Inorganic Chemistry Communications 95 (2018) 22–26

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

Two anionic low-connectivity microporous indium-organic frameworks with selectivity adsorption of CO_2 over CH_4

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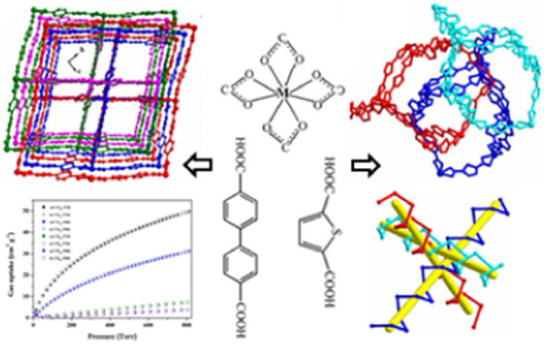
GRAPHICAL ABSTRACT

Two novel anionic low-connectivity microporous In(III)-organic frameworks were successfully prepared. Complex 1 exhibits selectivity adsorption of CO_2 over CH_4. Complex 2 shows a chiral structure with dia net.



ARTICLE INFO

Keywords:
Metal-organic framework
Anionic
Low-connectivity
Microporous
Selectivity adsorption

ABSTRACT

Up to now, the synthetic development of metal-organic frameworks (MOFs) continues to attract much attention because of their intriguing structural topologies and potential applications. Herein, two anionic low-connectivity microporous indium-organic framework materials (named complex **1** and complex **2**) have been solvothermally synthesized, which were further characterized by single-crystal X-ray diffraction, powder X-ray diffraction (PXRD), elemental analysis, thermogravimetric analysis (TGA), and gas sorption in detail. In addition, complex **1** exhibits high selectivity adsorption of CO_2 over CH_4 at ambient conditions.

Recently, the synthetic development of porous coordination polymers (PCPs) or metal organic frameworks (MOFs) continues to attract much attention because of their intriguing structural topologies and potential applications in gas storage and separation [1–6], sensing [7–11], optical devices [12–14], enzyme immobilization [15–17], and heterogeneous catalysis [18–21]. The low connectivity of framework building blocks (3 or 4 connected) is closely associated with open architecture and porosity in three-dimensional (3D) framework materials [22]. The design strategy in low-connectivity microporous MOFs is that tetrahedral metal centers (*e.g.*, Zn^{2+}, In^{3+}) are connected by different linear ligands to form such structures. Generally, this type of materials demonstrates outstanding properties in gas storage and separation because the guest molecules in the pores are easily removed and their framework stability at high temperatures.

The successful in the synthesis of low connectivity MOFs often appear interpenetration structures in the past several decades. Sometimes the framework interpenetration, which would reduce the capacity of an MOF, could help to increase the stable and porous crystalline structures.

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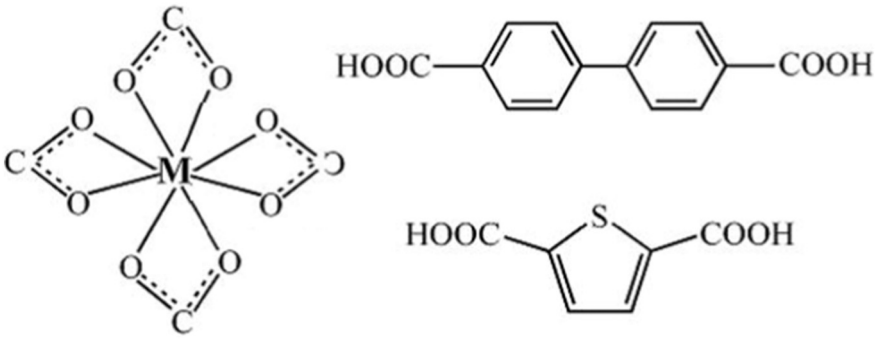
https://doi.org/10.1016/j.inoche.2018.06.023
Received 4 May 2018; Received in revised form 27 June 2018; Accepted 29 June 2018



Scheme 1. The structural building blocks in this work.

