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Syntheses, characterizations, and properties of five coordination compounds based on ligand tetrakis (4-pyridyloxymethylene)methane

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Abstract: A nonplanar tetrahedral pyridine ligand has been synthesized and applied to assemble five metal-organic frameworks (MOFs) with novel structural features under solvothermal conditions, namely, $\{[Cu_2(TPOM)(adi)_2](H_2O)_4\}_n$ (**1**), $\{[Zn_2(TPOM)(glu)_2](H_2O)_8\}_n$ (**2**), $\{[Cd_2(TPOM)(1,4\text{-chdc})_2(H_2O)_4](H_2O)_4\}_n$ (**3**), $\{[Ni(TPOM)(suc)(H_2O)_2](H_2O)_2\}_n$ (**4**), and $\{[Zn_2(TPOM)(1,4\text{-chdc})(NO_3)_2](H_2O)_2\}_n$ (**5**) (TPOM = tetrakis(4-pyridyloxymethylene)methane, adi = adipic acid, glu = glutaric acid, chdc = 1,4-cyclohexanedicarboxylic, suc = succinic acid). These compounds were characterized by elemental analyses, IR spectra and X-ray single-crystal diffractions. Compounds **1** and **3** reveal 3-fold interpenetrating 3D frameworks with *sqc969* and new topology, while compound **2** possesses a 2-fold interpenetrating 3D framework with *qtz* topology. Compound **4** exhibits a non-interpenetrating 3D structure with the extension of the cage structure, in which there are only two pyridine nitrogen atoms in TPOM involved in the coordination. It is different from compounds **1-3**, showing that they may take distinct coordination modes under different conditions. In compound **5**, the coordination mode of TPOM is

also different from those of compounds **1-3**, it is a 2D structure with 2-fold interpenetrating framework.

Introduction

MOFs which emerge as a very promising type of materials[1] have attracted more and more research interest and become one of the important research fields of inorganic and organic chemistry. Recently, a large number of MOFs based on mixed ligands have been subsequently reported,[2] and most of them are constructed utilizing the ligands that contains nitrogen and/or carboxylic acid. Novel structures can be obtained using mixed ligands, especially when the ligands are flexible.[3,4] So far, MOFs containing mixed ligands still need the accumulation of plenty of research work, because polytype ligands and complex coordination modes make it more difficult for the final composition and spatial structures to be predicted. What's more, the syntheses of metal-organic frameworks can be influenced by many factors such as the nature of metal ions and linkers, condition of reactions, counterions, as well as molecular interaction including hydrogen bonds and π-π interaction that can be used to control the process of self-assembly.[5] In order to get novel structures for required products, much effort has been dedicated to controlling the assembled motifs and modifying the building blocks via selecting different metal ions and organic ligands.[6]

Among the N-donor bridging ligands, TPOM is a good candidate for the construction of MOFs with diverse structures, since four pyridine N atoms of TPOM ligand can serve as four potential coordination nodes and the four pyridine groups can freely twist around the quaternary carbon atom.[7] In this paper, we report five new metal–organic frameworks based on TPOM and other auxiliary ligands, namely $\{[Cu_2(TPOM)(adi)_2]\cdot(H_2O)_4\}_n$ (**1**), $\{[Zn_2(TPOM)(glu)_2]\cdot(H_2O)_8\}_n$ (**2**), $\{[Cd_2(TPOM)(1,4\text{-chdc})_2(H_2O)_4]\cdot(H_2O)_4\}_n$ (**3**), $\{[Ni(TPOM)(suc)(H_2O)_2]\cdot(H_2O)_2\}_n$ (**4**), and $\{[Zn_2(TPOM)(1,4\text{-chdc})(NO_3)_2]\cdot(H_2O)_2\}_n$ (**5**). In addition, we also describe the details of their characterizations and thermal stabilities.

Experimental section

Materials and Measurements. All commercially available chemicals were of reagent grade and used as received without further purification. TPOM ligand was prepared by literature methods.[8] IR absorption spectra of the compounds were recorded in the range of 400-4000 cm^{-1} on a Nicolet (Impact 410) spectrometer with KBr pellets. C, H and N analyses were carried out with a Perkin Elmer 240C elemental analyzer. Thermogravimetric analysis (TGA) was performed under a N_2 atmosphere with a heating rate of 10 $K\cdot min^{-1}$ by using a Perkin Elmer thermogravimetric analyzer, with an empty Al_2O_3 crucible being used as the reference. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Mo-Kα radiation (λ = 0.71073 Å), in which the X-ray tube was operated at 40 kV and 40 mA.

Synthesis of compound $\{[Cu_2(TPOM)(adi)_2]\cdot(H_2O)_4\}_n$ (1). A mixture of $Cu(NO_3)_2\cdot 6H_2O$ (29.5 mg, 0.1 mmol), H_2adi (14.6 mg, 0.1 mmol), and TPOM (22.2 mg, 0.1 mmol) was dissolved in mixed solution consisting of H_2O (6 ml) and DMF (3 ml). The reaction mixture was sealed in a PTFE-lined stainless-steel vessel under autogenous pressure and heated at 120 °C for 3 days. Large quantities of blue block crystals were obtained after cooling, and crystals were filtered off, washed with quantities of distilled water, and dried under ambient conditions. The yield of the reaction was ca. 67% (based on TPOM ligand). Calcd for $C_{37}H_{48}Cu_2N_4O_{16}$: C, 47.64%; H, 5.15%; N, 6.01%. Found: C, 47.61%; H, 5.20%; N, 5.93%. Main infrared spectra data (KBr, cm^{-1}): 3450 (s), 2946 (w), 2365 (w), 1613 (s), 1509 (m), 1468 (w), 1396 (w), 1295 (m), 1208 (m), 1037 (m), 877 (w), 836 (m), 545 (w).

