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Cobalt(II) metal–organic framework micro-nanoparticles: Molecular self-assembly from layers to micropores showing the conjunctive orientation of carboxyl groups

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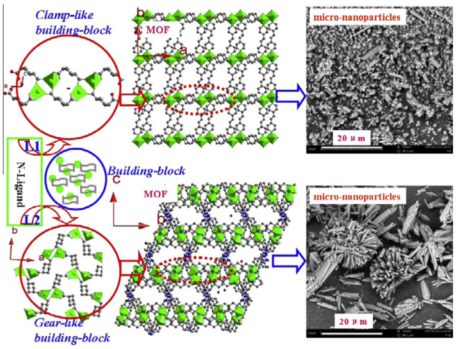
HIGHLIGHTS

- Cobalt metal–organic frameworks were assembled in a MeOH–H_2O solvent system.
- MOFs' structures exhibited from layers to micropores.
- N-ligand can regulate and control the conjunctive orientation of carboxyl groups.
- MOFs' micro-nanoparticles were investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

Cobalt metal–organic framework (MOF) materials CoL(1,4-chdc)·mH_2O (1,4-chdc = 1,4-cyclohexanedicarboxylic acid, L1 = 1,2-di(4-pyridyl)ethylene, and $m = 0$ for **1Co**; L2 = 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene and $m = 2$ for **2Co**) were assembled in a MeOH–H_2O solvent system. They crystallized in a monoclinic system with space group $P2(1)/c$, $Z = 4$, $a = 9.479(4)$ Å, $b = 13.704(6)$ Å, $c = 14.455(6)$ Å, and $\beta = 99.424(6)°$ for **1Co**, and $a = 14.349(11)$ Å, $b = 12.088(9)$ Å, $c = 26.62(2)$ Å, and $\beta = 97.255(11)°$ for **2Co**. It was shown that N-ligand can regulate and control the conjunctive orientation of carboxyl groups in these MOFs; thus, the MOFs exhibited structures that ranged from layers to micropores. Furthermore, the micro-nanoparticles of **1Co** and **2Co** were investigated for new potential applications of micro-nano MOFs.

Introduction

Metal–organic frameworks (MOFs) are a new class of crystalline supramolecular materials composed of metal cations or clusters bridged by organic electron donor linkers [1–4]. These porous materials exhibit high surface areas, and tunable pore sizes and functionalities. Research into these compounds is expanding rapidly; the materials show great potential for application in gas storage and gas separation, catalysis, chemical sensing, and medical applications [5–12] because of their exciting combination of porous properties and stability. Several methods for synthesizing different types of MOFs have been developed [13–18]. As solid-state materials, MOFs are typically formed by solvent (i.e., liquid-phase) reactions, and crystallization from the liquid phase involves the surface chemistry of building blocks. The construction of meso-MOFs using elongated ligands [19,20] or bulky secondary building blocks [21] is of great interest. However, increasing the

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pore size and framework stability of MOFs remains a major challenge. More recently, great efforts have been made to design nanoscale MOFs with different morphologies, such as spheres, cubes, rods, and wheels [22–28]. The evolution of the full innovative potential of MOFs requires a fundamental understanding of the formation process of MOFs, particularly for nanotechnology and device integration. Furthermore, control of the crystal growth of MOFs and nanoparticles in size- and shape-selected crystals, and MOF heterostructures in a given system in a well-defined and oriented manner is necessary.

Cobalt dicarboxylates are very promising materials because of their versatile coordination geometries. As good candidates for MOFs, 1,2-di(4-pyridyl)ethylene (bpe) and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (bpd) are club-bridged ligands suitable for the synthesis of porous materials. Herein we report cobalt 1,4-cyclohexanedicarboxylate MOF materials with layer structures (Co(bpe)(1,4-chdc), **1Co**) and microporous structures (Co(bpd)(1,4-chdc)·$2H_2O$, **2Co**). Two complexes **Co** self-assembles from a layered structure into a microporous structure, indicating that the conjunctive orientation of carboxyl groups is controlled by the N-ligand. Furthermore, in this study, the morphology and size of the micro-nanoparticles were controlled during fabrication by the system, the solution, and the surfactant. The results of this study demonstrate that the hydrophilic surfactant favored monodispersion and that the solution of smaller molecules facilitated the formation of the micro-nanoparticles. Furthermore, N_2 adsorption–desorption isotherms were studied.

Experimental section

In a typical experiment, a mixture of 1,4-chdc (0.1033 g, 0.6 mmol), NaOH (0.048 g, 1.2 mmol), $Co(NO_3)_2$ (0.1746 g, 0.6 mmol), and distilled water (20 mL) were stirred to obtain a Co-chdc aqueous solution, which was subsequently transferred to a test tube. Then, 4 mL of a MeOH solution containing bpe (0.1093 g bpe dissolved in 20 mL MeOH) was carefully layered on top of the Co-chdc aqueous solution (4 mL) through a 2-mL buffer solution consisting of H_2O and MeOH in a volume ratio of 1:1 in the test tube. After three weeks, hexahedral light-red crystals $[Co(C_8H_{10}O_4)\ (C_{12}H_{10}N_2)]_\propto$ (**1Co**) suitable for single crystal X-ray diffraction analysis were obtained. The synthesis procedure for the light-red crystals of $[Co(C_8H_{10}O_4)\ (C_{12}H_{10}N_4)]_\propto$ (**2Co**) was the same as that for **1Co**, except that bpd (0.1261 g) was used instead of bpe (0.1093 g).

