Controllable Assembly of Three Copper-Organic Frameworks: Structure Transformation and Gas Adsorption Properties

Xiuling Zhang^{1,2}, Peng-fei Liu¹, Na Wang¹, Da-Shuai Zhang^{2}*

¹College of Chemical Engineering, Qingdao University of Science and Technology,
Qingdao, 266000 P. R. China

²Key Laboratory of Coordination Chemistry, Functional Materials in Universities of
Shandong (De Zhou University), De Zhou, 253023 P. R. China

*

Corresponding author. E-mail: dashuai_74@163.com.

To Polyhedron

Abstract

Mixtures of three new MOFs, $[\text{Cu}(\text{Hdpt})(\text{tdc})(\text{H}_2\text{O})]_n$ (**1**), $\{[\text{Cu}_2(\text{Hdpt})_2(\text{tdc})_2] \cdot 2\text{DMF}\}_n$ (**2**) and $[\text{Cu}_2(\text{dpt})(\text{tdc})]_n$ (**3**) (H_2tdc =thiophene-2,5-dicarboxylic acid, Hdpt =4,4'-(1H-1,2,4-triazole-3,5-diyl)bis-Pyridine), have been prepared by hydrothermal method and characterized by single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), IR, TGA, and EA. Through precisely modulating the reaction conditions, pure samples of the three MOFs could be separately obtained, and regularity of reaction conditions impacting the resulted product was founded as well. Interestingly, it reveals that under moderate temperature and high DMF/ H_2O ratio, **1** firstly crystalized very quickly, and gradually transformed to **3** as time grows, which could be eye-monitored and demonstrated by PXRD as well. Moreover, the gas adsorption properties have also been investigated, which show potential applications in gas storage and separation. This work may set an example for the controllable synthesis of MOFs in systems that easily afford mixed-crystals.

Keywords

Metal-organic frameworks; Synthesis; Crystal structure; Structure transformation; Gas adsorption

1 Introduction

Metal-organic frameworks (MOFs) are a kind of newly emerged crystalline porous material, which are assembled by the coordination of inorganic metal ions/clusters and organic linkers. Sharply increasing attention in the past two decades is helping MOFs fuel a boom in research and development [1-2]. Owing to their tunable pore structures [3, 4] and excellent chemical/physical properties, MOFs could be potentially used as functional materials in various domains [5], such as gas storage, separation [6-9], catalysis [10-13], sensing [14-17] and drug delivery [18-21]. However, to apply MOFs for practical utilization, the effective synthesis is still a big challenge and should be the prime concern, since high productivity and purity would be needed for the subsequent property studies. On the other hand, the flexibility and diversity of coordination modes of the metal part and organic ligand often lead to the formation of a variety of MOFs with different structures and properties in the same reaction system, which make it very difficult to separate them from each other, thus restricting their application. This problem is common but undesired. Therefore, study on the controllable synthesis of MOFs with desired structures and properties is of great necessity and could be helpful in comprehending the assembly process of MOFs so that exploiting the performances of MOFs will be more freely.

Some recent developed methods showed demonstrations for solving this issue, such as solvent-assisted separation of mixed MOFs based on the density difference and seed-mediated synthesis of phase-pure MOFs, which encouraged us for more investigations in this field [22-25]. As we know, there are many other factors impacting the reaction process, for example, temperature, pH, solvent ratio, time, respectively or a synergistic combination of them. Especially in the systems that easily afford mixed-MOFs, great attention should be paid on all the possible influence factors for minor changes may cause different results.

