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Two solvent-dependent porous coordination polymers with –OH decorated ligand: unusual non-crystallographic net and *fsh* topology

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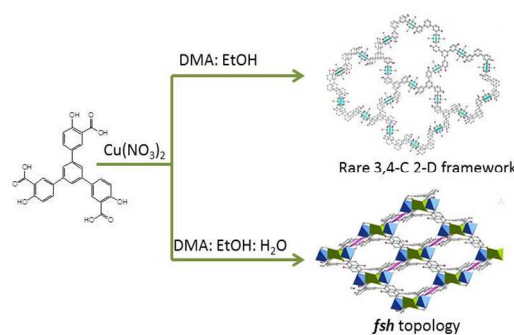
Two new porous coordination polymers (PCPs), $[\text{Cu}_6(\text{L})_4 \cdot (\text{H}_2\text{O})_6] \cdot 10\text{DMA} \cdot 4\text{EtOH}$ (**1**), $[\text{Cu}_5(\text{L})_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_2 \cdot \text{DMA}] \cdot 2\text{DMA} \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ (**2**), were solvothermally synthesized and structurally characterized. Interestingly, their variable architectures controlled by solvent system exhibit a structural progression from an unusual non-crystallographic (NC) net to a (4, 6)-connected framework with *fsh* topology. Moreover, the combination of 3D channels of about 3.0×7.2 , 4.7×9.5 , and $6.3 \times 7.8 \text{ \AA}^2$, and functional –OH groups in **2** lead to good selectivity of CO_2 toward CH_4 (26–55 by IAST) at 273 K.

Porous coordination polymers (PCPs), with tunable nature of their structure and properties, are excellent rivals to other porous materials, such as zeolites and activated carbon, for gas storage and separation.¹ However, the rational control of coordination assemblies remains a challenge.^{1a, 1g, 2} Because, many factors (reactant stoichiometry, temperature, pH, solvent, reaction time and template agents) may affect the final architectures.³ Among them, solvent systems have been found to produce more dramatic effect on self-assembly.⁴ This is because, by acting as a template or a second ligand, traditional coordination geometry that preferred by metal center could be changed.⁵ The generated structure cannot follow the rule of reticular chemistry, even based on the well-designed ligands. Thus, further investigation of solvent systems in formation of coordination polymers is very essential.

In addition, exposed functional sites and optimized pore size play important roles in selective gas capture, as the enhanced ability of host-guest interaction and also the maximum size exclusive effects.⁶ To immobilize functional sites (such as, open metal sites and alkylamine) into PCPs were considered as rational design.⁷ Moreover, by introducing some specific substituent groups, e.g. $-\text{NH}_2$, $-\text{COOH}$ on the pore surface also work well.⁸ However, there is a dearth of research on the investigation of impact of open –OH groups in PCPs, since the difficulty of getting open –OH sites after the coordination assembly.⁹

We are interested in the design and construction of porous coordination polymers with functional pore for recognition of energy gas molecules, and identifying a series of water and chemical stable frameworks for expected feasible gas storage and separation.¹⁰ Here, in continue our work, we report the syntheses of two new PCPs, $[\text{Cu}_6(\text{L})_4 \cdot (\text{H}_2\text{O})_6] \cdot 10\text{DMA} \cdot 4\text{EtOH}$ (**1**, the desolvated solid named as **1'**), $[\text{Cu}_5(\text{L})_2(\text{OH})_2 \cdot (\text{H}_2\text{O})_2 \cdot \text{DMA}] \cdot 2\text{DMA} \cdot \text{EtOH} \cdot 2\text{H}_2\text{O}$ (**2**, the desolvated solid named as **2'**), ($\text{H}_6\text{L} = 1,3,5\text{-tris}(3\text{-carboxy-4-}$

hydroxyphenyl)benzene), based upon a ligand with functional –OH group. Interestingly, their variable architectures controlled by solvent system exhibit a structural progression from an unusual NC net to a (4, 6)-connected framework with *fsh* topology. In addition, PCP **2** bearing suitable pore size, as well as open –OH site shows high selectivity of CO_2 toward CH_4 (25–55) at 273 K.



