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Pillar-layered Zn–triazolate–carboxylate frameworks tuned by the bend angles of ditopic ligands

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ABSTRACT

In the utilization of three ditopic ligands with different bend angles as pillars, we reported herein three pillar-layered Zn–triazolate–carboxylate frameworks, namely, $[Zn_2(ATRZ)_2(BDC)]_n$ (**1**), $[Zn_2(ATRZ)_2(TPDC)]_n \cdot 2n$DMF (**2**) and $[Zn_2(ATRZ)_2(ADDC)]_n$ (**3**) (ATRZ = 3-amino-1,2,4-triazole, H_2BDC = 1,4-benzenedicarboxylic acid, H_2TPDC = 2,5-thiophenedicarboxylic acid, and H_2ADDC = 1,3-adamantanedicarboxylic acid). Single crystal structural analyses demonstrate that different geometries of ditopic carboxylate pillars not only result in Zn–ATRZ layers adopting various corrugated configurations, but also give rise to 3,4-connected self-interpenetrated net of **1** and non-interpenetrated nets of **2** and **3**. All these compounds exhibit high thermal stability and blue photoluminescence.

Crystalline metal–organic frameworks (MOFs) have attracted tremendous interest in the past decades due to their potential applications in gas storage/separation, heterogeneous catalysis, drug delivery and so on [1]. Among various approaches to construct porous MOFs, pillared-layer method is promising since the layer structural motif is usually not affected by the alteration of the pillars, but 1D, 2D, or even 3D open channels may be controlled and adjusted by use of different pillars [2,3]. Moreover, the introduction of functional pillars can also produced available chemical and physical properties such as hydrophilic/hydrophobic character, hydrogen bonding, and open metal sites [4,5].

One of the most rational methods to construct pillared-layer MOF structures is to apply rigid carboxylate ligands to bridge 2D layers formed by metal ions and amines [6,7]. The rigid carboxylate ligands have a great ability to adopt different bonding modes and satisfy many metal coordination preferences, which undoubtedly enrich the structural diversity of MOFs with pillared-layer structures. Take the 2D layer into account, except the well-known metal-pyridine system, metal-1,2,4-triazolate motifs are of great interest [8,9]. Up to now, a lot of 2D metal–triazolate networks exhibiting diverse topologies have been reported [10].

As an extension of our systematic investigation on metal-1,2,4-triazolate coordination frameworks [11–13], we speculate that the introduction of rigid carboxylate ligands to the 2D metal–triazolate system may be a feasible way to construct 3D porous pillared-layer frameworks. In our strategy, three rigid ditopic carboxylate ligands with different bend angles, that is, the 1,4-benzenedicarboxylic acid (H_2BDC), 2,5-thiophenedicarboxylic acid (H_2TPDC), and 1,3-adamantanedicarboxylic acid (H_2ADDC) were chosen as the starting materials together with Zn salt and 3-amino-1,2,4-triazole (ATRZ). Under the hydrothermal conditions, a series of fluorescent 3D pillared MOFs were successfully synthesized, namely, $[Zn_2(ATRZ)_2(BDC)]_n$ (**1**), $[Zn_2(ATRZ)_2(TPDC)]_n \cdot 2n$DMF (**2**) and $[Zn_2(ATRZ)_2(ADDC)]_n$ (**3**).

The hydrothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$, ATRZ and corresponding ditopic carboxylate ligands in DMF–water mixtures at 120 °C or 150 °C afforded compounds **1**–**3** [14], and they were analyzed by single crystal X-ray crystallography study, X-ray power diffraction, elemental analysis, infrared absorption spectra, and thermogravimetric analyses. The powder X-ray diffraction patterns of compounds **1**–**3** are well consistent with the simulated ones on the basis of single crystal structures, indicating the phase purity of the as-synthesized samples (Fig. S1). FT-IR spectra display characteristic absorption band for the main functional groups of complexes **1**–**3** (Fig. S2). The strong and broad peaks around 3400 cm^{-1} indicate the presence of $-NH_2$ group. The bands in 3010–3135 cm^{-1} and 1170–1300 cm^{-1} are related to ν(C–H) and ν(C–N) or ν(N–N) of the ATRZ ligand. Moreover, the absorption bands in the range of 1340–1630 cm^{-1} are assigned to the ν_{as}(C–O) and ν_{sym}(C–O) of carboxylate groups.