Synthesis of compound $\{[Zn_2(TPOM)(glu)_2]\cdot(H_2O)_8\}_n$ (2). The preparation of compound **2** was similar to that of **1** except that $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol) and H_2glu (13.0 mg, 0.1 mmol) were used instead of $Cu(NO_3)_2\cdot 6H_2O$ and H_2adi, respectively. Large quantities of colorless lump crystals were obtained after cooling, and crystals were filtered off, washed with quantities of distilled water, and dried under ambient conditions. The yield of the reaction was ca. 52% (based on TPOM ligand). Calcd for $C_{35}H_{52}N_4O_{20}Zn_2$: C, 42.91%; H, 5.31%; N, 5.72%. Found: C, 42.76%; H, 5.23%; N, 5.79%. Main infrared spectral data (KBr, cm^{-1}): 3430 (s), 2968 (w), 1612 (s), 1511 (m), 1467 (w), 1439 (w), 1399 (m), 1342 (w), 1294 (s), 1212 (s), 1033 (s), 875 (w), 842 (m), 672 (w), 537 (w).

Synthesis of compound $\{[Cd_2(TPOM)(1,4\text{-chdc})_2(H_2O)_4]\cdot(H_2O)_4\}_n$ (3). A mixture of $Cd(NO_3)_2\cdot6H_2O$ (34.4 mg, 0.1 mmol), 1,4-H_2chdc (17.2 mg, 0.1 mmol), and TPOM (22.2 mg, 0.1 mmol) was dissolved in mixed solution consisting of H_2O (6 ml) and DMF (3 ml). The reaction mixture was sealed in a PTFE-lined stainless-steel vessel under autogenous pressure and heated at 120°C for 3 days. Large quantities of colorless lump crystals were obtained after cooling, and crystals were filtered off, washed with quantities of distilled water, and dried under ambient conditions. The yield of the reaction was ca. 43% (based on TPOM ligand). Calcd for $C_{41}H_{60}Cd_2N_4O_{20}$: C, 42.67%; H, 5.20%; N, 4.86%. Found: C, 42.71%; H, 5.24%; N, 4.80%. Main infrared spectra data (KBr, cm^{-1}): 3063 (w), 2932 (w), 2857 (w), 1605 (s), 1569 (m), 1538 (m), 1507 (m), 1433 (m), 1401 (m), 1293 (s), 1211 (s), 1023 (m), 823 (w), 778 (w), 536 (w), 472 (w).

Synthesis of compound $\{[Ni(TPOM)(suc)(H_2O)_2]\cdot(H_2O)_2\}_n$ (4). A mixture of $Ni(NO_3)_2\cdot6H_2O$ (29.1 mg, 0.1 mmol), H_2suc (8.61 mg, 0.1 mmol), and TPOM (22.2 mg, 0.1 mmol) was dissolved in mixed solution consisting of H_2O (6 ml) and DMF (3 ml). The reaction mixture was sealed in a PTFE-lined stainless-steel vessel under autogenous pressure and heated at 120°C for 3 days. Large quantities of light green lump crystals were obtained after cooling, and crystals were filtered off, washed with quantities of distilled water, and dried under ambient conditions. The yield of the reaction was ca. 52% (based on TPOM ligand). Calcd for $C_{29}H_{36}N_4NiO_{12}$: C, 50.34%; H, 5.21%; N, 8.10%. Found: C, 50.30%; H, 5.24%; N, 8.13%. Main infrared spectra data (KBr, cm^{-1}): 3385 (s), 2951 (w), 2908 (w), 1605 (s), 1521 (m), 1481 (m), 1382 (m), 1280 (s), 1210 (s), 1206 (s), 1038 (s), 815 (s), 73 3(w), 670 (m).

Synthesis of compound $\{[Zn_2(TPOM)(1,4\text{-chdc})(NO_3)_2]\cdot(H_2O)_2\}_n$ (5). A mixture of $Zn(NO_3)_2\cdot6H_2O$ (29.7 mg, 0.1 mmol), 1,4-H_2chdc (17.2 mg, 0.1 mmol), and TPOM (22.2 mg, 0.1 mmol) was dissolved in mixed solution consisting of H_2O (6 ml) and DMF (3 ml). The reaction mixture was sealed in a PTFE-lined stainless-steel vessel under autogenous pressure and heated at 120°C for 3 days. Large quantities of colorless lump crystals were obtained after cooling, and crystals were filtered off, washed with quantities of distilled water, and dried under ambient conditions. The yield of the reaction was ca. 50% (based on TPOM ligand). Calcd for $Zn_2C_{33}H_{38}N_6O_{16}$: C, 43.81%; H, 4.20%; N, 9.29%. Found: C, 43.76%; H, 4.25%; N, 9.26%. Main infrared spectra data (KBr, cm^{-1}): 3430 (s), 2968 (w), 1612 (s), 1511 (m), 1467 (w), 1439 (w), 1399 (m), 1342 (w), 1294 (s), 1212 (s), 1033 (s), 875 (w), 842 (m), 672 (w), 537 (w).