Scheme 1 Synthetic Procedures of PCP **1** and **2**

A solvothermal reaction of H_6L and $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DMA/EtOH afforded the green crystals, $[\text{Cu}_6(\text{L})_4 \cdot (\text{H}_2\text{O})_6] \cdot 10\text{DMA} \cdot 4\text{EtOH}$. Phase purity of it was confirmed by comparing their experimental powder X-ray diffraction pattern to that calculated based on the single-crystal structures. X-ray diffraction analysis reveals that the L^{3-} ligand in **1** was connected by three copper paddlewheels, and each cluster was bridged by four carboxylate groups from four different ligands, forming a high symmetrical *fan-like* sub-structure (Fig. 1). The double layers *fan-like* structure shared their edges to each other to generate a 1-D channel with the diameter of 15.6 Å. In addition, all of the inserted –OH groups are well-aligned inside the channels of **1** (Fig. 1d). For the easy understanding of connection of this structure, we simply the $\text{Cu}_2(\text{ArCOO})_4$ as 4-connected nodes and whereas L^{3-} as 3-connected linkers. The 3-c nodes come in pairs in which each of them is connected to the same three 4-c nodes. Clearly there is a net automorphism that simply involves interchanging those two vertices leaving the rest fixed¹¹. Thus, the generated topology of **1** is an example of a non-crystallographic (NC) net that is different with another two (3,4)-connected net of HKUST-1(*tbo*)¹² and MOF-14(*sqc*)¹³. This significant change can be explained as the shift of coordination site from 4- to 3-position at benzene ring. The total accessible volume of desolvated **1** is ca. 71.1%, calculated using the PLATON program.¹⁴ Additionally, power

X-ray diffraction (PXRD) pattern showed that the peak

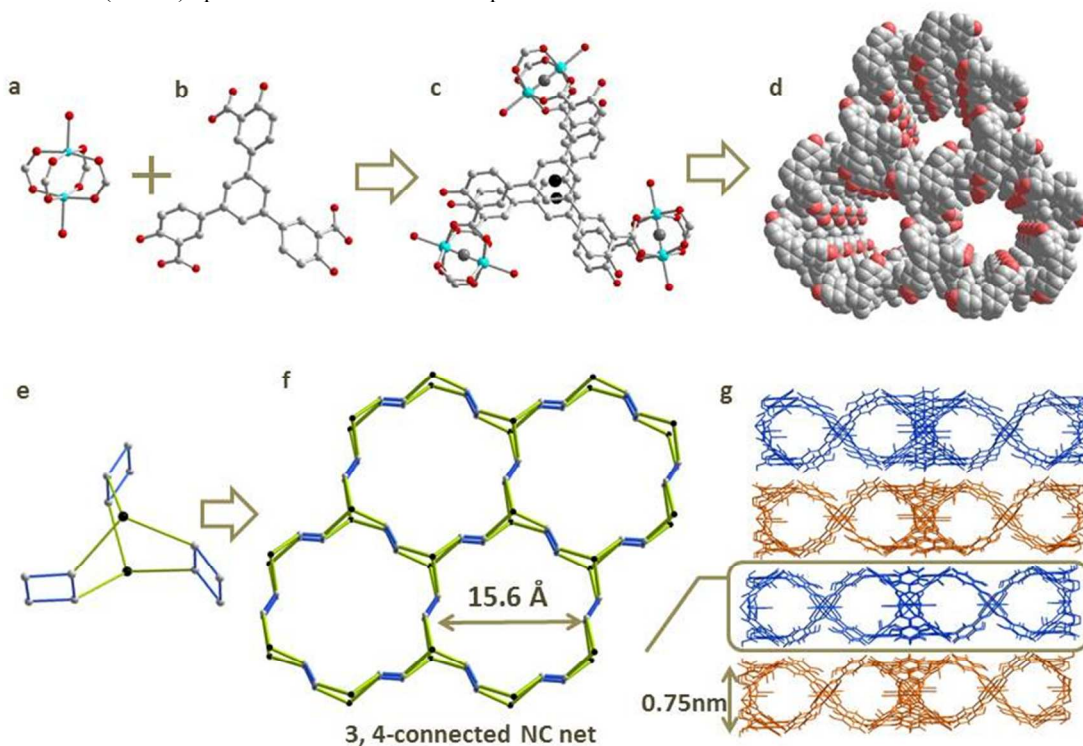


Fig. 1 The structure of 1: (a) the dicopper cluster; (b) H_6L ligand; (c) double layered fan-like structure; (d) functional and free -OH groups aligned inside the 1-D channel (O atoms from -OH groups were highlight by red color); (e) the simplification method; (f) unusual 3, 4-connected NC net; (g) the packing of the 2-D framework with 0.75 nm layer height.

