



Three 3D metal coordination polymers based on triazol-functionalized rigid ligand: Synthesis, topological structure and properties



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ABSTRACT

By using a triazol-functionalized tricarboxylate, three novel metal coordination polymers, namely, $[\text{Zn}_2\text{L}(\text{OH})] \cdot 0.5\text{H}_2\text{O}$ (**1**), $[\text{Co}_2\text{L}(\text{OH})(\text{H}_2\text{O})] \cdot 5.5\text{H}_2\text{O}$ (**2**), $[\text{Cu}_2(\text{HL})]$ (**3**) $\text{L} = [5-(3-(4\text{-carboxyphenyl})-5\text{-methyl-4H-1,2,4-triazol-4-yl})\text{isophthalate}]$ were synthesized under hydrothermal reactions. All the compounds were characterized by element analysis, IR spectroscopy, thermogravimetric analysis, power X-ray diffraction and single-crystal X-ray diffraction. Structural analysis reveals that compounds **1** and **2** have 3D networks with *flu* topologies where rigid triazol-functionalized ligands as 4-connected nodes and $\text{Zn}_4(\text{COO})_6$ or $\text{Co}_4(\text{COO})_6$ clusters serves as 8-connected secondary building units. Compound **3** has 3D network with *pcu* topology where $\text{Cu}_4(\text{COO})_4$ clusters serve as 6-connected secondary building units. Gas adsorption studies reveal that desolvated compound **1** exhibits high H_2 absorption capacity at 77 K and highly selective separation abilities of CO_2 and C_3H_8 over CH_4 at room temperature. The results suggest that **1** has potential application in gas storage and separation. In addition, the magnetic properties of compound **2** were also investigated.

1. Introduction

Over the last two decades, metal coordination polymers (MCPs) as a new class of porous material have quickly developed into a fruitful research field, such as adsorption, separation as well as magnetism [1–7]. These materials are constructed through the formation of coordination bonds between metal ions (or metal clusters) as nodes and organic ligands as spokes, and possess open framework structures with inherently high microporosity [8,9]. Utilization of polynuclear metal clusters as building blocks to construct highly connected frameworks has already proven to be a practicable route, owing to the fact that the metal clusters usually contain many more coordination points and share more electron pairs that can readily accommodate more organic linkers [10–12]. Moreover, the choice and design based on the geometries of new bridging organic linkers to coordinating inorganic metal clusters is very important, to date, great effort has been devoted to the design of multidentate ligands. The specific symmetry and rigidity/flexibility are crucial for controlling and adjusting the architectures of MOFs. The size and shape within the ligand can affect the structure as well [13,14].

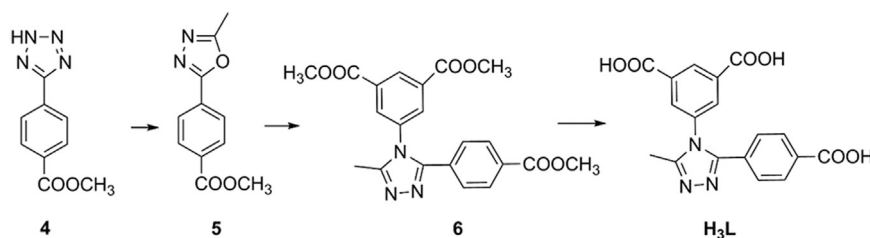
In addition, some organic linkers contain Lewis basic sites (LBSs) such as pyrazoles, imidazoles, triazoles and tetrazoles can be tailored to

the application, because these LBSs have high thermal and chemical stabilities [15–18]. Most recently, ligands containing both LBSs and multi-carboxylates have been proven to be an effective strategy to construct intriguing MOFs and these microporous materials have been successfully applied in gas storage, due to the fact that carboxylic acid groups can provide reliable coordination modes to regulate pore size and LBSs can enhance host-guest interactions meanwhile [19–24]. Krautscheid and co-workers have successfully synthesized a triazol-functionalized microporous metal-organic framework with high H_2 (3.05 wt%) and CO_2 (40.5 wt%) adsorption at ambient pressure. Our group has fully used and designed two *rht* topology MOFs containing high density triazine [25] or s-heptazine LBSs with excellent gas storage and separation properties [26]. For all of the above reasons, it would be attractive to develop synthetic approaches towards new N-containing MOF materials.