Micro-nanocrystalline samples of **1Co** and **2Co** were synthesized under different conditions. The N-ligand bpe (0.1093 g, 0.6 mmol) or bpd (0.1261 g) was added to an alcohol (20 mL) solution in a 250-mL round-bottom flask to obtain a clear homogeneous solution. The light-red Co-1,4-chdc solution was then continuously injected into the magnetically stirred aforementioned N-ligand alcohol (20 mL) solution at room temperature using an injection pump. Furthermore, the alcohol-phase solvents methanol and ethanol, surfactants tween 40 and OP-10, and reaction time were all selected to control the sizes and morphologies of the micro-nanocrystals. The red micro-nanocrystals were collected for characterization.

Results and discussion

The IR spectra show ν_{CH} stretching peaks at 3054, 3006, 2970, 2912, and 2835 cm^{-1} for **1Co** and 3054, 2929, and 2855 cm^{-1} for **2Co**. The broad band at 3380 cm^{-1} in the spectrum of **2Co** was attributed to ν_{OH} stretching of H_2O. The expected strong characteristic peaks indicating the stretching vibration of carboxyl groups were observed at 1603, 1559, 1435, and 1384 cm^{-1} in the spectrum of **1Co** and at 1605, 1482, 1453, and 1425 cm^{-1} in the spectrum of **2Co** (Fig. S1). The thermogravimetric analysis (TGA) curve of **1Co** shows a weight loss of 79.14% (cal: 85.58%) because of incomplete decomposition of the sample. The TGA curve of **2Co** shows a weight loss of 7.0% (cal: 7.57%) from room temperature to 309 °C, which is attributed to the removal of water molecules. The weight losses associated with incompletely decomposed ligands are 12.89% from 309 to 350 °C and 32.82% from 384 to 492 °C (Fig. S2).

As shown in Fig. 1, **1Co** crystallizes in monoclinic space group $P2(1)/c$ and exhibits a 2-D net-like structure (Table S1). Only one crystallographically independent Co(II) is located in the six-member coordination environment. Four oxygen donors provided by carboxyl groups coordinate to the cobalt ions in equatorial positions, and two nitrogen atoms from bpe link to the cobalt atom in axial positions. The Co–O bond lengths range from 2.015 to 2.187 Å, and the Co–N bond lengths are 2.144 and 2.168 Å. The O–Co–O, O–Co–N, and N–Co–N bond angles vary from 59.78° to 152.88°, 86.19° to 95.00°, and 175.19° (Table S2), respectively. One of the carboxyl groups of 1,4-chdc chelates to a cobalt ion, and the other bridges two other cobalt ions. The $Co_2(1,4\text{-chdc})_4$ of cobalt 1,4-cyclohexanedicarboxylate is a clamping building block (Fig. S3); it clamps to other building blocks to form infinite ladders along the *b*-axis. The ladders link club ligand bpe to form a 2-D network MOF structure along the *c*-axis (Fig. 2); the channels of this structure are approximately 9.1×13.7 Å^2.

2Co is constructed by two Co(II) ions, two 1,4-chdc ligands, two bpd ligands, and four H_2O molecules. Each Co(II) ion is coordinated in its equatorial positions by four oxygen atoms from three 1,4-chdc ligands and in its axial positions by two nitrogen atoms provided by bpd. The bpd ligand coordinates to one Co(II) ion as a bridging ligand. The Co–O bond lengths range from 2.009 to 2.350 Å, and the Co–N bond lengths range from 2.149 to 2.170 Å. The O–Co–O, O–Co–N, and N–Co–N angles vary from 57.88° to 154.55°, 86.19° to 95.90°, and 176.10° to 179.10° (Table S3), respectively. The carboxyl groups of 1,4-chdc link cobalt ions in the same manner as those of **1Co**, although the $Co_2(1,4\text{-chdc})_4$ of cobalt 1,4-cyclohexanedicarboxylate is a gearing building block (Fig. S8). These gearing building blocks infinitely connect with each other and result in wave-layers along the *a*-axis (Fig. S10). The club ligand bpd link the wave-layers to form a 3-D microporous structure along the *a*-axis (Fig. 2); the pore size of this structure is

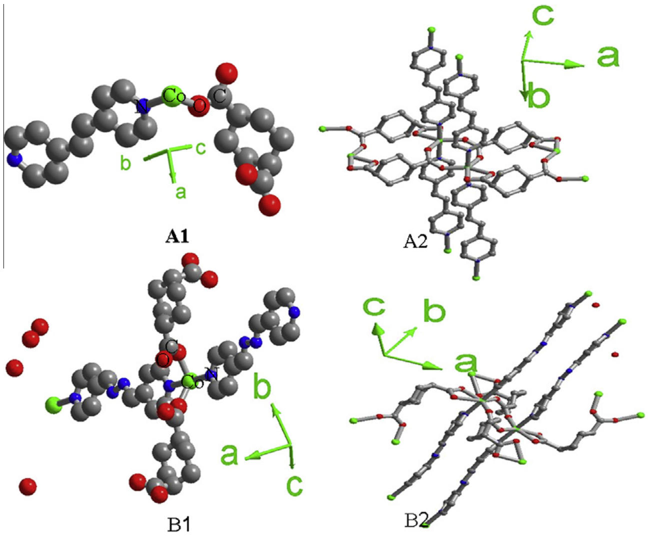

Fig. 1. ORTEP drawings of **1Co** and **2Co** showing the coordination environments of the Co^{2+} ions.