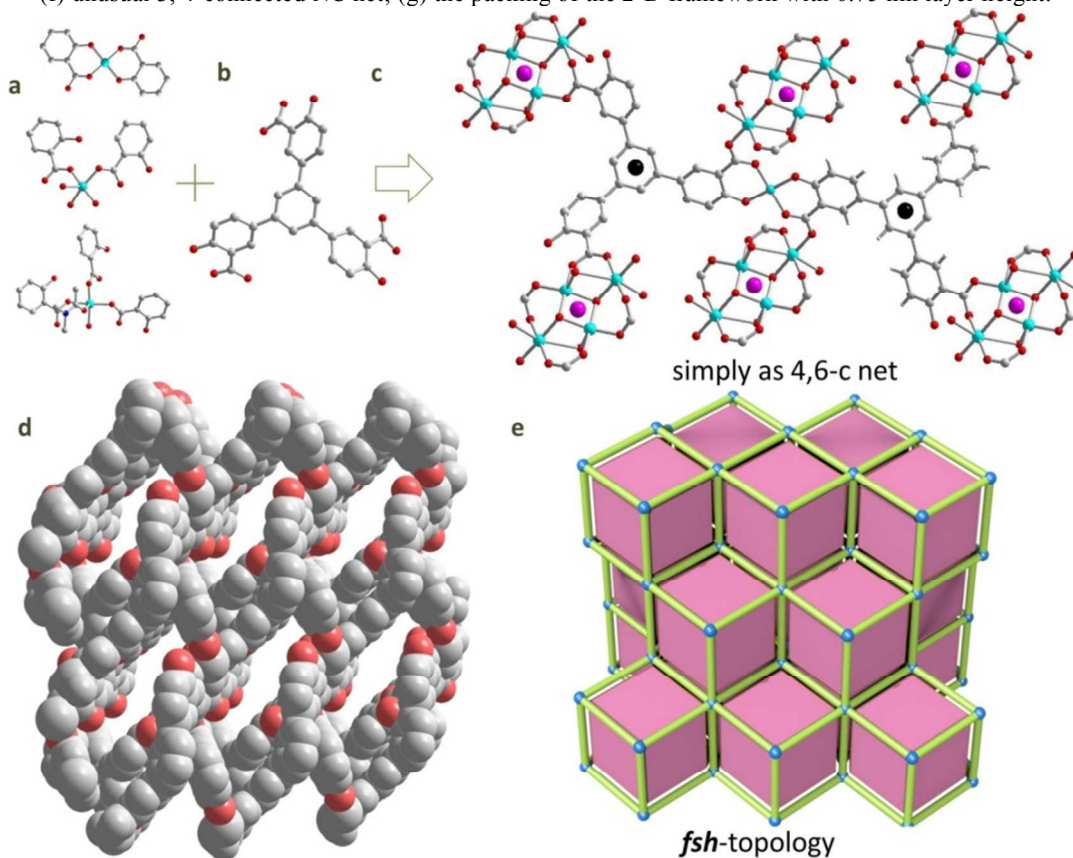


Fig. 2 The structure of 2: (a) three different coordination geometries of Cu^{2+} atoms ; (b) H_6L ligand; (c) the simply method; (d) functional -OH groups aligned inside the 1-D channel (O atoms from -OH group were highlight by red color); (e) fsh topology

with one kind of tiling.

positions of as-synthesized phase are same as the simulated data, but the peak intensity, especially for [2 0 0] peak, is different. This is because **1** exhibits the stronger preferential orientation along the [2 0 0] direction.¹⁵ Meanwhile, with very good reliability factors ($R_p = 0.0252$ and $R_{wp} = 0.0553$), Le Bail analysis of PXRD shows that the refined parameters are very close to the data from the single crystal, reflecting good phase purity and also well-defined structure (Fig. S8).

