

## Short communication

## Design and synthesis of porous 3D MOFs hybrid functional materials encapsulating macrocyclic metal complexes

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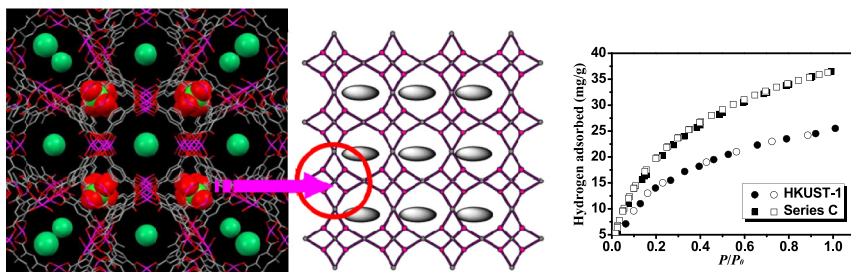
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## GRAPHICAL ABSTRACT

A series of 3D MOFs encapsulating functional macrocyclic metal complexes were obtained from the simple one-step solvothermal reaction of zinc nitrate or copper nitrate, benzenetricarboxylate (BTC) and certain macrocyclic metal complexes. In the Zn-BTC or Cu-BTC-based frameworks, the coordinatively unsaturated metal centers of macrocyclic metal complexes can increase capacity of hydrogen adsorption. It has provided a new strategy for the orientated construction of new crystalline functional hybrid materials and for the rational design of exposed metal centers.



## ARTICLE INFO

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## ABSTRACT

A series of remarkable crystalline compounds were obtained from the simple one-step solvothermal reaction of zinc nitrate or copper nitrate, benzenetricarboxylate (BTC) and certain macrocyclic metal complexes. In these compounds, the macrocyclic metal complexes were alternately arrayed as noncoordinating guests in the cages of a Zn-BTC or Cu-BTC-based metal organic framework host matrix. Powder X-ray diffraction analysis, ICPAES, EDS, H<sub>2</sub> adsorption studies demonstrated the validity of encapsulation of macrocyclic metal complexes and the enhancement of hydrogen capacities. It is the first time that the construction of metal-organic frameworks (MOFs) is based on macrocyclic metal complexes as templates. Actually, it is worth to be noted that the introduction of macrocyclic metal complexes contributes to increasing the active sites or the adsorption sites interacting to hydrogen gas.

## 1. Introduction

Metal-organic frameworks (MOFs) have emerged as a unique class of porous materials due to their potential in many applications such as molecular separation [1], ion-exchanges [2], catalysis [3], gas

adsorption and storage [4]. A major impetus to advance MOF applications is the development of new pathways and strategies to construct made-to-order MOFs as platforms suitable for a desired application. Toward this effort, we developed a new approach or strategy for construction of MOFs based on the rigid organic ligands and metal ions

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used macrocyclic metal complexes as the templates. Actually, during the recent years MOFs are highly attractive all over the world in the area of hydrogen energy, particularly for hydrogen storage. Our new strategy has been proved to be much more effective than the former given hydrogen capacities [5].

Several groups have reported analogical work as introducing or encapsulating organic amine cations [6], inorganic alkali metal ions [7], polyoxometalates [8] and metalloporphyrin [9] into particular MOFs for certain functions. However, the encapsulation of macrocyclic metal complexes into MOFs has not been presented until now.

Herein, we tried several kinds of metal ions, organic ligands and macrocyclic metal complexes to detect the rules of encapsulation of macrocyclic metal complexes into porous three-dimensional MOFs. First, the appropriate size and figure of pores are crucial which framework is chosen as host matrix of macrocyclic metal complexes. Second, the particular type of macrocyclic metal complexes is required to be thermodynamically stable keeping itself integral during the assembly process. Third, the negative-charge framework is much more advantageous than the neutral-charge owing to the charge balance rule.

Accordingly, we successfully prepared a series of compounds based on the metal-BTC host framework and macrocyclic metal complexes which served as guests and filled in the pores. Besides, we presented the use of a MOF as platform to anchor macrocyclic metal complexes, which allows enhancement of its hydrogen capacities in Fig. 1.

## 2. Experimental section

### 2.1. Materials and physical measurements

The requisite macrocyclic metal complexes  $[\text{NiL}_1](\text{ClO}_4)_2$ ,  $[\text{CuL}_2](\text{ClO}_4)_2$  and  $[\text{CoL}_2](\text{ClO}_4)_3$  ( $\text{L}_1 = 5,7,7,12,14,14$ -hexamethyl-1,4,8,11-tetra-azacyclo-4,11-tetradecadiene and  $\text{L}_2 = 5,7,7,12,14,14$ -

hexamethyl-1,4,8,11-tetra-azacyclotetradecane) were synthesized according to the literature method [10]. All the other reagents of analytical grade were obtained from commercial sources and used without further purification. The powder X-ray analyses were recorded on a Bruker D8 ADVANCE X-ray diffractometer. The composition of the prepared compounds was analyzed by Energy dispersive spectrometer (EDS) (Thermal field emission environmental SEM-EDS-EBSD, model Quanta 400 F). Thermal gravimetric analysis (TGA) data were collected on a Netzsch TG-209 instrument under nitrogen atmosphere in the temperature range of 20–800 °C with a heating rate of 10 °C/min. Gas sorption isotherms were measured on a volumetric adsorption apparatus (Bel-max). The relative Inductively Coupled Plasma-atomic Emission Spectrometry is TJA IRIS (HR) (Scheme 1).

