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A new anionic metal-organic framework for highly efficient removal of cationic pollutant in water

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ABSTRACT

A novel 3D anionic microporous metal-organic framework, $Cu_2(H_4DCPPA)$ (**ZJU-71**, H_4DCPPA=[1,1′:2′,1′′-terphenyl]-4,4′,4′′,5′-tetracarboxylic acid, ZJU=Zhejiang University), has been synthesized and structurally characterized. **ZJU-71** possesses one-dimensional channels along ***a*** axis and a ***scu*** type topology. The negative electricity of the framework makes **ZJU-71** an candidate for effective elimination of cationic contaminants.

1. Introduction

It is well-known that the presence of trace amounts of endocrine disrupting chemicals (EDCs) is harmful to environment and living creatures, even can cause some changes in endocrine function. Therefore, quick removal of trace amounts of EDCs from aquatic environment is extremely significance. Because the endocrine disrupting chemicals are stable to light, heat and oxidation reactions, the effective elimination of water containing EDCs is very difficult [1–5]. Several technologies such as chemical, physical and biological methods have been used to remove the trace amounts of EDCs. The adsorption technology is considered as one of the most competitive technologies among the proposed methods because of economic feasibility, high-efficiency, convenient and simple operation. However, conventional adsorption materials may not reach suitable removal efficiencies [6,7]. So it is an importance challenge to develop new porous materials for efficient and quick removal of trace amounts of EDCs.

Metal-organic frameworks (MOFs) can be easily self-assembled from metal ions/metal containing clusters and organic bridging linkers through coordination bonding [8–22]. As a new type of functional porous materials, MOFs have been widely used in various fields, such as gas separation/storage [9], luminescence [10–12], electrode materials [13], catalysis [14,15], magnetism [16] and drug delivery and biomedicine [17]. Due to large surface areas, high porosity and systematically tunable/controllable pore sizes and shapes [11–16], MOFs are also very promising porous materials for the pollutant adsorption/removal. It has been found that numerous MOFs have been utilized for treatment of water containing high concentration methylene blue [22,23], nevertheless, the lack of specific interaction sites restricts their adsorption for trace amounts of methylene blue. Because the methylene blue (MB) can be regarded as a cationic contaminants, so the anionic MOFs can serve as a host to preferably accommodate methylene blue by electrostatic interactions. With this in mind, we design and synthesize a new anionic metal-organic framework, $[Cu_2(H_4DCPPA)(H_2O)](C_3H_7NO)_4$ $(H_2O)_4$ (**ZJU-71**; H_4DCPPA =[1,1′:2′,1′′-terphenyl]-4,4′,4′′,5′-tetracarboxylic acid, ZJU=Zhejiang University). **ZJU-71** possesses one-dimensional channels along ***a*** axis and a ***scu*** type topology. By the design of interactions between the host and guest, the effective removal of trace amounts of pollutants from the aqueous solution at room temperature was realized with **ZJU-71**.

2. Experimental

2.1. Synthesis of ZJU-71

ZJU-71 compounds were obtained by dissolving H_4DCPPA (2 mg, 0.0049 mmol) and $Cu(NO_3)_2 0.2 \cdot 5H_2O$ (4.8 mg, 0.0199 mmol) in DMA/DMF/EtOH/H_2O (2.8 mL, 15:5:2:6, v/v) with

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a spot of HBF_4 (60 μL) in a screw-capped vial. The vial was screwed down and placed in an oven at 80 °C for 72 h. The blue cuboid-shaped single crystals were got and washed with DMF a few times to give **ZJU-71**. Elemental analysis: calcd. for $[Cu_2(C_{22}H_{10}O_8)(H_2O)][(C_3H_7NO)_4(H_2O)_4]$ ($C_{34}H_{48}N_4O_{17}Cu_2$): C, 44.78; H, 5.31; N, 6.14; Found: C, 44.83; H, 5.16; N: 6.73.

2.2. Details of MB absorption test

The mother solution of methylene blue (MB) (1000 ppm) was received by dissolving methylene blue ($C_{16}H_{18}ClN_3S$, MW: 373.9) in deionized water. The solutions of MB with different concentration (1–100 ppm) were obtained by continuous dilution of the mother solution with deionized water. The MB concentrations were calculated by absorbance (at 665 nm) of the MB solutions measured through a spectrophotometer (Hitachi UV spectrophotometer, UV-4100).

Before adsorption, the **ZJU-71** was dried 2.5 h at 100 °C under vacuum and maintained in a drying vessel. An exact amount of the MOFs (5 mg) was weighted and then was put in the solutions of MB (10 mL) with the concentrations of 5 ppm. The MB solutions including the adsorbents were mixed well in constant temperature shaking table (YZQ-A, velocity: 170 rpm) and kept for a fixed time (from 5 min to 12 h) at room temperature. The solution was obtained from the adsorbents using a syringe filter (PTFE, hydrophobic, 0.22 μm) after adsorption for a determined time. The MB concentration was calculated by contrasting the UV–vis absorbance to the standard curve, after dilution (if necessary).