[Cu₅(L)₂(OH)₂·(H₂O)₂·DMA₂]_xGuest (**2**) was harvested from the DMA/EtOH/H₂O solvent system. Interestingly, crystallographic analysis revealed that **2** crystallizes in *P*-1 space group (Fig. 2). The asymmetric unit of **2** includes one half Cu(II) atom (Cu1) on an inversion centre, two other Cu(II) atoms in general positions, one partially deprotonated L ligand, one -OH group, one coordinated water molecule and one coordinated DMA molecule (Fig. 2a). The coordination numbers of these three copper atoms are 4, 5 and 5, respectively. The coordination geometry of Cu1 is a slightly distorted pentahedron, and which was completed by two oxygen atoms from bridged -OH groups, two oxygen atoms from the carboxylate groups, and one coordinated water molecule, meanwhile, coordination geometry of Cu2 was completed by one oxygen atoms from bridged -OH groups, three oxygen atoms from the carboxylate groups, and one coordinated DMA molecule. Last but not least, a rare and planar coordination square around Cu3 was finished by two phenols oxygen atoms and two carboxylate oxygen atoms. In addition, one ligand was connected by five Cu atoms, forming a porous 3-D framework. Thus, high density of open metal sites can be expected in **2**, since the existence of original open metal site and also the sites from the removal of coordinated DMA and water. In addition, the free -OH groups can also be found inside the channel as shown in Fig. 2d. Compared with the significant channel in **1**, the structure of **2** with 3-D intercrossed channels of about 3.0 × 7.21, 4.72 × 9.52, and 6.37 × 7.81 Å² indicates the suitable pore size for CO₂ separation (kinetic parameter of CO₂: 3.3 Å). The total accessible volume of desolvated **2** is ca. 41.5%, calculated using the PLATON program.¹⁴ In addition, after soaking **2** inside water for 1 days, the PXRD profiles show the integrity of the framework (Fig. S9), and which is rare result for carboxylate- and Cu-based PCPs. In order to further understand the connection of **2**, the Cu₄(ArCOO)₄(OH)₂ and Cu(ArCOO)₂(ArO)₂ clusters was simplified as 4- and 2-connected nodes, where, L⁴⁻ ligands is 4-connected linkers (Fig. 2c). However, it is usual to subsume 2-connected vertices into the link, and then the generated basic unit of **2** was assigned as a hexatopic carboxylate linker that joined 4-connected nodes. Considering the 4-c branch points of L⁴⁻ unit, the framework shows an (4,6)-c net with *fsh* topology (Fig. 2e).

Interestingly, compared the synthesis conditions of those two PCPs (changed solvent systems, while the other conditions were intentionally held constant), we found that the solvent systems induced the changed coordination of ligand and as well as the structural progression. In order to confirm

this point, the following experiments were conducted and

Table 1. Experimental matrix of PCPs syntheses.

Temperature, time and solvent	DMA:EtOH:H ₂ O			
	4:2:0	4:2:0.5	4:2:2	4:2:12
65 °C, 48h	1	2	2	×
90 °C, 48h	×	×	2	×
130 °C, 48h	×	×	×	×

observations from PXRD (Fig S7 and S11) are detailed in Table 1: (1) when DMA/EtOH (2 mL, 4:2) is used as solvent systems, **1** with phase purity can be obtained at 65 °C, but not under 90 °C and 130 °C; (2) when very small amount of water was added inside the DMA/EtOH system (2 mL, DMA:EtOH:H₂O = 4:2:0.5), we can get purified **2** at 65 °C; (3) when we increase the amount of water of the solvent system from 4:2:0.5 to 4:2:2, only **2** can be generated at 65 and 90 °C. (4) When the amount of water increase to very high level (4:2:12), no any PCPs can be formed at these three temperature. Thus, different solvent systems regulate the formation of different environment for the assembly of Cu(II) and linking modes of H₆L ligand. In **1**, only the carboxylate groups coordinated to the Cu(II) paddlewheel nodes, whereas, in **2**, three different coordination geometries were bridged by the carboxylate groups and also a -OH group from the ligand. Therefore, the ligand can be simplified as three- and four-connected linkers in **1** and **2**, respectively. Then, a structural progression from an unusual NC net to a (4, 6)-connected framework with *fsh* topology were well observed (Fig. 3). Herein, more theoretical and experimental efforts are required for finding the roles of water in influencing coordination self-assembly, but we can make a preliminary conclusion: the volumetric ratio of water in a mixed solvent system may influence the solvation process and coordination kinetics in solution. This is maybe due to the water is one kind of special ligand that can result in new balance of kinetic and thermodynamic of final product.^{4, 16}

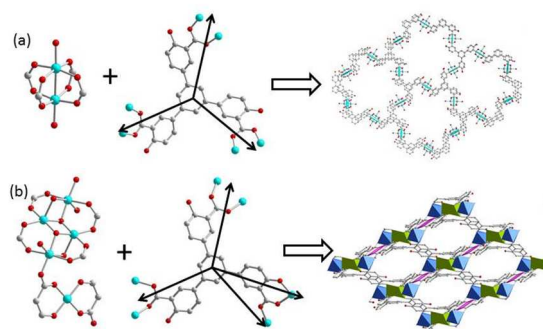


Fig. 3 The coordination of metal and ligand in PCP **1** (a) and **2** (b)