In this paper, three new MOFs, namely, $[\text{Cu}(\text{Hdpt})(\text{tdc})(\text{H}_2\text{O})]_n$ (**1**), $\{[\text{Cu}_2(\text{Hdpt})_2(\text{tdc})_2] \cdot 2\text{DMF}\}_n$ (**2**) and $[\text{Cu}_2(\text{dpt})(\text{tdc})]_n$ (**3**), have been synthesized as crystal mixtures using the same ligands thiophene-2,5-dicarboxylic acid (H_2tdc) and 4,4'-(1H-1,2,4-triazole-3,5-diyl)bis-Pyridine (Hdpt) and metal ions $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ under one reaction system [26-29]. Through precisely modulating the reaction conditions, pure samples of the three MOFs could be separately obtained, and regularity of reaction conditions impacting the

resulted product was founded as well: two drops of HBF_4 are essential for the synthesis of these MOFs; low temperature and low water content tends to generate **1** with a two dimensional (2D) structure; high temperature and low water content benefited the formation of **3** with a 3D porous framework; high water content help to obtain **2** with a 3D framework. Interestingly, it reveals that under moderate temperature and high DMF/ H_2O ratio **1** crystalized firstly, and gradually transformed to **3** as time grows. This work may set an example for the controllable synthesis of MOFs in systems that easily afford mixed-crystals. Herein, we report the controllable synthesis of three metal-organic frameworks. Moreover, the gas adsorption properties have also been investigated, which show potential applications in gas storage and separation.

2. Experimental

2.1. Materials and methods

All the chemical reagent of analytical grade were commercially available, and used without further purification. The Elementar Vario Micro Cube analyzer was used to carry out the elemental analyses (C, H, N). Infrared (IR) spectrometric analyzer were were measured on a Thermo Nicolet IR200 FT-IR spectrometer using KBr pellets (range of $4000\text{--}500\text{ cm}^{-1}$). A SHIMADZU DTG-60 thermo analyzer was used to perform the thermogravimetric analyses (TGA) under nitrogen at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ from room temperature to $700\text{ }^\circ\text{C}$. Powder X-ray diffraction (PXRD) data under the 2θ range $5\text{--}50^\circ$ were recorded using $\text{Cu-K}\alpha$ radiation ($k = 0.1542\text{ nm}$) on a Bruker D8A A25 X-ray diffractometer, with the X-ray tube operated at 40 kV and 40 mA at room temperature. N_2 , H_2 , CO_2 and CH_4 adsorption measurements were performed on an Autosorb-3.0 (Quantachrome) volumetric analyzer and the N_2 , H_2 , CO_2 , CH_4 gases were of 99.999% purity quality.

2.2. Preparation of the complexes

The three complexes could be afforded by the solvothermal reactions of Hdpt, H_2tdc and $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ in a HBF_4 added solvent of DMF and H_2O under certain range of temperature. Synthesis of the pure samples are as follows.

2.2.1 Synthesis of pure samples of $[\text{Cu}(\text{Hdpt})(\text{tdc})(\text{H}_2\text{O})]_n$ (**1**)

In a 20 mL glass vial, 19.9 mg of $\text{Cu}(\text{CH}_3\text{COO})_2\cdot\text{H}_2\text{O}$ (0.1mmol), 11.2 mg of Hdpt (0.05 mmol) and 8.6 mg of H_2tdc (0.05 mmol) were dissolved in mixed solvent of DMF (5.5 mL) and H_2O (0.5

mL). Then, 2 drops HBF₄ (50 wt% aqueous solution) was added into mixture and stirred. The vial was sealed and placed in a 55 °C oven for 2 days. Blue block crystals of **1** were obtained in 46% yield (based on Cu), washed with DMF and air dried. Elemental anal. Calcd for C₁₈H₁₃CuN₅O₅S (%): C, 45.52; H, 2.76; N, 14.75; Found: C, 45.98; H, 3.07; N, 14.43. IR (KBr, cm⁻¹): 3430(s), 2362(w), 1653(s), 1619(s), 1574(s), 1525(m), 1385(s), 1359(s), 1101(m), 1026(w), 992(w), 852(w), 776(w), 727(w), 668(w), 518(w).

