



## Co(II)-tricarboxylate metal–organic frameworks constructed from solvent-directed assembly for CO<sub>2</sub> adsorption

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### ABSTRACT

A series of Co(II)-tricarboxylate metal–organic frameworks (MOFs), {Co<sub>3</sub>O(HBTC)<sub>2</sub>(H<sub>2</sub>O)(DMF)}<sub>n</sub> (**1**), {Co<sub>2</sub>(BTC)Cl(DEF)<sub>3</sub>}<sub>n</sub> (**2**), {Co<sub>3</sub>O(BTB)<sub>2</sub>(DMF)·2(N(CH<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O))<sub>n</sub> (**3**), and {Co<sub>3</sub>(HCOO)(BTB)<sub>2</sub>(DEF)·(N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>n</sub> (**4**) (BTC = 1,3,5-benzenetricarboxylate, BTB = 4,4',4''-benzene-1,3,5-triyltribenzoate, DMF = *N,N'*-dimethylformamide, DEF = *N,N'*-diethylformamide), were synthesized by solvothermal reaction in the presence of phthalic acid under different solvents (DMF and DEF). Synthetic investigations and structural analyses reveal that the two pairs of MOFs show distinct frameworks with remarkable solvent-directed feature, although they were assembled from the same starting materials, i.e., CoCl<sub>2</sub>·6H<sub>2</sub>O with tricarboxylate-BTC for **1** and **2**, or with expanded derivative BTB for **3** and **4**. The CO<sub>2</sub> adsorption properties of these MOFs were investigated and the results indicate that the activated MOF **1** presents the highest CO<sub>2</sub> uptake capability of 85.8 cm<sup>3</sup> g<sup>-1</sup> at 1 atm and 273 K.

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## 1. Introduction

Sharp increase of anthropogenic CO<sub>2</sub> emission has seriously influenced the global climate and therefore the fabrication of CO<sub>2</sub> adsorbents becomes vital technology on the way towards a sustainable low-carbon future [1–6]. Due to high porosity, large surface area, and adjustable pores size, metal–organic frameworks (MOFs) have become highly promising materials for gas adsorption, especially for CO<sub>2</sub> capture and storage [3–8]. The CO<sub>2</sub> capture performance is normally affected by the frameworks of selected MOFs. It is still a challenge for synthetic chemists to predict and control the assembly processes during the framework formations, since such processes are highly dependent on the coordination geometry of the metal ions, the flexibility of the ligand backbones, metal/ligand ratios, and the presence of counterions and solvents [9–13]. Among these factors, the solvent effect on the assembly process is of particular interest, which was also observed in the most synthetic processes for the preparations of zeolites and molecular sieves [14–16]. When using the same reactants with the same metal/ligand ratios, only slight changes in the solvents may lead to the formations of distinct frameworks. Thus, the investigations on the solvent-directed assembly from the same

materials are fundamentally important for exploring ultimate MOFs possessing the best performance for CO<sub>2</sub> capture and storage.

Tricarboxylate organic ligands, such as BTC and BTB (BTC = 1,3,5-benzenetricarboxylate, BTB = 4,4',4''-benzene-1,3,5-triyltribenzoate) are sophisticated organic linkers for the construction of MOFs [17–20]. Based on solvent-controlled assembly process, two pairs of new MOFs, {Co<sub>3</sub>O(HBTC)<sub>2</sub>(H<sub>2</sub>O)(DMF)}<sub>n</sub> (**1**) and {Co<sub>2</sub>(BTC)Cl(DEF)<sub>3</sub>}<sub>n</sub> (**2**), {Co<sub>3</sub>O(BTB)<sub>2</sub>(DMF)·2(N(CH<sub>3</sub>)<sub>2</sub>·(H<sub>2</sub>O))<sub>n</sub> (**3**) and {Co<sub>3</sub>(HCOO)(BTB)<sub>2</sub>(DEF)·(N(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>n</sub> (**4**) (DMF = *N,N'*-dimethylformamide, DEF = *N,N'*-diethylformamide) were synthesized and subsequently used for CO<sub>2</sub> adsorption. Herein, we report the synthetic investigations and structural analyses of the two pairs of Co(II)-tricarboxylate MOFs constructed from solvent-directed assemblies and their performance on CO<sub>2</sub> adsorption.

