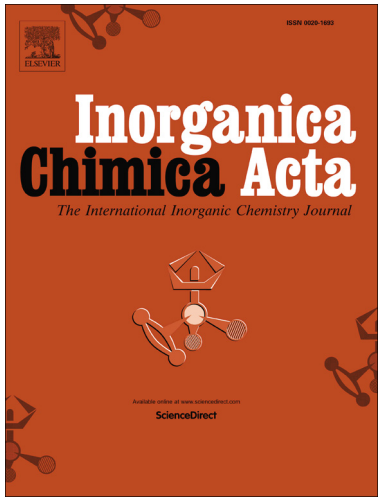

Research paper

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PII: S0020-1693(18)30027-6
DOI: https://doi.org/10.1016/j.ica.2018.05.039
Reference: ICA 18290

To appear in: *Inorganica Chimica Acta*

Received Date: 5 January 2018
Revised Date: 1 May 2018
Accepted Date: 28 May 2018

Please cite this article as: A-L. Cheng, J. Zhang, L-L. Ren, E-Q. Gao, A new anionic metal-organic framework based on tetranuclear zinc clusters: selective absorption of CO_2 and luminescent response to lanthanide (III) ions, *Inorganica Chimica Acta* (2018), doi: https://doi.org/10.1016/j.ica.2018.05.039

A new anionic metal-organic framework based on tetranuclear zinc clusters: selective absorption of CO_2 and luminescent response to lanthanide (III) ions

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Keywords: anionic; metal-organic framework; ultra-microporous; gas adsorption; luminescent

Abstract: A new anionic metal-organic framework, $\{[H_3O]_2[Zn_4(\mu_4\text{-}O)(NSBPDC)_4]\cdot 16(H_2O)]\}_n$ **(1)**, was synthesized under solvothermal conditions using a predesigned multifunctional dicarboxylic acid (H_2NSBPDC = 6-nitro-2,2'-sulfone-4,4'-dicarboxylic acid**)**. Complex **1** contains 4-connected tetrahedral $[Zn_4(\mu_4\text{-}O)(CO_2)_8]$ clusters, which are further linked by the bridging ligands, generating a three-fold interpenetrated diamond-like network with ultra-microporous channels. Gas adsorption studies reveal that **1** has good adsorption selectivity for CO_2 over CH_4 and N_2. In addition, **1** can serve as a host to incorporate lanthanide cations via a targeted ion-exchanged process. Notably, the structure of **1** can be dehydrated and rehydrated reversibly.

1. Introduction

Metal−organic frameworks (MOFs), as a new class of hybrid organic-inorganic materials, has attracted considerable attention owing to their structural diversity and promising applications in adsorption and separation, ion-exchange, catalysis, sensing and so on [1-8]. Therefore, a plethora of MOFs with intriguing structures have been constructed by rational selection of metal ions (or metal clusters) and organic ligands [9-11]. Significantly, polynuclear metal clusters (di-, tri-, tetranuclear and even higher-nuclear clusters) usually possess high rigidity and well-established geometries, which can be viewed as secondary building units (SBUs) to construct robust high-connected MOFs with predictable topologies [12-14]. Among the various kinds of SBUs, dinuclear copper and tetranuclear zinc clusters have been widely studied for the generation of desirable MOFs. In particular, with the 6-connected octahedral $[Zn_4O(COO)_6]$ as SBUs, a series of **pcu** type MOFs (IRMOFs) have been successfully synthesized by using different linear decarboxylases as the ligands [13]. Additionally, by replacing the linear dicarboxylates with slightly bent ligands [fluorene-2,7-dicarboxylate and *N*,*N*′-bis(4-carboxyphenyl)urea], a rare 3D **kag** type framework (**2**) and an unconventional flexible pcu type framework (**3**) based on $[Zn_4O(COO)_6(sol)_2]$ (sol = DMSO/DMF) clusters have been obtained, respectively [15, 16]. The above results indicate that the slight bending of the dicarboxylate ligands would affect the