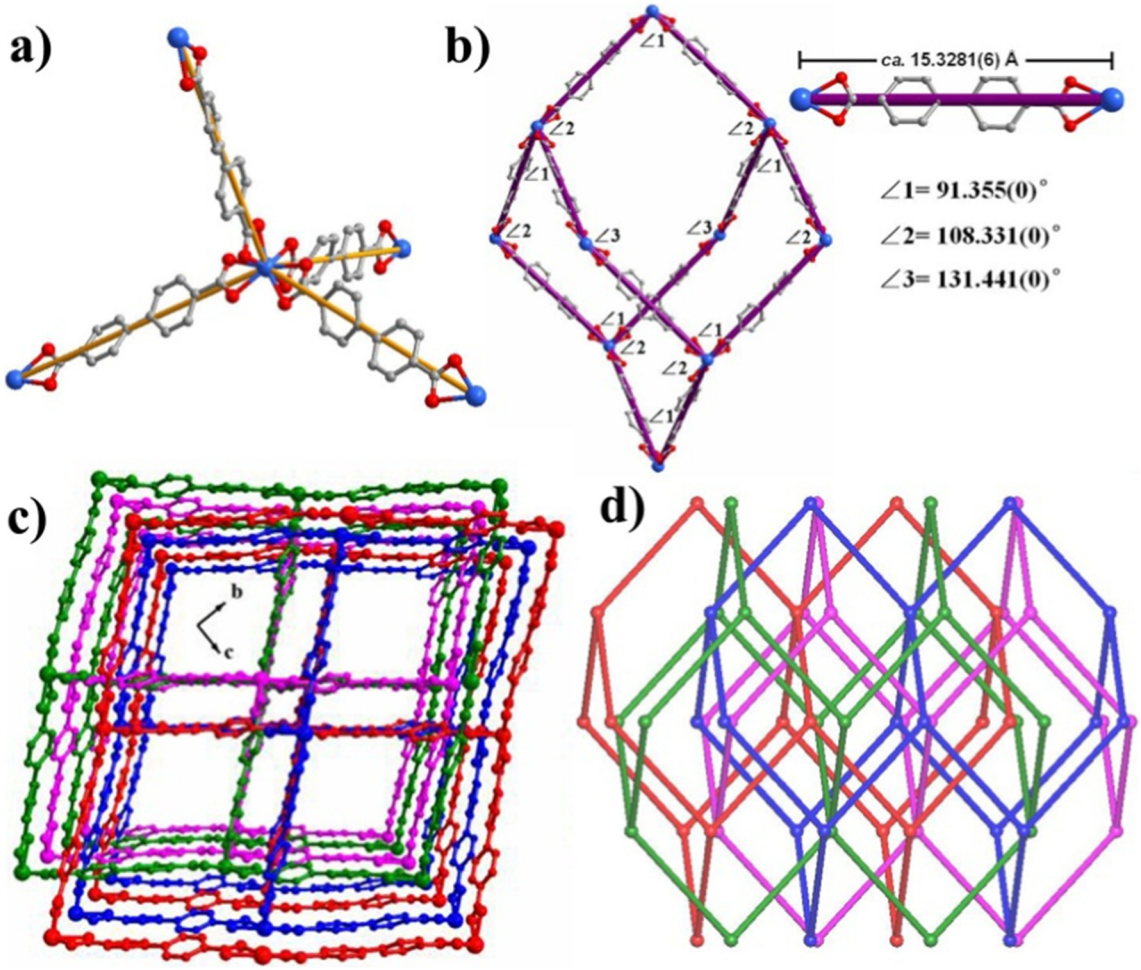


Fig. 1. (a) Coordination environments of In(III); (b) the coordination angle in complex **1**; (c) the four-fold interpenetration of complex **1** network; (d) the 4-connected **dia** net; (The hydrogen atoms are omitted for clarity and C, gray; O, red; In, blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In addition, ionic liquid is a very good solvent in the synthesis of MOFs, but difficult to remove as template molecules with high boiling point and taking too much pore volume as cation to balance the charge [23].

Thus, according to the synthetic strategies of low-connectivity microporous MOFs, we employed Indium nitrate, 4, 4′-biphenyldicarboxylic acid (H_2bpdc) and thiophene-2, 5-dicarboxylic acid (H_2thb) successfully to design and synthesis two anionic low-connectivity framework $[NH_2(CH_3)_2][In(bpdc)_2]\cdot 2DMF$ (named complex **1**) and $[N(CH_3)_4][In(thb)_2]\cdot 2H_2O$ (complex **2**). The synthetic strategies of complex **1** and complex **2** as show in Scheme 1, every metal center is connected with four dicarboxylates, and every dicarboxylate is linked with two metal centers. Complex **1** is a four-fold interpenetration structure, and complex **2** is a three-fold interpenetration structure, which are both belong to **dia** topology. Complex **1** was successfully synthesized by heating H_2bpdc, *D*-camphoric acid and $In(NO_3)_3\cdot 6H_2O$ in a mixed solvent of triethanolamine and *N*,*N*-dimethylformamide (DMF) for three days at 160 °C. Complex **2** could be achieved by heating H_2thb, 1,4-Diazabicyclo[2.2.2]octane (DABCO) and $(CH_3)_4NCl$ in acetonitrile (MeCN) and DMF at 120 °C for two days [24, 25].

The single-crystal X-ray diffraction analysis [26] reveals that complex **1** crystallizes in the orthorhombic space group *P*nna and a three-dimensional (3D) coordination framework. In the asymmetric unit, it