Rational construction of defects in a metal–organic framework for highly efficient adsorption and separation of dyes

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HIGHLIGHTS

- Defective UiO-66 was prepared by modulated synthesis and acid treatment.
- The defective UiO-66 shows highest surface area among all the reported UiO-66.
- The defective UiO-66 shows high adsorption capacity for Safranin T.
- The defective UiO-66 shows high selectivity for Safranin T over Crystal Violet.

GRAPHICAL ABSTRACT
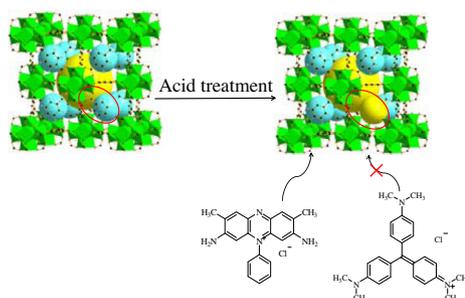
ABSTRACT

In this work, UiO-66 with defects was successfully prepared by a synthesis strategy of using benzoic acid as a modulator and postsynthetic acid treatment. The defective frameworks can be confirmed by N_2 adsorption–desorption analysis and ^1H NMR. It is observed that this strategy can effectively enlarge the surface area and pore volume of stable UiO-66 through the removal of coordinated benzoate ligands. The resulting defective UiO-66 shows high BET surface area and total pore volume (1890 m^2/g and 0.88 cm^3/g), which are both larger than those of defect-free sample (1200 m^2/g and 0.49 cm^3/g) as well as all the reported UiO-66s with defects so far to the best of our knowledge. This MOF exhibits significantly improved capture ability (366 mg/g) toward Safranine T (ST) compared with the defect-free UiO-66 (39 mg/g) and most of reported adsorbents. Meanwhile, it also shows high selectivity for ST over Crystal Violet (CV) due to the size-exclusion effect constructed from the defects in the framework. The results show that this work provides a promising strategy to rationally design novel MOFs for separating large molecules.

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1. Introduction

Porous solid materials including zeolites, activated carbon, and mesoporous silica have attracted tremendous attention owing to their various applications [1]. In the past decades, a class of crystalline nanoporous materials known as metal–organic frameworks (MOFs), composed of metal-containing nodes and organic linkers, has emerged as an alternative to zeolites due to their fascinating performances in many areas, including adsorption, separation, and catalysis [2]. Generally, MOFs have high surface areas, regular permanent porosity, and designable chemical functionality [3,4]. More interestingly, compared with traditional porous solids such as zeolites, MOFs have relative ease of tailoring their structures and functions at the molecular level [5]. In recent years, some stable MOFs have been synthesized and investigated in various

applications [6–9], making these new materials more promising for practical applications. However, the majority of these stable MOFs are microporous [6–9], thus preventing them from adsorbing large molecules such as dyes. Theoretically, pore sizes of MOFs could be expanded by choosing longer organic linkers. The resulting MOFs, however, are usually instable toward water [10] and/or have interpenetrating structures, which could significantly decrease the pore sizes [11]. In addition, from the viewpoint of cost, synthesis of long linkers is usually too complex and expensive. Therefore, it is a great challenge to enlarge the pore sizes of MOFs easily and conveniently without losing their stability.

Recently, introduction of various types of defects into MOFs has received considerable attention as these defects not only help in overcoming diffusion limitations but also result in active sites [12]. Zhou and De Vos's groups reported that coordinated modulator molecules in UiO-66, such as acetic acid and trifluoroacetic acid, could be removed through thermal activation to generate defects in the frameworks [13,14]. The defects could enhance not only the CO_2 adsorption capacity at high pressure by increasing the porosity and surface area [13] but also catalytic activity [14]. Li's group reported that creation of ordered metal vacancies and linker vacancies by hydrolysis could increase pore sizes of Zn_4O $(PyC)_3$ (PyC = 4-pyrazolecarboxylate) [15]. In addition, Farrusseng's group synthesized MOF-5 with structural defects by fast precipitation [16]. The resulting MOF has active catalytic centers for selective alkylation of large aromatics.

Recently, our group successfully prepared various hierarchical-pore MOFs (H-MOFs) with defects by *in-situ* self-assembly strategy using metal–organic assemblies as the templates [17]. The resulting H-MOFs have size-tunable mesopores (40–120 Å) for the capture of several large molecules. In addition, several groups reported that surfactants such as cetyltrimethylammonium bromide could also be used to synthesize mesoporous MOFs [18–20]. However, compared with pristine samples, these resulting H-MOFs with large defects sometimes show poor crystallinity and thus low surface areas.

