Kagomé type extra-large microporous solid based on a paddle-wheel Cu^{2+} dimer†

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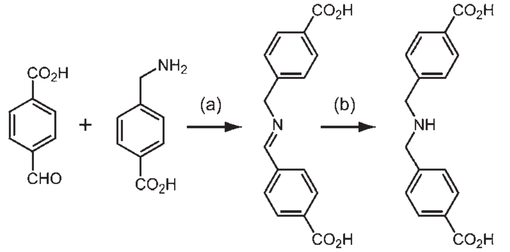
A robust extra-large microporous coordination polymer with a Kagomé type structure was synthesized by carboxylate/amine multifunctional ligand with a Cu^{2+} cluster and the hexagonal 1D channels (~15 Å) showed type I and IV adsorption isotherms for gas molecules.

Metal–organic coordination polymers with open frameworks (porous coordination polymers: PCPs) have been an area of intense research due to their rich structural chemistry and potential applications in storage, catalysis and separation processes.[1] Generally porous solids with a pore diameter of less than 2 nm are microporous and those in the range from 2 to 50 nm are mesoporous materials.[2] Although the immense variety of reports on PCPs has been updated in recent years, in fact, almost all structures cover the microporous region with pore diameters of less than 1 nm and there are still few guidelines to create an extra-large microporous or mesoporous framework with a pore diameter of >1.5 nm, because ligand extension is often accompanied by thermal unstability or framework interpenetration. The large micropores with complete crystalline pore walls have been desired because of their functional significance for high performance catalysis, the separation of large molecules and also as drug delivery systems.[3] The crystalline extra-large microporous solids have been limited to inorganic motifs such as silicates or phosphates,[4] and recently a couple of reports on the creation of PCPs with large pore diameters have been observed.[5]

It is well known that the paddle-wheel type cluster $M_2(COO)_4$ with a bicarboxylate and an N-donor linker affords 3D porous networks with high thermal stability.[6] The coordination geometry of the equatorial and axial positions of the cluster provides a square grid type open framework with high designability. Herein we present a new synthetic approach for an extra-large microporous framework by employing the Cu^{2+} paddle-wheel cluster and a newly synthesized ligand (4-bcba-H3: bis(4-carboxy-benzyl)amine) which has two carboxylate groups at the terminal position, and one aliphatic amine group between the benzoxy groups. These different coordination groups would react with equatorial and axial positions of paddle-wheel type dimer to extend an open 3D framework. The 4-bcba-H3 was synthesized *via* two steps (Scheme 1). 4-(Aminomethyl)benzoic acid in MeOH was added to a MeOH solution of terephthalaldehydic acid. Then $NaBH_3CN$ was added to an imine product in dehydrated MeOH at 273 K and after stirring the solution for 20 h, the 4-bcba-H3 was collected with a yield of 85.4%.†



Scheme 1 Preparation of bis(4-carboxy-benzyl)amine (4-bcba-H3). Conditions: (a) MeOH, 25 °C, 14 h; (b) $NaBH_3CN$, MeOH, 0 °C, 20 h.

The three-dimensional porous compound, $\{[Cu(4\text{-bcba-H})]\cdot H_2O\}_n$ (**1⊃H₂O**) was prepared by reaction of $Cu(NO_3)_2\cdot 2.5H_2O$ with 4-bcba-H3 and excess Et_3N in DMF at room temperature and obtained as blue hexagonal single crystals. The crystal structure of **$1\supset H_2O$** around the Cu^{2+} center is shown in Fig. 1a.§ The asymmetric unit consists of one Cu^{2+}, 4-bcba-H and a guest water molecule. The equatorial position of the Cu^{2+} ion in the paddle-wheel cluster is coordinated to the carboxylate group and the axial position is occupied by N atoms of the amine group of 4-bcba-H. The ligands are bending to connect each Cu^{2+} dimer to form 1D chains along the *c* axis and the chains are linked *via* another carboxy-benzyl group to construct a robust 3D framework (Fig. 1b). As a result, the structure of **$1\supset H_2O$** has two kinds of straight 1D channels which are large and hexagonal with dimensions of 14.3×13.2 Å² and triangular with dimensions of 3.3×4.2 Å², both along the *c* axis. This network on the *ab* plane is a Kagomé-type structure[7] and the pore diameter of ~15 Å is in the range of an extra-large micropore. The estimated solvent-accessible void volume is 63.9% of the total crystal volume by PLATON program.[8]