X-ray crystallography. Single crystals of **1-5** were prepared by the methods described in the synthetic procedure. X-ray crystallographic data of **1-5** were collected at room temperature using epoxy-coated crystals mounted on glass fiber. The water molecules of compounds **2** and **5** were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules.[9] The numbers of solvent molecules in compounds **2** and **5** were obtained by element analyses. X-ray crystallographic data of these complexes were collected on a Bruker Apex Smart CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Structure solutions were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedures based on F^2 values.[10] The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. Compounds **1-5** crystal data and structure refinement parameters are listed in Table 1, and the main bond lengths (Å) and bond angles (°) are listed in Table S1.

Results and discussion

Crystal structure of compound 1. Single crystal diffraction data shows that compound **1** possesses a three-dimensional (3D) structure and crystallizes in monoclinic crystal system of *P*42/*n*. The asymmetric unit contains 1/2 Cu atom, 1/4 TPOM ligand, 1/2 adipic acid ligand and one solvent water molecule, and Cu sits on the twofold axis, and the central carbon of TPOM lies on the fourfold axis (Figure 1a). The coordination geometry about each Cu atom is a quadrilateral plane, with two O atoms come from adipic acid ligands and two N atoms come from TPOM ligands. The bond lengths of Cu1-O and Cu1-N are 1.951(4) Å and 2.011(4) Å, respectively, which are all similar to the values found in other Cu compounds.[11]

In compound **1**, the adipic acid adopts bis-monodentate coordination modes to bridge two Cu atoms to form a chain, which are connected by the TPOM ligands to generate 3D framework (Figure 1b). A topology analysis reveals that the structure can be represented as a (4,4)-connected node 3D network topology, with the Schäfli symbol $\{6^4.8^2\}_2\{6^6\}$ and *sqc969* topology type. The potential voids are large enough to generate a 3-fold interpenetrating architecture (Figure 1c).

According to the studies by Ryan et al.,[12] the distortion of TPOM can be assessed by comparing the N···C_{core}···N angles defined by the central carbon atom of the TPOM core (C_{core}) and the nitrogen atoms of the pyridyl groups, as well as the torsion angle of C_{core}-CH_2-O-Cpyridyl. In compound **1**, the flexible ligand TPOM adopts a conformation that bears four pyridyl groups in a highly distorted tetrahedral orientation. The angles of N···C_{core}···N are 3×83.760° and 3×123.666°, indicating that the ligand deviates significantly from tetrahedral geometry. The -CH_2O spacers that connect each pyridyl group to the core adopt orientations that are not fully extended, with C_{core}-CH_2-O-C torsion angles being 4×117.642°.