Therefore, in this work, we proposed a strategy to rationally construct MOF with missing-linker defects to obtain larger pore size. UiO-66(Zr) was selected in consideration of its excellent chemical and thermal stability [8]. UiO-66 itself comprises tetrahedral and octahedral cages (about 8 and 11 Å, respectively) [21]. Each octahedral cage is connected to eight corner tetrahedral cages through triangular windows with a free diameter of about 6 Å. As a result, UiO-66 should have great pore interconnectivity. By using benzoic acid (HBC) as a modulator and postsynthetic acid treatment, defective UiO-66 was synthesized with larger pore and higher surface area than defect-free sample without losing the stability and crystallinity. In addition, to explore the accessibility of defects, we performed adsorption experiments toward two probe molecules (Safranine T, ST, about 9.2×11.4 Å in size; Crystal Violet, CV, about 12.3×13.9 Å in size) with different sizes. The results show that the resulting MOF could selectively capture ST from mixture of ST and CV due to the size-exclusion effect, which indicates that this strategy is useful for the effective separation of large molecules with different sizes.

2. Materials and methods

2.1. Preparation of MOFs

All general reagents and solvents are commercially available and used without further purification except for N,N′-dimethylformamide (DMF), which is treated by activated 4A zeolite to remove water.

UiO-66-X (X represents the equivalent of HBC with respect to 1,4-benzendicarboxylic acid (H_2BDC)) were synthesized by dissolving $ZrCl_4$ (0.120 g, 0.5 mmol), H_2BDC (0.161 g, 1 mmol), and different equivalents of HBC (0, 5, 10, 15, and 20 mmol) with respect to H_2BDC in DMF (20 ml) in a Teflon liner at room temperature. The vessel was sealed and placed in an oven. The system was heated to 120 °C at a rate of 1 °C/min, and held at 120 °C for 24 h. After cooling to room temperature at a rate of 1 °C/min, the resulting white solids were isolated by centrifugation, washed with DMF and acetone five times, and dried. Then the solids were immersed in 1 M HCl solution (10 ml) for 30 min. The solids were centrifuged and washed with water, DMF, and acetone, and then dried under vacuum at 150 °C to obtain UiO-66-X powder (X = 0, 5, 10, 15, and 20, respectively).

Previous report indicates that the near defect-free UiO-66 would be obtained when the synthesis temperature is 220 °C [22]. So the non-defective UiO-66 (UiO-66-ND) was synthesized under the similar condition. $ZrCl_4$ (0.932 g, 4.0 mmol), H_2BDC (1.329 g, 8.0 mmol), and DMF (24 ml) were mixed in a Teflon liner at room temperature, then concentrated HCl (0.67 ml) was added. The vessel was sealed and placed in an oven. The system was heated to 220 °C at a rate of 1 °C/min, and held at 220 °C for 16 h. After cooling to room temperature at a rate of 1 °C/min, the resulting white product was filtered off, washed with DMF to remove the excess of unreacted reactants, then it was washed again with acetone five times and dried under vacuum at 150 °C.

2.2. Characterization techniques

The powder X-ray diffraction (PXRD) patterns were recorded on a BRUKERD8-Focus Bragg–Brentano X-ray Powder Diffractometer equipped with a Cu sealed tube (λ = 1.54178 Å) at room temperature. The 2θ range from 5° to 50° was scanned with a step size of 0.02°. Nitrogen adsorption–desorption measurements at 77 K were performed on an Autosorb-iQ-MP (Quantachrome Instruments) surface area analyzer. Thermal gravimetric analysis (TGA) data were obtained on a TGA-50 (SHIMADZU) thermogravimetric analyzer with a heating rate of 2 °C/min in N_2 atmosphere. The morphologies of the MOFs were characterized using a Hitachi S-4700 scanning electron microscope (SEM) with an accelerating voltage of 20.0 kV. ^{1}H NMR spectra were recorded on a Bruker AV-600 (600 MHz) at 298 K. The FT-IR spectroscopy was recorded on Nicolet 6700 FTIR spectrophotometer. The slice was made with powder constituted of KBr and sample by a tablet machine and the spectra data were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.3. Chemical stability test of MOF

About 0.050 g of sample was immersed in 4 ml of water for 7 d and 1 M HCl for 24 h. Then the samples were collected and washed with methanol three times, and then dried under vacuum at 150 °C.

2.4. Adsorption of dyes

MOFs were washed with deionized water until the pH value of the solution is larger than 5.5. The samples were dried overnight at 150 °C before adsorption to remove the guest molecules in the pores. A stock solution of 1000 ppm ST or CV was prepared by dissolving solid ST or CV in deionized water. To initiate the experiments, 0.010 g adsorbent was put into the aqueous dye solutions (10 ml) with fixed initial dye concentrations from 10 to 800 ppm. After adsorption on a vibration shaker at 25 °C for 24 h, the adsorbent was separated from the solutions by centrifugation. Then the concentrations of residual ST or CV in the supernatant solutions were analyzed by using a double beam model PERSEE TU-1901 UV–vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China) at the calibrated maximum wavelength of 554.0 nm or 585.0 nm.