2.2.2 Synthesis of pure samples of {[Cu₂(Hdpt)₂(tdc)₂]·2DMF}_n (**2**)

In a 20 mL glass vial, 19.9 mg of Cu(CH₃COO)₂·H₂O (0.1 mmol), 11.2 mg of Hdpt (0.05 mmol) and 8.6 mg of H₂tdc (0.05 mmol) were dissolved in mixed solvent with DMF (1 mL) and H₂O (5 mL). Then, 2 drops HBF₄ (50 wt. % aqueous solution) was added into mixture and stirred. The vial was sealed and placed in a 100 °C oven for 5 hours. Aquamarine blue block crystals of **2** were obtained in 46% yield (based on Cu), washed with DMF and air dried. Elemental anal. Calcd for C₄₂H₃₆Cu₂N₁₂O₁₀S₂ (%): C, 47.59; H, 2.13; N, 13.46; Found: C, 47.44; H, 2.31; N, 13.52. IR (KBr, cm⁻¹): 3425(s), 2922(w), 1676(m), 1617(s), 1577(s), 1450(w), 1381(m), 1356(s), 1332(m), 1089(m), 1024(w).

2.2.2 Synthesis of pure samples of [Cu₂(dpt)(tdc)]_n (**3**)

In a 20 mL glass vial, 19.9 mg of Cu(CH₃COO)₂·H₂O (0.1 mmol), 11.2 mg of Hdpt (0.05 mmol) and 8.6 mg of H₂tdc (0.05 mmol) were dissolved in mixed solvent with DMF (5.5 mL) and H₂O (0.5 mL). Then, 2 drops HBF₄ (50 wt. % aqueous solution) was added into mixture and stirred. The vial was sealed and placed in an 85 °C oven for 3 days. Dark blue block crystals of **3** were obtained in 42% yield (based on Cu), washed with DMF and air dried. Elemental anal. Calcd for C₁₈H₁₁Cu₂N₅O₄S (%): C, 41.54; H, 2.13; N, 13.46; Found: C, 42.01; H, 2.31; N, 13.52. IR (KBr, cm⁻¹): 3448(s), 2362(w), 2339(w), 1652(s), 1620(s), 1560(m), 1487(m), 1094(s), 935(w), 843(w), 546(m).

2.3 X-ray Structure Determination and Structure Refinement

X-ray diffraction data of the single crystals was collected on a Bruker SMART APEXII CCD diffractometer equipped with a graphite monochromated Mo K α radiation (λ = 0.71073 Å). The SADABS programs was used to apply the empirical absorption correction. Direct methods and full-matrix least-squares methods on F² were performed to solve and refine the structure using the

program SHELX-2014 [30, 31]. The single suite Olex2 [32] was used as an integrated system for all the crystallographic programs. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms which positions and thermal parameters were fixed during the structure refinement were located by geometrically calculations. The crystallographic data and details of selected bond lengths and angles are summarized in Table S1 and Table S2, respectively. For complexes, the volume fractions of disordered solvent in the pores could not be modelled in terms of atomic sites and were treated using the SQUEEZE routine in the PLATON [33] software package.

2.4 Gas adsorption measurement

Before gas adsorption measurements, the as-synthesized samples of **1**, **2** and **3** were soaked in methanol for 3 days and in anhydrous dichloromethane for another 3 days to exchange the solvent molecules involved their frameworks. The samples were collected by decanting and dried in air. Before the gas adsorption tests, solvent-exchanged samples were loaded in a sample tube and further activated under high vacuum at an optimized temperature of 30 °C for 6 h. Finally, 112 mg (**1**), 97 mg (**2**) and 78 mg (**3**) of degassed samples were used for gas sorption measurements. The gas adsorption isotherm measurements were proceeded at 77 K in a liquid nitrogen bath, at 273 K in an ice-water bath and at 298 K in a water bath.