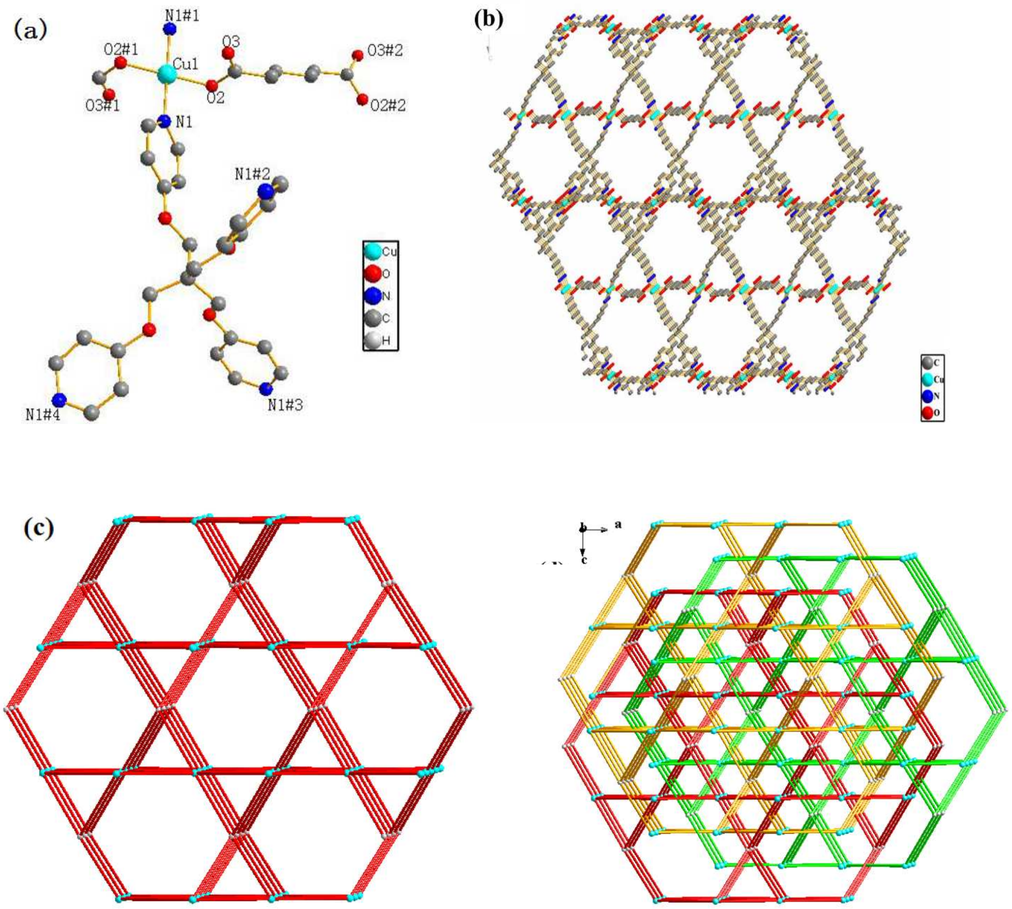


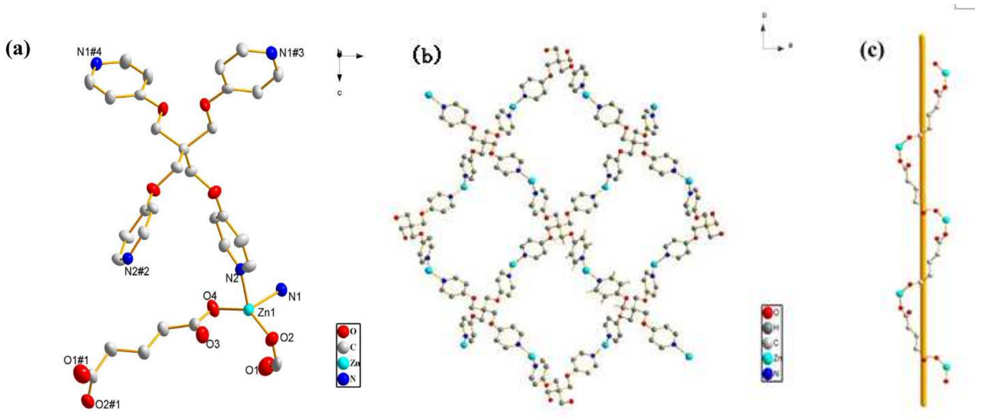
Figure 1. (a) Coordination environment of compound **1**. The hydrogen atoms are omitted for clarity (50% ellipsoid probability. Symmetry codes: #1 = 1 - *x*, 1 - *y*, -*z*; #2 = 1.5 - *x*, 0.5 - *y*, *z*; #3 = 1.5 - *x*, 1.5 - *y*, *z*; #4 = 1.5 - *y*, *x*, 1.5 - *z*; #5 = *y*, 1.5 - *x*, 1.5 – *z)*. (b) Views of the 3D network along the b axis. (c) Schematic view of topology (left) and 3-fold interpenetrating structure (right).

Crystal structure of compound 2. Single crystal diffraction data shows that compound **2** crystallizes in orthorhombic crystal system of the $P2_12_12$ space group (chiral space group). The asymmetric unit of **2** contains one independent Zn cation, 1/2 TPOM ligand, one glutaric acid ligand and four solvent-water molecules squeezed by PLATON, and the central carbon of TPOM is located on the twofold axis. As shown in Figure 2a, each Zn atom is four-coordinate with distorted tetrahedral geometry by two carboxylic O atoms (O2, O4) and two nitrogen atoms (N1, N2) from

TPOM ligands. The values of distance for Zn1-O2, Zn1-O4, Zn1-N1 and Zn1-N2 are comparable to those reported in the literature. [13]

If we only consider TPOM ligands, zinc ions connect with TPOM ligands to form latticed two-dimensional planar structures (Figure 2b). Similarly, if we only consider glutaric acid, adjacent zinc ions link with the glutaric acid to form a chiral helical chain (Figure 2c), which connects the adjacent 2D layers to form the 3D framework structure (Figure 2d). A topology analysis reveals that the structure can be represented as a (4,4)-connected node 3D network topology, with the Schäfli symbol $\{6^4.8^2\}$ and *qtz* topology type. The potential voids are large enough to be filled via mutual interpenetration of an independent equivalent framework, resulting in a 2-fold interpenetrating 3D architecture (Figure 2e).

The conformation of TPOM in compound **2** is similar to that in compound **1**. The N···C$_{core}$···N angles are in the range of 84.715-119.162°, showing that the TPOM ligand in **2** deviates from tetrahedral geometry, and the corresponding C$_{core}$-CH$_2$-O-C torsion angles are 2×117.863° and 2×117.989°.



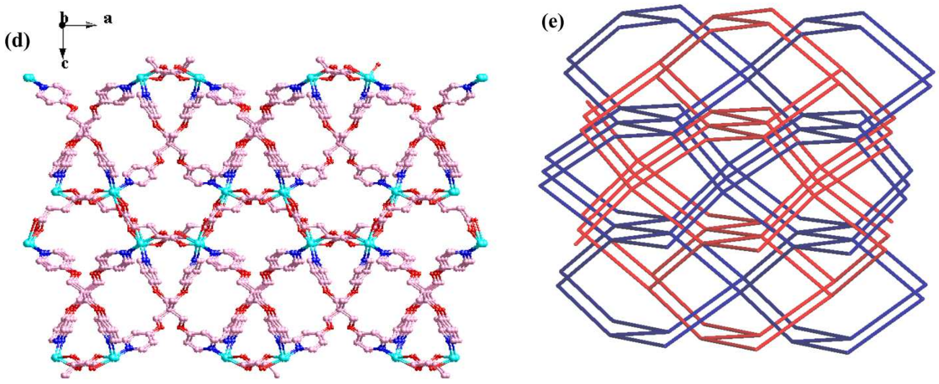


Figure 2. (a) Coordination environment of compound **2**. The hydrogen atoms are omitted for clarity (50% ellipsoid probability).Symmetry codes: #1= -0.5 + *x*, 1.5 - y, 2 - *z*; #2= -*x*, -2 - *y*, *z*; #3= 0.5 - *x*, 0.5 + *y*, -*z*; #4= -0.5 + *x*, 1.5 - *y*, -*z*. (b) View of the 2D network only TPOM ligands are considered. (c) Helical chains of connection of zinc ion and glutaric acid. (d) View of the 3D structure of compound **2**. (e) 2-fold interpenetrating structure of compound **2**.