Evacuation procedure at 140 °C for **$1\supset H_2O$** provided the dehydrated sample of **1**. The thermal stability of **1** was checked

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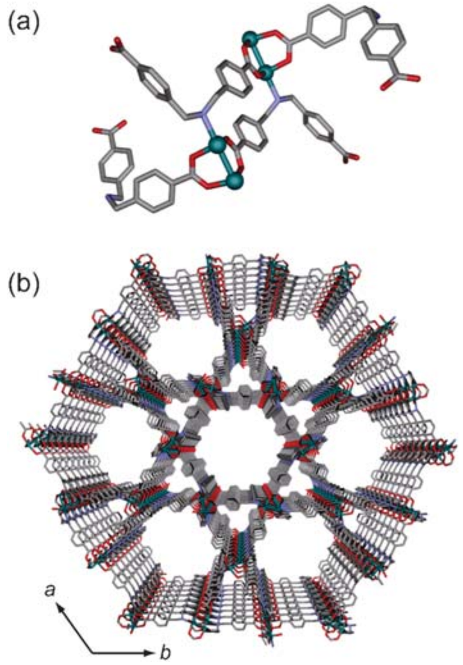

Fig. 1 Crystal structure of $\mathbf{1} \supset \mathbf{H_2O}$ showing (a) the coordination environment around the Cu^{2+} dimers, (b) the 3D assembled porous framework along the *c* axis. Guest waters and H atoms are omitted and Cu, C, O, N are green, red, gray and blue.

by thermogravimetric analysis (Fig. 2), which revealed a temperature range (300 to 510 K) of stability with no observable weight loss. We also measured variable temperature X-ray powder patterns for **1** (Fig. 3). In the range of 90 to 400 K, the powder patterns show sharp peaks and do not change at all, matching the simulation from single crystal X-ray analysis. This indicates that the porous framework possesses high crystallinity and robustness over a wide range of temperatures.

We estimated the adsorption property for **1**. The N_2 isotherm at 77 K (Fig. 4a) exhibits a type-I profile, which means the presence of permanent micropores. The adsorption amount is 500 mL g^{-1} (STP) at $P/P_0 = 0.9$ and the desorption profile does not show any hysteresis and the BET (Brunauer–Emmett–Teller) surface area of **1** calculated from the N_2 adsorption isotherm is 1715 m^2 g^{-1} (Fig. 5a).† The small triangular pore is too narrow to pass gases and only the hexagonal pore acts as a gas accommodation channel. The pore size distribution of **1**, which was calculated by DFT methods in Fig. 5b, showed a pore diameter of only 15 Å dominating the distribution, which is consistent with the crystallographic results of large hexagonal 1D channels.†

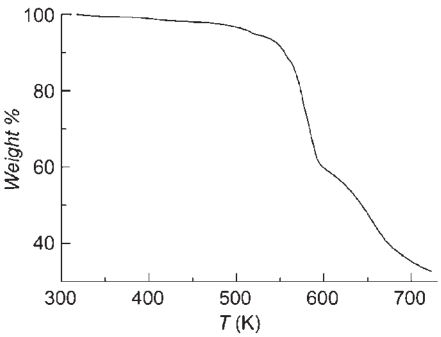

Fig. 2 Thermogravimetric analysis of **1** over the temperature range from 300 to 723 K at a heating rate of $\beta = 5$ K min^{-1}.