3 Results and Discussion

3.1 Crystal Structure Description

(Insert Fig.1)

3.1.1 [Cu(Hdpt)(tdc)(H₂O)]_n (**1**)

Structure analysis reveals that complex **1** crystallized in the monoclinic system with space group P21/c. The asymmetric unit of complex **1** contains one Cu(II) ion, one tdc²⁻ ligand, one Hdpt ligand and one water molecule. In compound **1**, Cu(II) ion is coordinated by four O atoms of which three are from different tdc²⁻ ligands and one from water molecule, and two pyridyl N atoms from Hdpt ligand to form an atactic octahedron geometry (Fig. 1a). The Cu-O bond distances are in the range of 1.945(2)-2.284(3) Å, and the Cu-N bond distance is 2.019(3) Å. The bond angles between the donor atoms around the Cu (II) center range from 87.84(10) to 168.32(12) (Table S2). As shown in Fig. 2, different linear organic ligands (tdc²⁻ and Hdpt) connect to each other by centering on the

single Cu(II), and form a typical grid layer structure. These grid structures further generate a reticular 3D supramolecular structure through hydrogen bonds with 1D channels along *a* and *c* axis, and the porosity ratio of the complex was 51.7% after removing the solvent molecules as estimated by PLATON.

(Insert Fig.2)

3.1.2 {[Cu₂(Hdpt)₂(tdc)₂]·2DMF}_n (**2**)

Single-crystal structure analysis reveals that complex **2** crystallized in the P2₁/n space group of monoclinic system. The asymmetric unit of **2** consists of two Cu(II) ions, two Hdpt ligands and two tdc²⁻ ligands. Cu1 and Cu2 ions are all five-coordinated with similar coordination environments, which are bridged by a pair of carboxyl oxygen groups to form a binuclear Cu(II) unit. Cu1 ion is surrounded by three carboxyl oxygen atoms from three different tdc²⁻ ligands and two nitrogen atom from three different Hdpt ligands (Fig. 1b). The Cu1-O bond distances are in the range of 1.982(2)-2.270(3) Å and the Cu1-N distances are 2.010(3)-2.026(3) Å respectively, indicating that the geometry of Cu1 ion is nearly in between square pyramid and trigonal bipyramid. Cu2 ion has a similar coordination environment with Cu1, with the Cu2-O and Cu2-N bond distances in the range of 1.971(2)-2.358(3) and 2.014(3)-2.010(3) respectively (Table S2). Interestingly, there contains internal cavities instead of open channels, which was caused by the formation of helical chains inside the framework. As shown in Fig. 3, the cavity was composed of alternating unit of three pairs of Hdpt ligand, four Cu(II) clusters and two pairs of tdc²⁻ ligands, with the help of hydrogen bonds. Inside the cavity was encapsulated one DMF molecule, just like a snake hunting for its food. So, although no obvious channels could be found along with all directions of the structure, it still has a void volume of 25.4%, which is estimated by the PLATON software.

(Insert Fig.3)

3.1.3 [Cu₂(dpt)(tdc)]_n (**3**)

Single-crystal structure analysis reveals that complex **3** crystallized in the orthorhombic system with space group Pccn. The asymmetric unit of complex **3** contains two mixed-valence Cu(I/II) ions [6-connected Cu1(II) and 2-connected Cu2(I)], one tdc²⁻ ligand, and one dpt⁻ ligand. In complex **3**, Cu1(II) ion is coordinated by four O atoms from different tdc²⁻ ligands and two N atoms of pyridyl from different dpt⁻ ligand to form an octahedral geometry (Fig. 1c). The Cu1(II)-O bond

distances are in the range of 1.917(4)-2.363(6) Å. The bond angles between the donor atoms around the Cu1(II) center range from 58.42(17) to 170.0(3) (Table S2.). The in-situ formed Cu2(I) reveals a nearly linear coordinate mode (angles: 170.37) connecting two N atoms of triazole groups from different dpt⁻ ligands. The Cu(I)-N bond [Cu(2)-N(3)#5-1.881(5) and Cu(2)-N(4)-1.831(5)] is shorter than the Cu(II)-N bond [Cu(1)-N(5)#3-2.014(5) and Cu(1)-N(1)-2.007(5)], which are similar to those found in coordination polymers. As shown in Fig. 4a, each dpt⁻ ligand connects four Cu(I/II) ion, of which N1 and N5 of pyridyl groups link two Cu1(II) with N3 and N4 linking two Cu2(I) ions, leading to a 2-D grid-like layer structure (as layers), while each tdc²⁻ ligand (as pillars) connects the two Cu1(II) atoms of the adjacent layers to generate a 3D “pillar-layer” structure. On the other hand, the overall structure of **3**, which shows a 3D porous framework, also could be simplified into an infinite (4,4)-connected **cds** topological network with a Schläfli symbol (6⁵.8) (Fig. 4c), if taking the dpt⁻ ligand and the Cu1(II) atom as 4-connected nodes respectively. In addition, looking along the *c* direction of the framework, two kinds of rectangular pores (Fig. 4b) could be observed with distinct sizes. The B-type pores has a size of 4.6×10.3 Å, which is a little bigger than the A-type ones (4.5×8.6 Å), considering the van der Waals radius of atoms. Moreover, the accessible volume of complex is 51.4%, estimated by PLATON.