Crystal structure of compound 3. Single crystal diffraction data shows that compound **3** crystallizes in monoclinic crystal system of the *P2/c* space group. The asymmetric unit contains one Cd ion, 1⁄2 TPOM ligand, one 1,4-chdc^{2-} anion, two coordinated water molecules and two solvent water molecules, the central carbon of TPOM is on the twofold axis (Figure 3a). Cd1 and Cd2 are both six coordination configurations: two pyridine N atoms from TPOM ligands [Cd-N bond lengths varying from 2.321(3) to 2.361(3) Å][21] and four O atoms, of which two come from coordinated water molecules, and the remaining come from carboxylic acid ligands [Cd-O bond lengths varying from 2.269(3) to 2.3671(3) Å][14].

The TPOM ligands and Cd ions connect to each other to form two-dimensional layers (Figure 3b left), which are connected by 1,4-cyclohexanedicarboxylate to give rise to a 3D structure (Figure 3b right). In order to further understand the structure of the compound, we employ the topology analysis, revealing that the structure can be represented as a (4, 4)-connected 3D network (Figure 3c), with the Schäfli symbol $\{5.6^4.8\}\{5^4.6^2\}\{5^4.8^2\}$ and new topology type. As shown in Figure 3d, the potential voids in the single 3D network are big enough to be incorporated with two other identical networks to form a 3-fold interpenetrating network.

Like compounds **1** and **2**, the C_{core}-CH_2-O-C torsion angles of **3** varies from 116.976° to 119.018° which are also no fully extended. The TPOM ligand adopts a highly irregular conformation in which the N···C_{core}···N angles vary from 81.228° to 124.693°.

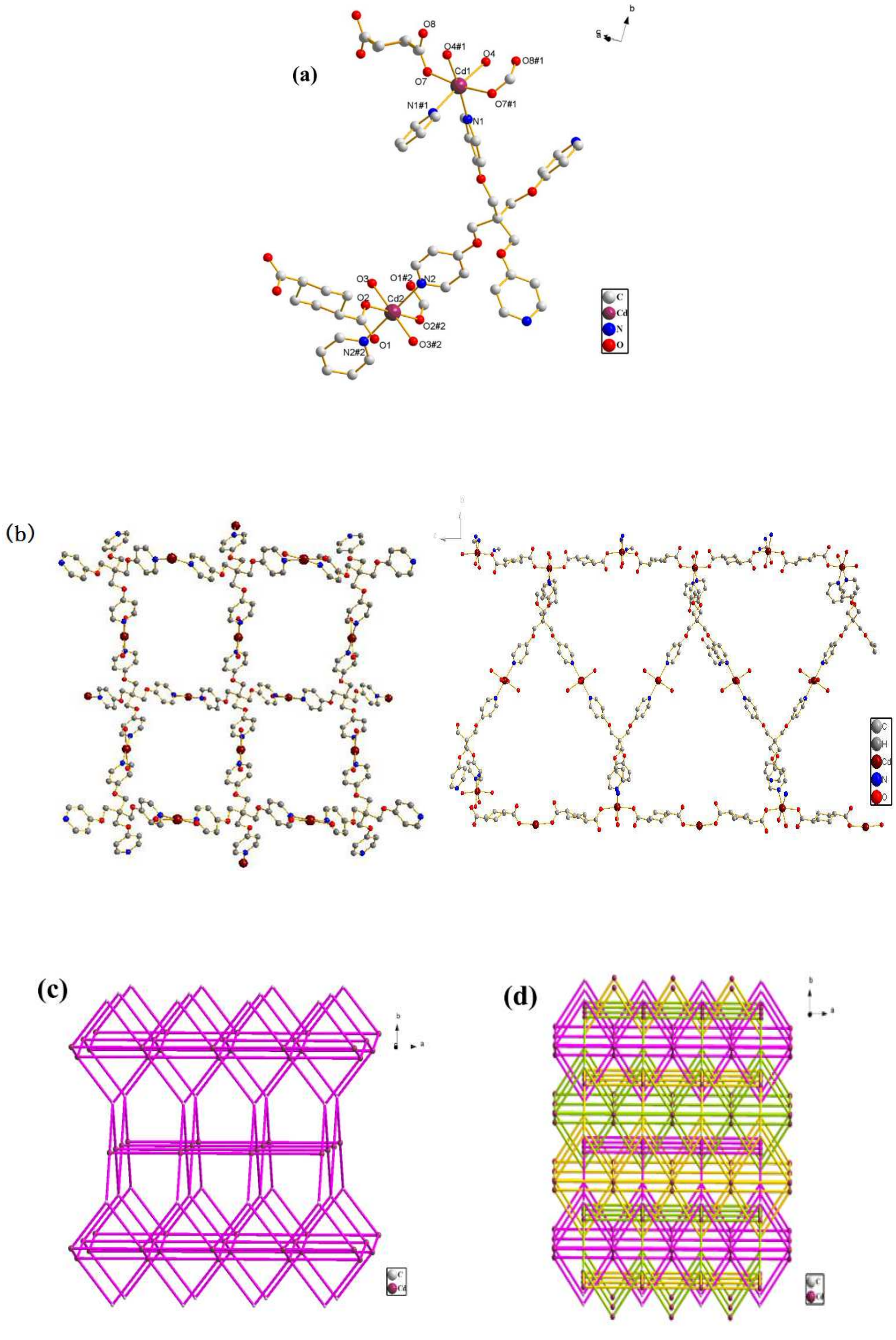


Figure 3. (a) Coordination environment of compound **3**. The hydrogen atoms are omitted for clarity (50% ellipsoid probability). Symmetry codes: #1= 1 - *x*, *y*, 0.5 - *z*; #2= -*x*, -*y*, 1 - *z*. (b) 2D structure chart of Cd connected TPOM (left) and 3D structure (right). (c) Topology of compound **3**. (d) 3-fold interpenetrating topological graph of compound **3**.

