and Fisher.¹⁹ The best fit parameters are $J = -0.22 \text{ cm}^{-1}$, $g = 2.14$, $\chi_p = 0.016$, and $R = 2.92 \times 10^{-5}$ ($R = \sum[(\chi_M)^{\text{obs}} - (\chi_M)^{\text{calc}}]^2 / [(\chi_M)^{\text{obs}}]^2$). In **3**, copper(II) ions are bridged by btr ligands with a neighbor $\text{Cu} \cdots \text{Cu}$ distance of 9.083 Å; the exchange interaction through the pathway provided by btr can be expected to be weak, which results in a small J value. **4** can be considered as a complex with a dinuclear unit as building block, and the $\text{Cu} \cdots \text{Cu}$ distance is 4.084 Å. The magnetic data has been fitted using the Bleaney–Bowers expression based on the Hamiltonian $\hat{H} = -JS_A \cdot S_B$ with $S_A = S_B = 1/2$, and the exchange interaction between the dinuclear units may be treated as an intermolecular exchange zJ' by a molecular field model. The best fit parameters are $J = -0.19 \text{ cm}^{-1}$, $g = 2.16$, $zJ' = -0.025$, and $R = 6.80 \times 10^{-6}$ ($R = \sum[(\chi_M)^{\text{obs}} - (\chi_M)^{\text{calc}}]^2 / [(\chi_M)^{\text{obs}}]^2$).

Conclusion

To provide a facile approach to control the assembly of 1D, 2D, and 3D extended solids, we have investigated a series of novel btr-M(II) ($M = \text{Cu}$ and Cd) complexes with a variety of 1D, 2D, and 3D frameworks, and novel topologies have been obtained. Subsequent preparation and structural characterization of the above complexes have indeed shown that novel types of bridged modes can be extended through this approach, and this offers the possibility to control the formation of such network structures by varying the anions and the metal centers.

This work was also undertaken to obtain more information on the coordination of the btr ligand, such as that compound **4**

is the first example of μ_3 - and μ_2 -btr simultaneity in a single system in triazole-metal complexes. Accordingly, our present findings will further enrich the crystal engineering strategies and offer the possibility of controlling the formation of the desired network structures; further efforts along this perspective are underway in our laboratory.

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Supporting Information Available: X-ray crystallographic files in CIF format and additional figures for **1–8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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