(Insert Fig.4)

3.2 Synthesis and structure transformation

Working on the controllable synthesis of targeted MOFs, we found that in DMF/H₂O/HBF₄ surroundings, the solvothermal reactions of Hdpt and H₂tdc ligands with Cu²⁺ tend to generate three different frameworks, that is compound **1**, **2** and **3**. As a result, normally the output products are mixture crystals of these MOFs. To purify these MOFs from each other, much more precise modulation of the reaction conditions were explored, which has been listed in table 1. Regularity of products was observed that 1) two drops of HBF₄ are essential for the synthesis of these MOFs (no crystals would be gained without HBF₄); 2) low temperature and low water content tend to generate **1** with a 2D layer structure; 3) high temperature and low water content benefit the formation of **3** with a 3D porous framework; 4) high water content helps to obtain the 3D framework of **2** with little effect by temperature.

As we know, higher pH values could benefit the deprotonation of the ligands, while Cu(II) ions

tend to generate precipitate with pH over 4.7. Therefore, lowering the pH value by adding a little acid to the system could inhibit the formation of precipitation. Take the synthesis of **2** as an example, pH value of the reaction system is tested to be about 6.0 without adding HBF₄, which afford an original mixture of suspension and no crystals were obtained at last (figure S7a). However, the mixture changed into clear solution with the addition of HBF₄ at the beginning and crystals would be obtained when the reaction is over (figure S7b). As we try, it seemed that two drops (about 60μL) of HBF₄ is just the best dosage to balance the deprotonation of the ligands and inhibition of precipitation, because the pH value in this case is just in the range of about 4.0-5.0, which is on or approaching the threshold of precipitation. If keep lowering the pH value by adding more acid, yield and quality of the crystals will be reduced, which might be attributed to the deprotonation decreasing of the ligands.

Along with DMF/H₂O ratio increasing and temperature declining, productivity of **1** increased gradually, and pure samples of **1** could be obtained below 65 °C when the solvent ratio is 5.5:0.5. Subsequently, blue-green crystals of **2** could be purified by reducing DMF/H₂O ratio to 2:4 in the given temperature ranges, with color changing to blue if keeping lowering the ratio. As for **3**, a condition of temperature >85 °C could yield pure samples with a DMF/H₂O ratio of 5.5:0.5.

Interestingly, it reveals that under moderate temperature (75~85 °C) and high DMF/H₂O ratio (5.5:0.5~5:1) bulk crystals of **1** crystalized quickly within about two hours, while gradually transformed to **3** as time grows. The transformation process could be monitored through PXRD patterns of the time-varying product (Fig. 6). Importantly, “transition state crystals” could be clearly observed as seen from picture of the product at eight hours—dark blue crystals of **1** was gradually fading, cracking and changing into crystals of **3**. This time-dependent single crystal to single crystal (SC-SC) [34-36] structure transformations is very rare in MOFs, so far as we know. Possible reasons for this unique transformation might be explained through comparison between the two structures that: 1) under this condition, **1** could be yield very fast with the existence of massive Cu²⁺; 2) as time goes by, part of the excessive Cu²⁺ was reduced into Cu⁺, which was then absorbed into the spaces among the layers of **1**; 3) the in-situ formed Cu⁺ induce a slight adjustment of the layer structures and then link the 2D layers into the 3D porous framework of **3** through coordinating with the triazole groups between different layers.