Crystal structure of compound 4. Single crystal diffraction data shows that compound **4** crystallizes in monoclinic crystal system of the *P2/c* space group. The asymmetric unit contains 1/2 Ni atom, 1/2 TPOM ligand, 1/2 succinic acid ligand, one coordinated water molecule and one solvent water molecule (Figure 4a). Ni is in a six-coordinated environment which is defined by four O atoms and two N atoms. Ni and the central carbon of TPOM are both on the twofold axis. Thereinto, two O atoms come from succinic acid molecules and the other two come from water molecules, with the Ni-O distance being from 2.0681(19)-2.0990(16) Å[15]. And the two N atoms derive from TPOM ligand, with the Ni-N being 2.1078(18) Å[15]. Although there are four N atoms in the TPOM ligand participating in the coordination in compounds **1-3**, there are only two pyridine N atoms involved in the coordination for compound **4**.

In compound **4**, Ni atoms connect with TPOM to construct a Zig-Zag chain (Figure 4b), the succinic acid link the 1D chain with different propagating direction to form a 3D framework (Figure 4c). By topology analysis, compound **4** can be represented as a *cds* network topology (with the Schäfli symbol $\{6^5.8\}$), and Ni atom and TPOM ligand can be represented as (4,4)-connected nodes. The potential voids are too small to form an interpenetrating architecture (Figure 4d).

In compound **4**, the TPOM ligand adopts a comformation holding the four pyridyl groups in an irregular orientation, the $N\cdots C_{core}\cdots N$ angles range from 81.585° to 124.456°. The $-CH_2O-$ spacers that connect each pyridylphenyl group to the core adopt a conformation that is not completely extended, with $C_{core}-CH_2-O-C$ torsion angles of 117.280° and 117.753°.

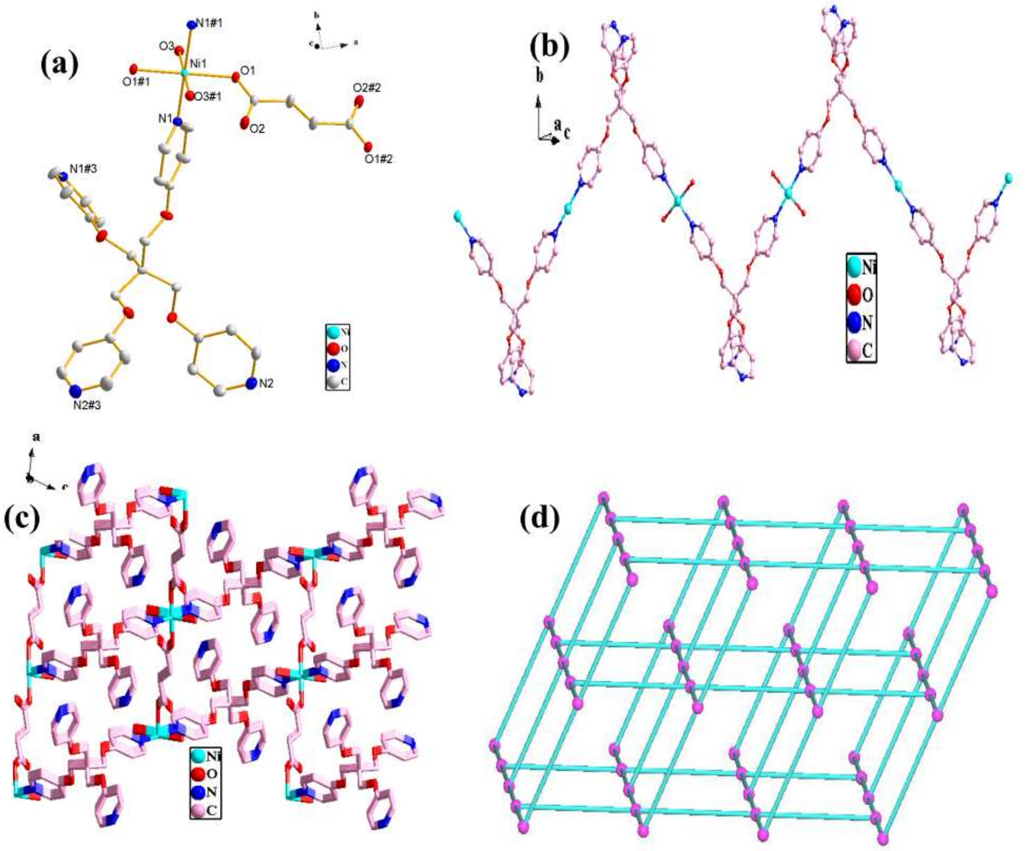


Figure 4. (a) Coordination environment of compound **4**. The hydrogen atoms are omitted for clarity (50% ellipsoid probability). Symmetry codes: #1= 0.5 - *x*, 2.5 - *y*, 1 - *z*; #2= 1 - *x*, 2 - *y*, 0.5 - *z*; #3= -*x*, *y*, 0.5 – *z*. (b) View of the 1D zig-zag chain in compound **4** (the succinic ligands are omitted). (c) The formation of 3D structure of compound **4**. (d) *cds* topological graph of compound **4**.