Encourage by the porous and functional sites, the gas adsorption of them were collected. Before the gas sorption experiments, the activation of these two structures were explored. Unfortunately, the desolvated **1'** collapsed, and did not show any gas uptake. Meanwhile, compound **2'** shows a little CO₂ gas uptake (25 cm³/g) at 1 bar and 195 K. The PXRD of desolvated **2'** indicated the structural change after the activation. However, interestingly, **2'** did not show any

uptakes of O₂, CH₄, C₂H₄ and C₂H₆ (Fig. S14). Thus, the unique gas adsorption isotherms show the possibility of selective capture of CO₂ by **2'**. Adsorption isotherms of CO₂ and CH₄ in **2'** were collected at 273K to 9 bar. The maximum uptakes of them reached 1.82 mmol/g and 0.35mmol/g, respectively. In order to explore the selectivity of **2'**, ideal adsorbed solution theory was employed to predict multi-component adsorption behaviors from the experimental pure-gas isotherms. The predicted adsorption selectivity for equimolar CO₂/CH₄ mixtures in **2'** as a function of bulk pressure was presented in Fig. 4. The selectivity of CO₂ over CH₄ is very sensitive to loading and which shows two steps in the changes of selectivity: a quick decrease of CO₂ selectivity at the low pressure region, and a slow increase at high pressure (22-55). This high selectivity can be explained as the well combination of suitable pore size, open metal sites and functionalized -OH groups in **2'**. In addition, based on the IAST model and similar conditions, these selectivities are higher than those of the reported adsorbent materials (Zn₂(NDC)₂(DPNI) (30),¹⁷ Zn₅(BTA)₆(TDA)₂ (37),¹⁸ Cu-BTC (6-10),¹⁹ zeolites 13X (2-24)²⁰ and comparable with the performance of our previous reported amide-functionalized materials of NJU-Bai3 (25-60),^{10b} indicating a selective removal of CO₂ from natural gas.

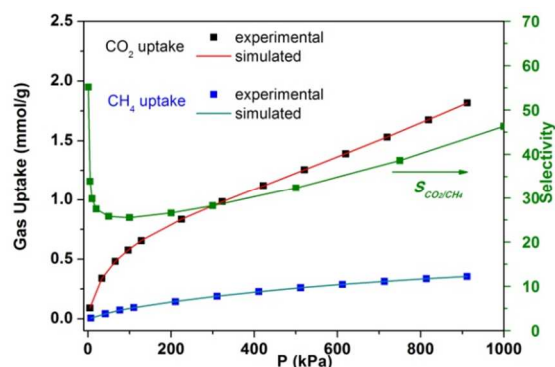


Fig. 4 High pressure gas adsorption isotherms and the Dual-site Langmuir-Freundlich fit lines of CO₂ and CH₄ in **2'** at 273K. The green lines show the IAST predicted selectivity of CO₂ over CH₄.

Conclusions

In summary, we have demonstrated the water-controlled assembly of two new porous coordination polymers originating from the variable coordination of the ligands around metal center. Interestingly, their variable architectures controlled by solvent systems exhibit a structural progression from an unusual non-crystallographic net to a (4, 6)-connected 3-D framework with *fsb* topology. While, PCP **2** possessing suitable pore size, functional -OH groups exhibits good gas selectivity of CO₂ (S_{CO_2/CH_4} : 22-55). Therefore, we believe that our results could enlarge the perspective of the chemistry of structural controlling and progression in PCP area.

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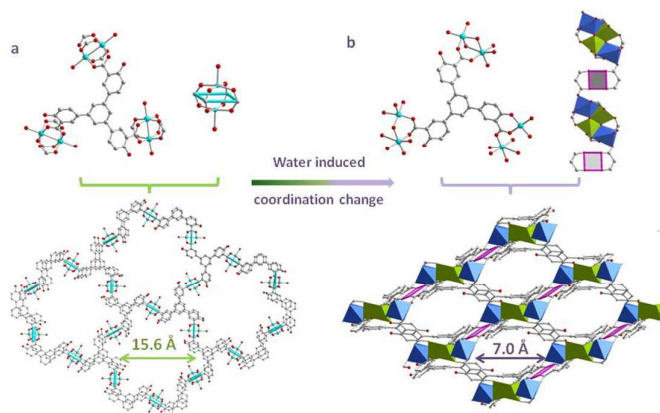
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Notes and references

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- †Electronic Supplementary Information (ESI) available: Synthesis and characterization of PCPs, PXRD, TGA, IR, sorption isotherms. CCDC for these two PCPs: 1023464-1023465. For ESI and crystallographic data in CIF or other electronic format. See DOI: 10.1039/b000000x/
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Graphic abstract



The variable architectures of two new porous coordination polymers (PCPs) can be controlled by solvent system, and they exhibit a structural progression from an unusual non-crystallographic net to a (4, 6)-connected framework with *fsh* topology.