All the results above could be confirmed by the Powder or single-crystal XRD (Fig. 5) and

crystal images of the products (Table 1).

(Insert Fig.5)

(Insert Fig.6)

(Insert Table 1)

3.3 PXRD

As shown in Figure S1, PXRD patterns of the pure samples of **1**, **2** and **3** agree well with their simulated ones, respectively, indicating the pure phases of these solid-state samples and further confirming the successful separation of the three frameworks. Moreover, the samples after solvent exchanged and gas adsorption are still as crystalline as the pure samples of the three compounds as proven by the PXRD patterns, suggesting the good stability of the three frameworks.

3.4 Gas adsorption

(Insert Fig.7)

In order to characterize the porosity, N₂ adsorption-desorption isotherms was measured at 77 K for activated samples of the three MOFs. As shown in Fig. 7a, complex **3** exhibit type I sorption isotherms, suggesting the microporosity of this material. The maximum N₂ uptake is around 235.9 cm³ g⁻¹ (STP) at 77 K and 1.0 bar for **3**. Based on the N₂ sorption data, the Brunauer-Emmett-Teller (BET) and Langmuir surface areas of complex **3** are estimated to be 793.5 and 832.8 m²g⁻¹, respectively. Moreover, the calculated H-K (Horvath-Kawazoe) pore size distributions range from 3.5 to 11.4 Å, corresponding to the pore sizes evaluated from the single-crystal X-ray structure. The pore volumes calculated from the maximum N₂ uptakes are 0.310 cm³ g⁻¹ for complex **3** which are close to the theoretical values of 0.322 cm³g⁻¹ calculated using PLATON software. In addition, compared with **3**, complex **1** and **2** are much less porous (Fig. 7a and Fig. S3).

The porous nature of **3** lead us to further investigate its capture and separation properties for other gases including CO₂, CH₄ and H₂. As shown in Fig. 7 b and c, **3** could uptake a moderate amount of CO₂ up to 95.7 cm³g⁻¹ (273 K) and 53.5 cm³g⁻¹ (298 K), while the uptake amounts of CH₄ are 35.1 cm³g⁻¹ (273 K) and 16.7 cm³g⁻¹ (298 K) at 1 atm, respectively. In spite of that the similar calculated void volumes between **1** and **3**, complex **1** reveals much less uptake amounts of CO₂ and CH₄, that is, 42.9 cm³ g⁻¹ (273 K) and 23.7 cm³ g⁻¹ (298 K) for CO₂, and 16.6 cm³g⁻¹ (273 K) and 5.8 cm³g⁻¹ (298 K) for CH₄ at 1 atm. In addition, CO₂ isosteric heats of adsorption (Q_{st}) for **1** and **3** were calculated based on the respective adsorption isotherms at 273 K and 298 K by employing the

Clausius-Clapeyron equation [37, 38]. The calculated Q_{st} values range is 58.1~30.5 kJ mol⁻¹ for **1** and 17.7~28.8 kJ mol⁻¹ for **3**, respectively, depending on the gas loading. Moreover, gas adsorptions of **1** and **3** both exhibit significantly different uptakes towards CO₂ and CH₄ at both 273 and 298 K. So the initial slopes of their adsorption isotherms were calculated over very low pressure ranges in order to estimate the CO₂ adsorption selectivity of them towards CH₄ (Fig. S4 a and b). The result CO₂/CH₄ selectivity is calculated to be 4.4:1 at 273 K and 4.0:1 at 298 K, which is comparable to many reported MOFs [39, 40]. As for complex **2**, almost no adsorption was obtained, which might be attributed to the reason that the twisted (non-open) channels with smaller sizes inside the framework extremely limited the entrance of CO₂ and CH₄ molecules with bigger sizes, given its low assessable volume.