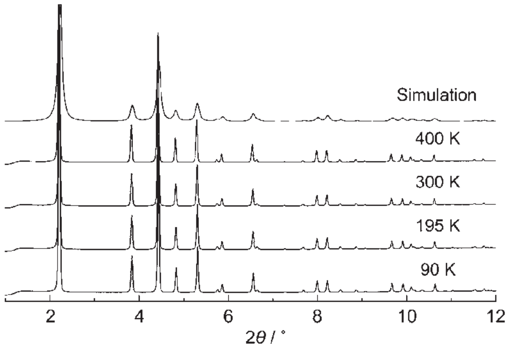

Fig. 3 Simulated and observed X-ray powder diffraction patterns of **1** for each temperature ($\lambda = 0.8$ Å).

The adsorption isotherms of guests are dependent on the shape and intramolecular interaction of the guests at each temperature. In the case of CO_2, the isotherm at 195 K in Fig. 4b shows a type IV isotherm with no hysteresis loop. The pore filling with multilayers of adsorptive molecules causes sharp capillary condensation observed at P/P_0 from 0.21 to 0.23 which indicates a narrow distribution of pores in the mesoscale range. The absence of hysteresis during desorption is a common feature of materials containing hexagonally aligned 1-D pores with widths of <40 Å.[9] For MeOH and MeCN (Fig. 4c and d) at 298 K, we also have type-IV isotherms without hysteresis. The relative pressure of capillary condensation of MeOH ($P/P_0 = 0.22$) is larger than that of MeCN and the saturated adsorption amount of MeOH is also larger than for MeCN. The extra-large micropores of **1** with high crystallinity provide the different adsorption profiles which are dependent on both the chemical and physical properties of the guest molecule.

In summary, we synthesized a robust, large microporous coordination polymer with a Kagomé type structure consisting of a carboxylate-amine ligand and a Cu^{2+} paddle-wheel cluster. This motif could be applied to create a crystalline guest-accessible space with intermediate region of micro- and mesoscale chemistry.

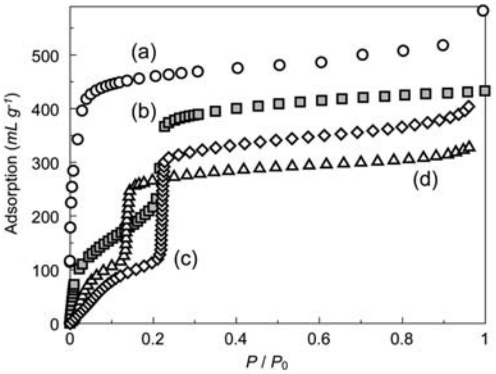

Fig. 4 Adsorption isotherms of **1** for (a) N_2 (77 K), (b) CO_2 (195 K), (c) MeOH (298 K) and (d) MeCN (298 K).

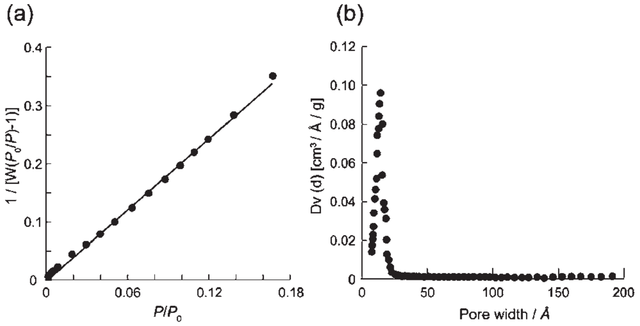

Fig. 5 (a) BET plot and (b) DFT/Monte-Carlo differential pore volume distribution of **1**, which were calculated from N_2 adsorption at 77 K.

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Notes and references

§ Crystal data for **1⊃H₂O**: $C_{16}H_{15}CuNO_5$, FW = 364.84, trigonal, space group R$\bar{3}$, a = 41.28(2) Å, c = 9.864(4) Å, V = 14556.3(115) Å^3, Z = 18, reflections collected: 56 084, independent reflections: 7391, T = 223 K, D_c = 0.745 g cm^{-1}; final R indices [$I > 2\sigma(I)$]: R_1 = 0.0830, wR_2 = 0.1480, GOF = 0.903. CCDC 685829. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b806616g

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