## 2. Experimental

### 2.1. Materials and general methods

All reagents for syntheses and analyses were purchased commercially and used as received. FT-IR spectra were recorded as KBr pellets on a SHIMADZU IR Prestige-21 spectrometer. Thermogravimetric analyses (TGA) were carried out on a TGA-Q500 thermoanalyzer with a ramp rate of 10 K/min from room temperature to 1023 K under nitrogen atmosphere. Powder X-ray diffraction (PXRD) measurements were taken on a SHIMADZU

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XRD-6000 Labx diffractometer using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at 40 kV and 30 mA. The data collection was carried out with a step size of  $0.04^\circ$  and counting time of 1 s per step, and the  $2\theta$  angular range is from  $5^\circ$  to  $50^\circ$ . The nitrogen and CO $_2$  sorption isotherms were measured on an autosorp-IQ instrument from Quantachrome Instruments Corporation.

## 2.2. Syntheses of MOFs 1–4

A mixture of CoCl $_2 \cdot 6\text{H}_2\text{O}$  (0.238 g, about 1 mmol, pretreated under vacuum at 333 K for 1 h), H $_3$ BTC (0.066 g, 0.4 mmol), and phthalic acid (0.033 g, 0.2 mmol) in DMF (10 mL) was added into a Teflon vessel (23 mL). After ultrasonication for 5 min, solvothermal reaction was carried out in stainless steel autoclave at 393 K for 2 days. Blue needle-shaped single crystals of {Co $_3$ O(BTC) $_2$ (H $_2$ O)(DMF) $_n$ } (**1**) were obtained when the autoclave was cooled down to room temperature naturally (yield = 87% based on Co). IR (KBr): 3454.5 s, 2374 m, 2342 m, 1654 s, 1627 s, 1560 s, 1521 s, 1508 s, 1436 s, 1388 s, 1375 s, 1340 m, 1253 m, 1197 w, 1109 m, 1062 w, 997 w, 925 w, 906 w, 754 s, 717 s, 663 s, 565 m, 518 m.

The synthetic method is similar to that of **1**, except that the organic solvent DMF was replaced by DEF. Blue blocked single crystals of {Co $_2$ (BTB)Cl(DEF) $_3$ } (**2**) were obtained (yield = 79% based on Co). IR (KBr): 3446 s, 2939 m, 2883 m, 2336 m, 1631 s, 1560 s, 1458 m, 1436 s, 1375 s, 1340 m, 1265 m, 1211 m, 1124 w, 1101 m, 1070 w, 999 w, 943 m, 825 m, 767 s, 717 s, 669 m, 659 m, 569 w, 528 w.

The synthetic method is similar to that of **1**, except that the organic ligand (BTC) was replaced by BTB. Blue blocked single crystals of {Co $_3$ O(BTB) $_2$ (DMF) $_2$ (N(CH $_3$ ) $_2$ )(H $_2$ O) $_n$ } (**3**) were obtained (yield = 78% based on Co). IR (KBr): 3415 s, 2931 m, 2374 m, 2331 m, 1646 s, 1610 s, 1544 m, 1436 m, 1386 s, 1330 m, 1253 m, 1176 w, 1103 s, 1060 m, 1016 m, 927 w, 856 m, 808 m, 785 s, 711 m, 680 m, 667 m, 609 m, 565 w, 503 m.

The synthetic method is similar to that of **3**, except that the organic solvent DMF was replaced by DEF. Pink blocked single crystals of {Co $_3$ (HCOO)(BTB) $_2$ (DEF)(N(C $_2$ H $_5$ ) $_2$ ) $_n$ } (**4**) were obtained (yield = 81% based on Co). IR (KBr): 3431 s, 2978 m, 2366 m, 2331 m, 1654 s, 1585 s, 1541 m, 1400 s, 1361 s, 1307 w, 1263 m, 1213 w, 1182 w, 1105 w, 1070 w, 1016 w, 943 w, 858 m, 808 m, 781 s, 705 m, 673 m, 642 w.

## 2.3. X-ray crystallography

Single-crystal X-ray diffraction data for MOFs **1–4** were collected on a Bruker CCD APEXII diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at about 290(2) K. The program SAINT was used for integration of the diffraction profiles [21], and all the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [22]. Metal atoms in each MOF were located from the *E*-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses, which were refined with anisotropic thermal parameters on  $F^2$ . The hydrogen atoms of the ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. The hydrogen atoms of the coordinated water molecules were generated using the difference Fourier method, others were generated theoretically. The solvent molecules in MOFs **1**, **3** and **4** were highly disordered and cannot be modeled, thus the SQUEEZE routine of PLATON was applied to remove the contributions of the solvent molecules to the scattering [23]. Further details of crystallographic data and structural analyses as well as selected bond lengths and angles for MOFs **1–4** are summarized in Tables S1–S4 of the Supplementary Data. CCDC 895679–895682 contain the supplementary crystallographic data