In addition, H₂ storage capacity was also measured under low pressure. As shown in Fig. 7d, the amount of H₂ uptake at 77K for **1**, **2** and **3** is 54.2 (0.5 wt%), 83.2 (0.7 wt%) and 176.5 (1.6 wt%) cm³ g⁻¹, respectively. Interestingly, although **2** is lower porous than **1**, it has a little higher H₂ uptake amount. Contrary to the case of CO₂ and CH₄ adsorption, the narrow twisted channels and internal cavities are just suitable for H₂ entrance and storage, thus enhancing the H₂ uptake ability of **2**. However, it should be pointed out that the H₂ uptake capacity of **2** is still far lower than **1**, which is mainly caused by the low porosity of **2**.

4 Conclusions

In summary, three new copper-organic frameworks with same ligands have been successfully separated from one reaction system, through precisely modulating the reaction conditions (temperature, pH, solvent ratio, time). Regularity of reaction conditions impacting the resulted product was founded as well. Importantly, an uncommon time-dependent SC-SC structure transformation could happen from **1** to **3** under suitable conditions. The transforming process was investigated and a possible mechanism was proposed as well. Moreover, the gas adsorption properties have also been investigated, which show potential applications in gas storage and separation. This work may pave a way for the controllable synthesis of MOFs in systems that easily afford mixed-crystals.

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Appendix A. Supplementary data

CCDC 1486881; 1504982 and 1486880 contains the supplementary crystallographic data for $[\text{Cu}(\text{Hdpt})(\text{tdc})(\text{H}_2\text{O})]_n$ (**1**); $\{[\text{Cu}_2(\text{Hdpt})_2(\text{tdc})_2] \cdot 2\text{DMF}\}_n$ (**2**) and $[\text{Cu}_2(\text{dpt})(\text{tdc})]_n$ (**3**), respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Captions to Figure and Tables

Table 1. Obtained products under different reaction conditions.

Fig. 1. Coordination environment of the three complexes: **1**(a); **2** (b); **3** (c) (most H atoms omitted for clarity).

Fig. 2. The packing diagram of **1** showing the hydrogen bonding interactions (purple dashed lines) and the typical 2D grid structure.

Fig. 3. The semi-closed cage in **2** (Purple molecule on behalf of DMF).

Fig. 4. (a) The tdc^{2-} ligands connect the 2-D grid-like layer structure into a 3D framework; (b) View of the pore along c axis in a 3D framework of complex **2**; (c) Schematic representation of the 4-connected topological net (the purple balls represent four-connected central Cu atom and green balls represent the four-connected ligand dpt^-).

Fig. 5. XRD patterns for the obtained products with different DMF/ H_2O ratio under temperatures from 55°C to 100°C.

Fig. 6. PXRD patterns and crystal images for the obtained products of different time during the transformation processes of **1** to **3** under moderate temperature (75~85 °C) and high DMF/ H_2O ratio (5.5:0.5~5:1).

Fig. 7. Gas sorption isotherms for **1**, **2** and **3**: (a) N_2 sorption isotherms of **3** at 77 K (inset, pore size distribution plot); (b) CO_2 at 273K and 298K; (c) CH_4 at 273 K and 298K; (d) H_2 at 77 K.

Table 1.

DMF:H ₂ O 6:0	DMF:H ₂ O 5.5:0.5	DMF:H ₂ O 5:1	DMF:H ₂ O 4:2	DMF:H ₂ O 3:3	DMF:H ₂ O 2:4	DMF:H ₂ O 1:5
100 °C						
×	3	×	2	2	2	2
85 °C
3	1→3		2	2	2	2
75 °C
3	1→3		2	2	2	2
65 °C						
×	1	1	2 with traces 1	2	2	2
55 °C						
×	1	1	2 with traces 1	2	2	×

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

(a)

(b)

(c)

(d)

Graphical abstract

Controllable Assembly of Three Copper-Organic Frameworks: Structure Transformation and Gas Adsorption Properties

Xiuling Zhang, Peng-fei Liu, Na Wang, Da-Shuai Zhang *