### 2.2. Preparation of complexes

#### 2.2.1. Series A

$[\text{Zn}_3(\text{BTC})_2](\text{DMF})_n$  (A1). A mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (0.145 g, 0.64 mmol),  $\text{H}_3\text{BTC}$  (0.090 g, 0.43 mmol) and DMF (10 mL) was sealed in a 20 mL Teflon-lined stainless steel autoclave and heated at 85 °C for 48 h, then cooled to room temperature at a rate of 5 °C/h. Transparent block-shaped crystals were obtained in ca. 40% yield based on Zn (II). This identical structure was reported by Qiu et al. [11].

$[\text{Zn}_3(\text{BTC})_2](\text{DMF})_n \supset [\text{NiL}_1](\text{ClO}_4)_2$  (A2). This kind of compounds were prepared by a similar procedure to A1 with the implementation of  $[\text{NiL}_1](\text{ClO}_4)_2$  (0.010 g, 0.019 mmol; 0.020 g, 0.038 mmol; 0.050 g, 0.093 mmol; 0.100 g, 0.186 mmol respectively). Yellow block crystals were obtained in ca. 37% yield based on Zn(II).

$[\text{Zn}_3(\text{BTC})_2](\text{DMF})_n \supset [\text{CuL}_2](\text{ClO}_4)_2$  (A3). These compounds were also synthesized by the above methods replacing  $[\text{CuL}_2](\text{ClO}_4)_2$  with  $[\text{NiL}_1](\text{ClO}_4)_2$ .

$[\text{Zn}_3(\text{BTC})_2](\text{DMF})_n \supset ([\text{CoL}_2](\text{ClO}_4)_3)$  (A4). These compounds

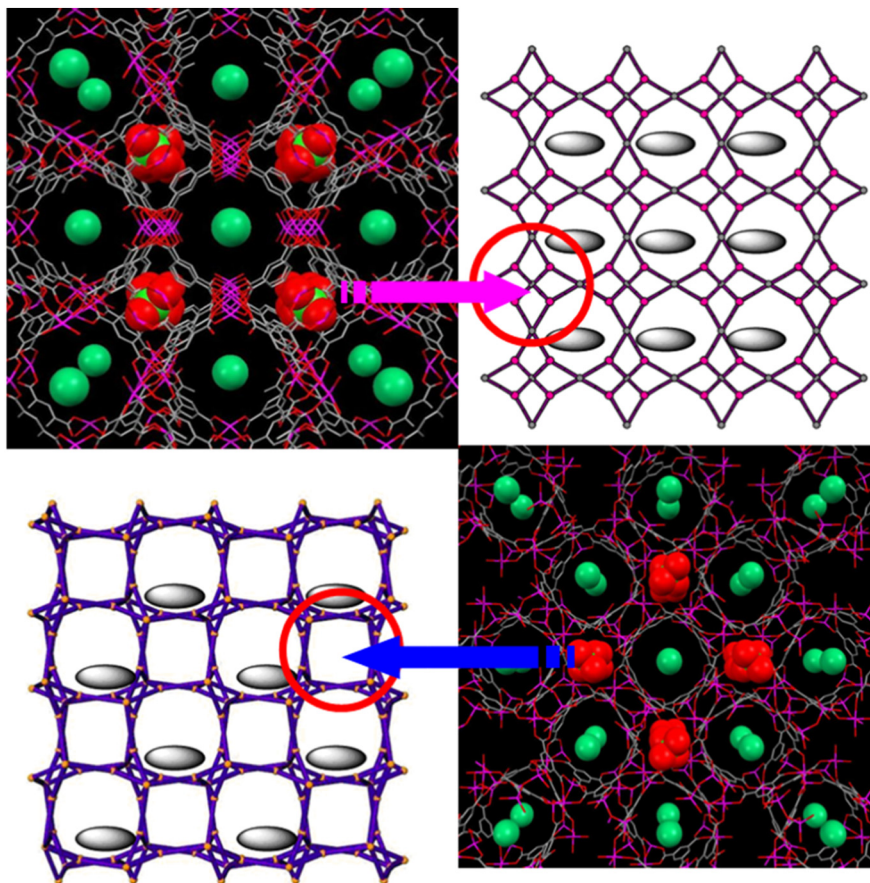


Fig. 1. Crystal structure and schematic presentation of Series A and C (HKUST-1 analog) (upper) and Series B (MOF-38 analog) (lower). The metal-BTC frameworks, and perchlorate anions are represented by wireframe and spacefill models, respectively. All H atoms and solvent molecules are omitted for clarity. Metal ions or ellipsoids represented for metal macrocyclic complexes with perchlorate anions are enclosed in two kinds of cages, respectively.

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