Single crystal analysis shows that compound **1** crystallizes in the tetragonal *P*4/*ncc* space group [15]. One zinc ion, one tridentate ATRZ ligand, and one BDC anion are observed in the asymmetric unit (Fig. S3(a)). The Zn center is 4-coordinated to one BDC oxygen atom and three nitrogen atoms from three individual triazolate ligands. Each ATRZ ligand binds to three Zn ions through typical $\mu_{1,2,4}$-bridging fashion, which leads to a two-dimensional Zn–triazolate layer (Fig. S4(a)) showing 4.8^2 topology as that of the known copper(I) and silver(I) triazolates [10] from the topological point of view. However, this 2D Zn–ATRZ layer is not planar but corrugated due to the existence

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of tetrahedrally coordinated Zn centers (Zn–N = 1.981(5)–2.045(5) Å and N–Zn–N = 98.9(2)–107.7(2)°). The 2D layers are connected by linear BDC pillars via the Zn–O coordinated bonds (Zn–O = 1.929(5) Å and O–Zn–N = 98.5(2)–133.2(3)°) giving an ABAB-stacking sequence along the *c*-axis direction, which ultimately generate the 3D pillar-layered structure of **1** (Fig. 1(a)). The linear BDC pillars are not perpendicular to the layer, which cross each other to form a self-interpenetration. In the view of topology, BDC ligands can be viewed as linkers. The tetrahedrally coordinated Zn(II) and tridentate ATRZ ligand can be simplified as 4- and 3-connected nodes (Fig. 1(b)), respectively, producing a (3,4)-connected self-penetrated net with $\{4\cdot8^2\cdot10^3\}\{4\cdot8^2\}$ point symbol.

When angular TPDC ditopic ligand was utilized instead of linear BDC, another pillar-layered compound (**2**) crystallizing in the orthorhombic *Pnma* space group [15] was obtained. The asymmetric unit of **2** contains one tetrahedral Zn center, one ATRZ, one TPDC and one guest DMF molecule (Fig. S3(b)). The Zn–N/O bond lengths and O/N–Zn–O/N angles are of 1.942(2)–1.995(3) Å and 98.11(10)–121.04(10)°, respectively. Similar to **1**, Zn and ATRZ link each other to give a $4\cdot8^2$ layer (Fig. S4(b)), which are connected by TPDC to give the 3D pillar-layered framework of **2** (Fig. 1(c)). Different to **1**, the 152° angle of TPDC effectively prevents the interpenetration. TPDC pillars basically parallel to each other, and support the layer vertically. Although the Zn atom and ATRZ ligand can also be regarded as 4- and 3-connected nodes like compound **1**, the angular TPDC linker generates a different topological net with the point symbol of $\{4\cdot6\cdot8\}\{4\cdot6^2\cdot8^3\}$ (Fig. 1(d)). 1D channels exist in this framework along the *a*-axis direction with the dimensions of about 5.5 × 8.5 Å^2, which are fully occupied by the guest DMF molecules.

To further understand the influence of bend angles of ditopic ligands on the pillar-layered framework, 1,3-adamantanedicarboxylic acid (H_2ADDC) was selected. As expected, the third pillar-layered framework (**3**) was produced. Compounds **2** and **3** both crystallize in the *Pnma* space group [15], however, the change of ditopic pillar ligands led to a dramatic variation of the unit cell parameters (*a* = 10.7020(3) Å, *b* = 26.6173(11) Å, *c* = 8.5189(4) Å for **2**; *a* = 12.89620(10) Å, *b* = 26.2341(2) Å, *c* = 13.15290(10) Å for **3**). Two unique Zn atoms and two ATRZ ligands link each other to form a 2D Zn–ATRZ layer (Fig. S4(c)), which are further connected by two unique ADDC anions to give the pillar-layer framework of **3** with the same topology of **2** (Fig. 1(e) and (f)). However, 1D channels are basically blocked by the adamantane groups.

Clearly, the bend angles of ditopic carboxylate ligands tuned not only the structure of 2D Zn–ATRZ layer, but also the topology of the whole pillar-layered frameworks. For the 2D layers in compounds **1**–**3**, the torsion angle between two adjacent four-membered rings varies from 74.9°, 86.1° to 82.1°, which are comparable to the similar pillar-layered frameworks constructed from other ditopic dicarboxylate pillars [16–18]. Also the distances between two near layers are changed with the bend angles of pillars, which are 9.2 Å for **1**, 8.1 Å for **2**, and 7.4 Å for **3**. The most distinctive feature is that the 3,4-connected topologies of these frameworks are effectively adjusted by the pillar ligands, which is interesting for further design of novel pillar-layered compounds.