Here we synthesized a novel triazol-functionalized ligand 5-(3-(4-carboxyphenyl)-5-methyl-4H-1,2,4-triazol-4-yl)isophthalic acid (**H3L**, Scheme 1) and successfully prepared three 3D MCPs, $[\text{Zn}_2\text{L}(\text{OH})] \cdot 0.5\text{H}_2\text{O}$ (**1**), $[\text{Co}_2\text{L}(\text{OH})(\text{H}_2\text{O})] \cdot 5.5(\text{H}_2\text{O})$ (**2**) and $[\text{Cu}_2(\text{HL})]$ (**3**). Diverse inorganic building blocks $\text{Zn}_4(\text{COO})_6$, $\text{Co}_4(\text{COO})_6$, $\text{Cu}_4(\text{COO})_4$ and functionalized ligand were self-assembled into 3D structures. Gas

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Scheme 1. A schematic preparation of H₃L ligand.

adsorption properties (N₂, H₂, CO₂, CH₄, C₂H₆ and C₃H₈) were examined at a series of temperatures. Magnetic properties were also investigated.

2. Experimental

2.1. Materials and measurements

All reagents were purchased commercially and used without further purification. The hydrothermal reaction was performed in a 15 mL Teflon-lined stainless steel bomb. Diffraction data collection was performed with Bruker SMART CCD diffractometer equipped with a graphite monochromator. IR spectra were measured with KBr pellets on a Bruker IFS-66 V/S FT-IR spectrometer. Thermogravimetric measurement was performed on pre-weighed samples in a nitrogen stream using a Netzsch STA 449 C apparatus with a heating rate of 10 °C min⁻¹. Powder X-ray diffraction (PXRD) data were obtained using a Rigaku D/Max 2550 automated diffractometer (Cu K α , 1.5418 Å). ¹H NMR was carried out on a Bruker Avance III spectrometer at 400 MHz. The magnetic measurements of the compounds were carried out in an applied magnetic field of 1000 Oe in the temperature range 2–300 K using a quantum designed SQUID magnetometer.

2.2. Synthesis of methyl 4-(5-methyl-1,3,4-oxadiazol-2-yl)benzoate (5)

4 was synthesized according to previous literature [27]. A suspension of 6.12 g (30 mmol) of **4** in 50 mL (54.42 g, 0.53 mol, 18eq) acetic anhydride was heated under reflux for 12 h. After cooling to ambient temperature the excess of anhydride and acetic acid was removed under reduced pressure yielding a brownish solid.

Yield: 98% of theory. ¹H NMR ([D₆] DMSO, 400 MHz): δ = 2.61 (3 H), 3.91 (3 H), 8.13 (2 H), 8.15 (2 H) ppm. Elemental analysis: calcd for C₁₁H₁₀N₂O₃ (218.07): C, 60.55; H, 4.62; N, 12.84; O, 22.00; found: C, 61.00; H, 4.17; N, 12.94; O, 21.90. ESI-MS: m/z (100%) 218.07 [M]⁺.

2.3. Synthesis of dimethyl 5-(3-(4-(methoxycarbonyl)phenyl)-5-methyl-4H-1,2,4-triazol-4-yl)isophthalate (6)

A suspension of 3.36 g (18.6 mmol) of 5-aminoisophthalic acid, 4.05 g (18.6 mmol) of **5** and 0.35 g (1.86 mmol) *p*-toluenesulphonic acid in 50 mL xylene was heated under reflux for 48 h under nitrogen atmosphere. After cooling to ambient temperature the solvent was decanted and the residue was purified by column chromatography on silica gel yielding a white solid. Yield: 80% of theory. ¹H NMR ([D₆] DMSO, 400 MHz): δ = 2.26 (3 H), 3.82 (3 H), 3.88 (6 H), 7.49 (2 H), 7.91 (2 H), 8.27 (2 H), 8.58 (H) ppm. Elemental analysis: calcd for C₂₁H₁₉N₃O₆ (409.13): C, 61.61; H, 4.68; N, 10.26; O, 23.45; found: C, 62; H, 4.27; N, 10.20; O, 23.51. ESI-MS: m/z (100%) 409 [M]⁺.