Crystal structure of compound 5. Single crystal diffraction data shows that compound **5** crystallizes in orthorhombic crystal system of the *Ibam* space group. The asymmetric unit contains one zinc atom, 1/2 TPOM ligand, 1/2 1,4-chdc acid ligand, one NO_3^- anion and one free water molecule that is squeezed by PLATON. Like compound **2**, the central carbon of TPOM is lying on the twofold axis. As shown in the Figure 5a, there are two different coordination environments for Zn(II) ions: Zn1 is in a tetrahedron coordination sphere, which is defined by two O atoms from 1, 4-chdc acid ligands and two N atoms from TPOM ligands. Zn2 is also in a four-coordinated environment where two NO_3^- groups repalce two 1, 4-chdc acid ligands compared with Zn1. The values of distance for Zn-O are in the range of 1.916(2)-2.046(3) Å[13], and those for Zn-N change in the range of 2.035(4)-2.048(3) Å[13], which are comparable to the values found in other reported similar compounds.[21] As is shown in Figure 5b, the TPOM ligand and 1,4-chdc acid ligand link Zn ions to form a 2D framework (Figure 5b). This structure is one of the possible modes of parallel interpenetration illustrated by Batten and Robson[16] (Figure 5c).

In these five compounds, the torsion angles of N···C_{core}···N of compound **5** are the most obvious, which range from 76.148° to 126.216°, showing that the TPOM ligand deviates from tetrahedral geometry. The -CH_2O- spacers that connect each pyridylphenyl group to the core adopt a conformation that is substantially extended with C_{core}-CH_2-O-C torsion angles of 2×141.307° and 2×139.306°.

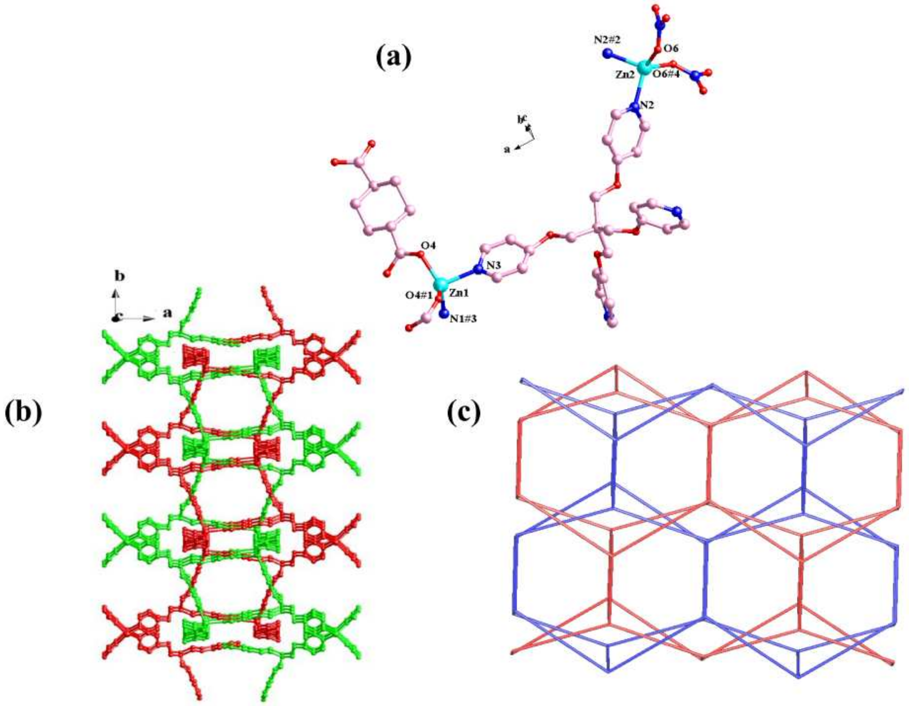


Figure 5. (a) Coordination environment of compound **5**. The hydrogen atoms are omitted for clarity (50% ellipsoid probability). Symmetry codes: #1= x, y, -z+1, #2 = x, -y+2, -z+3/2, #3= -x+1, -y+1, -z, #4= x, -y+2, -z+3/2. (b) 2D graphs of compound **5**. (c) 2-fold parallel interpenetration of compound **5**.

Thermal Analysis and XRD of compounds 1-5. To estimate the stability of the coordination architectures, their thermal behaviors were studied by TGA. As is shown in Figure 6, for compound **1**, a weight loss of 7.73% is observed from 15 to 125 °C which resulted from the loss of the solvent water, followed by a weight loss at 282°C which is attributed to the collapse of molecular skeleton. For compound **2**, the weight loss of 14.83% between 30 and 115°C resulted from the loss of the solvent water, and then the collapse of molecular skeleton occurs at 290°C. For compound **3**, there are two steps of weight loss, of which the first (6.02%) is observed in the range from 30 to 112°C owing to the loss of solvent water. The other occurs after 260°C which is attributed to the loss of coordinated water and the collapse of molecular skeleton occurs. Compound **4** displays three main steps of weight loss, the first step of weight loss (5.18%) in the range 20-115°C can be assigned to the loss of the solvent water, and the second step between 160-240°C is due to the loss of coordinated water, while the finally step is attributed to the collapse of molecular skeleton at higher than 300°C. The TGA curve of **5** is similar to that of **1**, the former step is the loss of free water and the latter is the collapse of molecular skeleton. The experimental values of weight loss of compounds **1-5** is close to the theoretical values (Table 2).