TGA results (Fig. S5) indicate that three pillar-layered frameworks all show high thermal stability. Compound **1** can stabilize up to about 400 °C, and a following weight loss corresponding to the decomposition of ATRZ and BDC ligands. The residue should be ZnO (exp. 47.53%; calcd. 46.50%). Two separate weight losses are observed for compound **2**. The first weight loss (22.60%) occurring in the temperature range of about 120–225 °C is attributed to the loss of free DMF molecules (calcd. 23.84%). The second weight loss of 33.80% (calcd. 33.51%) between 225 and 620 °C corresponds to the loss of TPDC and ATRZ ligands. Like

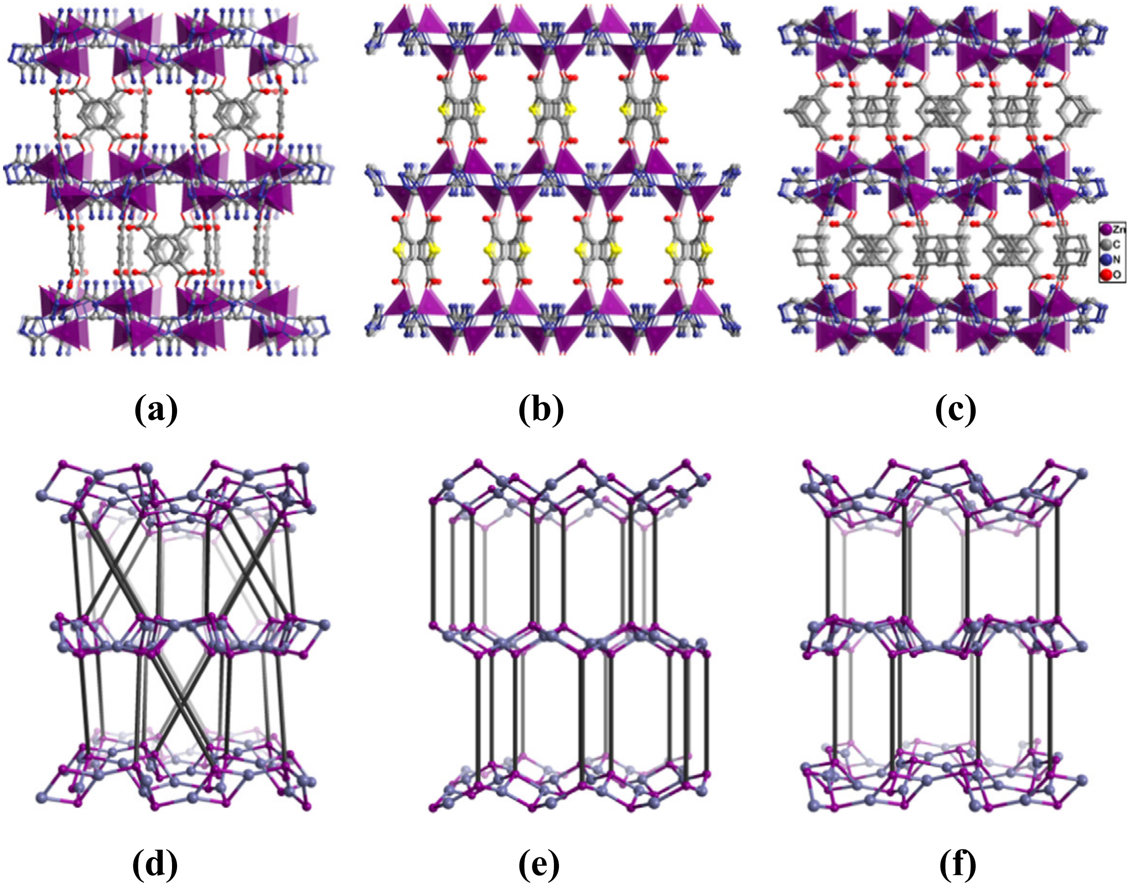

Fig. 1. 3D pillar-layered frameworks and their topological schematic plots: (a) and (d) for **1**; (b) and (e) for **2**; (c) and (f) for **3**.