3. Results and discussion

ZJU-71 was synthesized by the solvothermal reaction of organic ligand H_4DCPPA and $Cu(NO_3)_2 0.2 \cdot 5H_2O$ in a mixture solvent of DMA/DMF/EtOH/H_2O with addition of a small number of HBF_4 at 80 °C for 72 h as blue cuboid-shaped single crystals. The crystal structure of **ZJU-71** was characterized by single-crystal X-ray diffraction studies. As expect, the simulated Powder X-ray diffraction (PXRD) is perfectly consistent with the experimental PXRD (Fig. S1). The phase purity of the crystal material is independently determined by PXRD and TGA (thermogravimetric analysis, Fig. S2).

The single-crystal X-ray structure analysis shows that **ZJU-71** crystallizes in the monoclinic space group C2/m. As shown in Fig. 1, **ZJU-71** adopts a three-dimensional (3D) framework which is built from the $[Cu_4O_2(COO)_8]$ clusters (Fig. 1a) with H_4DCPPA linkers (Fig. 1b) via the carboxylate groups. The $[Cu_4O_2(COO)_8]$ clusters contains three type of Cu^{II} centers, two H_2O molecule and eight carboxylate groups. All Cu^{II} ions of the $[Cu_4O_2(COO)_8]$ clusters adopt a five-coordination mode. **ZJU-71** has one-dimensional channels along *a* axis of about 6.0 × 6.0 $Å^2$, taking into account the van der Waals radii, which are filled with guest molecules (Fig. 1c). The overall topology is a (4,8)-connected ***scu*** net if the organic linker and metal copper-containing cluster are taken as 4-connected and 8-connected nodes, respectively (Fig. 1d). The most interesting thing is that **ZJU-71** is an anionic framework because a small quantity of oxygen atoms (O9 and O5) (Fig. 1a) are exposed, not forming the coordination bond with copper atom.

The above structure feature of **ZJU-71** exhibits that anionic framework and large pore channel are suitable to encapsulate organic dyes. The performance of **ZJU-71** for the removal of MB from aqueous solution containing MB was detected. The little **ZJU-**

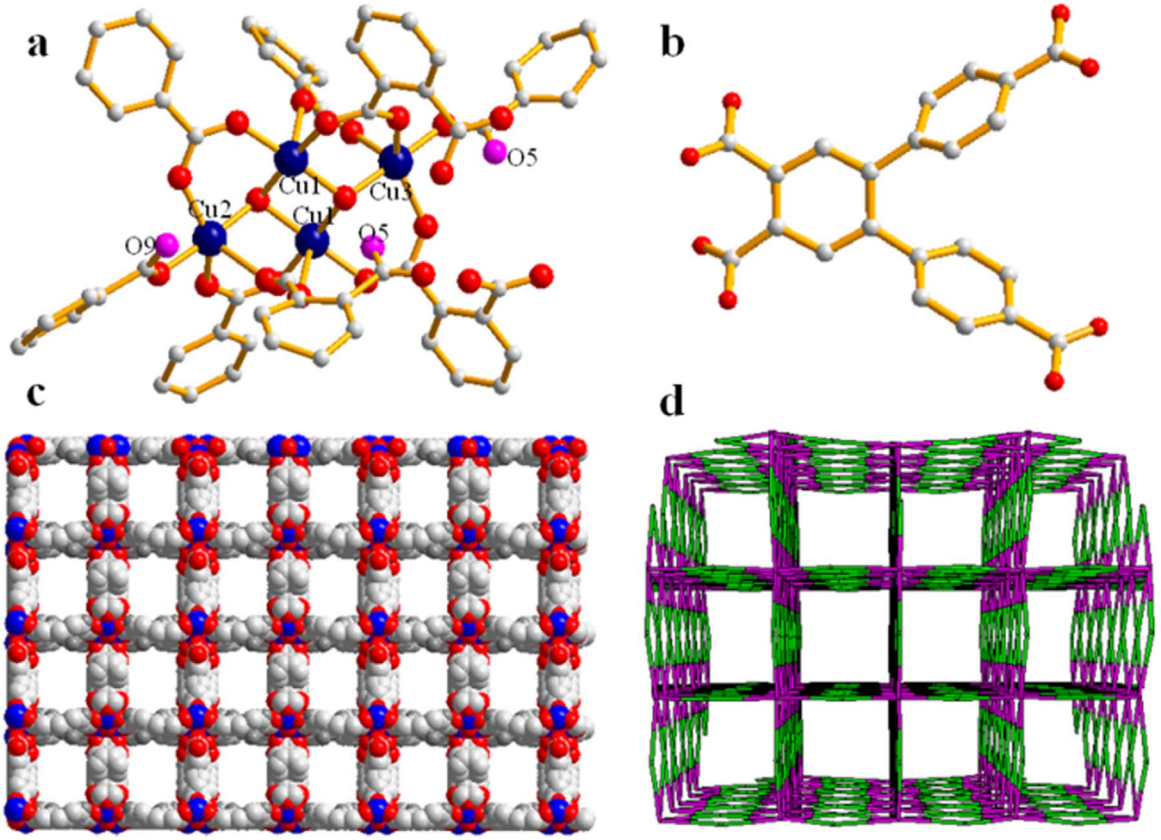

Fig. 1. X-ray single crystal structure of **ZJU-71** indicating (a) A view of the $[Cu_4O_2(COO)_8]$ clusters; (b) The carboxylate groups of linker can be divided into two categories of A and B; (c) the structure viewed along the *a* axes showing the square pores of about of 6.5 × 6.5 $Å^2$ in diameter; (d) showing the channel along *a* axis and (4,8)-connected topology with Schläfli symbol of $(^{416612})(4^46^2)_2$.