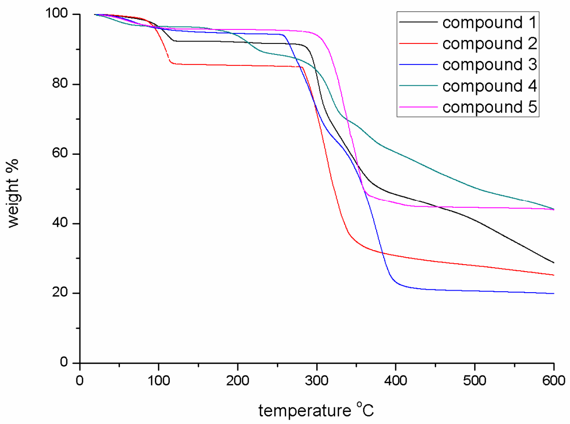


Figure 6. Thermogravimetric analysis plots of compounds **1-5**.

To confirm whether the crystal structures are truly representative of the bulk materials, XRD experiments for **1-5** were carried out. The XRD experimental and computer-simulated patterns of the corresponding complexes are shown in the supporting information (Figures S1-S5), and they show that the bulk synthesized materials are the same as the measured single crystals.

Conclusions

In summary, five new metal-organic frameworks have been successfully synthesized under solvothermal conditions. As we expected, the self-assembly of metal centers, TPOM and carboxylate ligands (adi, glu, suc or chdc) is an effective method to generate aesthetic architectures and topologies. Compounds **1-4** get the 3D structures, while compound **5** possesses a 2D structure through parallel 2-fold interpenetration. The results show that owing to the TPOM ligand containing more coordination sites and its flexible, it is easy to form the structure with high dimension or mutual penetration.

Supporting information available.

Selected bond lengths and angles, simulated, experimental X-ray powder diffraction patterns, and CCDC references: CCDC 973268-973272. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/

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Table 1. Crystallographic data and structure refinement details for compounds **1-5**

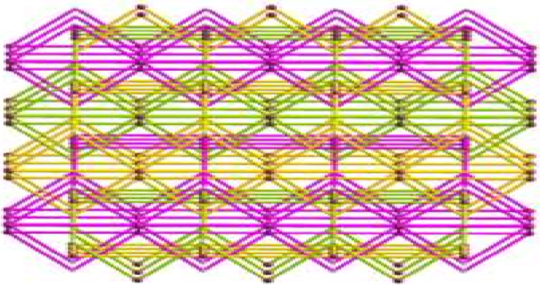
Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{37}H_{48}Cu_2N_4O_{16}$	$C_{35}H_{52}N_4O_{20}Zn_2$	$C_{41}H_{60}Cd_2N_4O_{20}$	$C_{29}H_{36}N_4NiO_{12}$	$Zn_2C_{33}H_{38}N_6O_{16}$
Formula weight	931.87	979.55	1153.73	691.33	906.56
Crystal system	Tetragonal	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	*P42/n*	*P21212*	*P2/c*	*C2/c*	Ibam
a (Å)	15.4019(10)	16.397(3)	11.4622(15)	17.334(2)	32.119(3)
b (Å)	15.4019(10)	18.642(3)	9.4091(12)	9.2474(10)	12.8479(10)
c (Å)	8.4768(11)	7.9656(13)	22.611(3)	20.562(2)	20.8244(16)
β (deg)	90	90	91.698(2)	108.815(4)	90
V (Å3)	2010.9(3)	2434.9(7)	2437.5(6)	3119.9(6)	8593.5(12)
Z	2	2	2	4	8
Dc (g cm^{-3})	1.539	1.336	1.572	1.472	1.344
μ(Mo Ka)(mm^{-1})	1.135	1.058	0.952	0.692	1.182
F(000)	968	1020	1180	1448	3568
Theta min-max (deg)	1.9 , 25.0	2.2, 26.0	1.8, 26.0	2.5, 25.0	2.0,26
Tot., Uniq. Data,	10740,1758	12983, 4784	12579, 4781	7553, 2738	22451, 4343
R(int)	0.034	0.037	0.098	0.053	0.025
Observed data $[I>2\sigma(I)]$	1320	4490	4061	2482	3330
Nref, Npar	1758 , 129	4784, 234	4781, 305	2738, 210	4343, 294
R, wR2 $[I>2\sigma(I)]$	0.0748,0.1792	0.0678, 0.1850	0.0459, 0.1302	0.0429, 0.1232	0.0560, 0.1511
S	1.03	1.17	1.05	1.10	1.06
Min. and Max Resd Dens (e·$Å^{-3}$)	-1.88, 0.96	-0.50, 1.01	-0.62, 1.16	-0.53, 0.87	-0.51, 0.71

Table 2 The theoretical and experimental values of weight loss of compounds **1-5**

Compound	**1**	**2**	**3**	**4**	**5**
theoretical values	7.73%	14.70%	6.24%	5.21%	3.97%
experimental values	7.73%	14.83%	6.02%	5.18%	4.11%

Graphical Abstract

Syntheses, Characterizations, and Properties of Five Coordination Compounds Based on Ligand Tetrakis (4-pyridyloxymethylene)methane



Base on Tetrakis (4-pyridyloxymethylene)methane (TPOM) and different carboxylates, five new MOFs with the structure of high dimension and mutual penetration have been successfully synthesized,