2.4. Synthesis of 5-(3-(4-carboxyphenyl)-5-methyl-4H-1,2,4-triazol-4-yl)isophthalic acid (H₃L)

A suspension of 2.045 g (5 mmol) **6** in 50 mL 6 M NaOH/THF (1:1 v/v) was heated under reflux for 24 h. After cooling to ambient temperature the resulting solution was adjusted to pH = 2 with HCl solution. The solid was collected by filtration, washed several times with distilled water and dried to give a white solid. Yield: 95% of theory. ¹H NMR ([D₆] DMSO, 400 MHz): δ = 2.267(3 H), 7.44 (2 H), 7.88 (2 H), 8.15 (2 H), 8.55 (H), 13.44 (3 H) ppm. Elemental analysis: calcd for C₁₈H₁₃N₃O₆ (367.08): C, 58.86; H, 3.57; N, 11.44; O, 26.13; found: C, 58.80; H, 3.63; N, 11.45; O, 26.12. ESI-MS: m/z (100%) 367[M]⁺.

2.5. Synthesis of [Zn₂L(OH)]·0.5H₂O (1)

Zn(NO₃)₂·6H₂O (30 mg, 0.1 mmol) and H₃L (18 mg, 0.05 mmol) were mixed in 8 mL acetonitrile/water (1:1, v/v). The mixture was placed in a Teflonlined stainless steel vessel and heated at 140 °C for 48 h, then cooled to room temperature over 24 h. Colorless crystals of **1** were obtained and collected by filtration, washed with water and then dried in air. Yield: 57% (based on H₃L). Anal. Calcd (%): C, 41.45; H, 2.30; N, 8.06. Found (%): C, 40.85; H, 2.42; N, 8.34. IR (KBr, cm⁻¹): 3494(s), 3037(s), 2342(m), 1977(s), 1888(m), 1853(s), 1633(s), 1570(m), 1529(m), 1488(m), 1405(w), 1356(m), 1019(m), 936(s), 874(w), 839(m), 791(s), 764(w), 729(s), 591(s), 543(s), 467(s).

2.6. Synthesis of [Co₂L(OH)(H₂O)]·5.5H₂O (2)

Co(NO₃)₂·6H₂O (29 mg, 0.1 mmol) and H₃L (18 mg, 0.05 mmol) were mixed in 6 mL acetonitrile/water (1:5, v/v). The mixture was placed in a Teflonlined stainless steel vessel and heated at 140 °C for 48 h, then cooled to room temperature over 24 h. Light red crystals of **2** were obtained and collected by filtration, washed with water and then dried in air. Yield: 60% (based on H₃L). Anal. Calcd (%): C, 16.51; H, 1.39; N, 19.33. Found (%): C, 16.92; H, 1.51; N, 19.62. IR (KBr, cm⁻¹): 3639(w), 3407(s), 3072(s), 1623(s), 1560(s), 1470(s), 1458(s), 1418(s), 1367(s), 1175(s), 1095(w), 1016(s), 926(m), 875(m), 847(w), 790(m), 744(m), 670(m), 575(w), 484(s), 456(m).

2.7. Synthesis of [Cu₂(HL)] (3)

Cu(NO₃)₂·6H₂O (24 mg, 0.1 mmol) and H₃L (18 mg, 0.05 mmol) were mixed in 3 mL ethanol/water (2:1, v/v). The mixture was placed in a Teflonlined stainless steel vessel and heated at 120 °C for 48 h, then cooled to room temperature over 24 h. Light yellow crystals of **3** were obtained and collected by filtration, washed with water and then dried in air. Yield: 45% (based on H₃L). Anal. Calcd (%): C, 43.90; H, 2.23; N, 8.53. Found (%): C, 43.23; H, 2.31; N, 8.71. IR (KBr, cm⁻¹): 3432(m), 3081(s), 2971(m), 2619(s), 2549(s), 2467(m), 2135(s), 1935(s), 1722(s), 1618(s), 1585(s), 1384(s), 1301(m), 1240(s), 1163(s), 1084(s), 1019(s), 923(m), 867(s), 819(m), 771(s), 722(s), 667(s), 591(s), 509(s), 419(s).

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