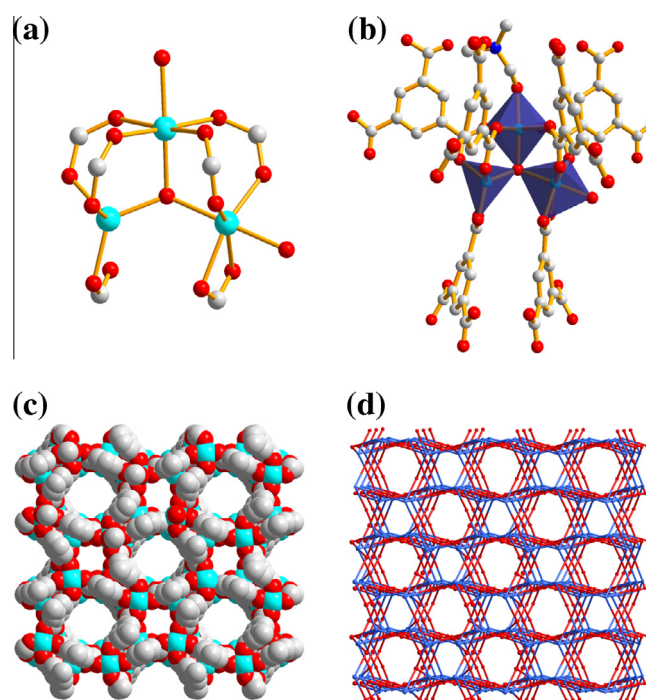
for MOFs **1–4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 3. Results and discussion

### 3.1. Crystal structure analyses of MOFs 1–4

X-ray crystallographic study shows that MOF **1** crystallizes in orthorhombic system with space group of *Iba*2 ( $a = 19.695(4)$ ,  $b = 21.188(4)$ ,  $c = 17.820(4) \text{ \AA}$ ,  $V = 7436(3) \text{ \AA}^3$ , and  $Z = 8$ ). Detailed structural analysis reveals that **1** is a three-dimensional (3D) porous MOF consisting of trinuclear Co $_3$  clusters and BTC ligands as well as coordinated water and DMF molecules, which is an isomorphism of reported Zn-BTC framework, MOF-CJ4 [24]. As shown in Fig. 1a and b, in each Co $_3$  cluster of **1**, three Co(II) ions bridged by a central  $\mu_3$ -O with the Co–O bond lengths of 1.927(14)–2.114(13)  $\text{ \AA}$  (Table S2) are arranged in a triangular form, in which two Co(II) ions are in octahedral CoO $_6$  coordination geometry and the third one is in a tetrahedral CoO $_4$  geometry. Then, one Co $_3$  cluster is extended by six coordinated BTC (Co–O bond lengths ranging in 1.985(12)–2.271(13)  $\text{ \AA}$ ) to form a 3D framework with one-dimensional (1D) channels ( $9.9 \times 10.3 \text{ \AA}^2$  in diameter) along *c* axis, which are filled by the coordinated water and DMF molecules on vertices of octahedrally formed Co(II) clusters (Fig. 1b and c). A better insight into the nature of the complicated framework was achieved by the application of a topological approach. Reducing the Co $_3$  cluster and BTC ligand to simple nodes, 3D framework of **1** can be considered as a net with the  $(4\cdot 6^2)(4^2\cdot 6^{10}\cdot 8^3)$  topology as shown in Fig. 1d [25–27].

From the same starting reactants through a similar synthetic procedure as MOF **1**, when DEF was used as organic solvent instead of DMF, single crystals of **2** were obtained. X-ray crystallographic study reveals that MOF **2** crystallizes in a cubic system with space group of *P*2 $_1$ 3 ( $a = 14.652(6) \text{ \AA}$ ,  $V = 3145(2) \text{ \AA}^3$ , and  $Z = 4$ ).



**Fig. 1.** Perspective views of the crystal structure **1**. H atoms are omitted for clarity. (a) the trinuclear Co $_3$  moiety; (b) the BTC-extended Co $_3$  moiety; (c) the porous framework of **1**, which shows 1D channels along *c* axis. The coordinated water and DMF molecules are omitted for clarity; (d) the  $(4\cdot 6^2)(4^2\cdot 6^{10}\cdot 8^3)$  topology of **1**.

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