

Electronic Supplementary Information

Postsynthetic ligand exchange for the synthesis of benzotriazole-containing zeolitic imidazolate framework

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EXPERIMENTAL SECTION

Materials and Reagents. Zinc nitrate hexahydrate (99%) and benzimidazole were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Benzotriazole (99%) was supplied by Alfa Aesar (Tianjin, China). Methanol (HPLC grade) and *N,N*-dimethylformamide (DMF) were obtained from Concord Fine Chemical Research Institute (Tianjin, China). Pure water was supplied by Wahaha Group Co. Ltd (Tianjin, China). Deuterated sulfuric acid was obtained from ACROS ORGANICS. The fused silica capillary was purchased from Yongnian Opic Fiber Plant (Hebei, China).

Instrumentation. The powder X-ray diffraction spectrometry (PXRD) patterns were recorded on a D/max-2500 diffractometer (Rigaku, Japan) using $\text{Cu}_{K\alpha}$ radiation ($\lambda = 1.5418 \text{ \AA}$) over the angular range from 3° to 80° . The BET surface areas of adsorbents were measured on Autosorb-iQ2 automated gas sorption analyzer (Quantachrome, USA) using CO_2 adsorption at 273 K. Thermogravimetric analysis (TGA) was performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 800°C at a ramp rate of $10^\circ\text{C min}^{-1}$. ^1H NMR spectra were recorded on Bruker AMX-400 spectrometers. The transmission electron microscopy (TEM) image was recorded on a JEOL 100CX II microscope (Akishima, Japan) operating at a 100 kV accelerating voltage. Gas chromatographic measurements were performed on an Agilent 7890 GC system with flame ionization detector (FID). The data acquisition and processing were controlled by ChemStation software. Nitrogen (99.999%) was used as the carrier gas. High performance liquid chromatography (HPLC) separations were performed on an HPLC system consisting of a Waters 600

pump, a Waters 2996 photodiode array detector, and an analytical reversed-phase column (C18, 25 cm long \times 4.6 mm i.d., BaseLine Co. Ltd, Tianjin, China) using methanol/water (1:1, v/v) as the mobile phase at a flow rate of 1.0 mL min⁻¹. Cd concentration was measured on a Hitachi 180-80 atomic absorption spectrometer equipped with a hollow cathode cadmium lamp at a wavelength of 228.8 nm and a slit of 1.3 nm. The flame conditions (2.2 L min⁻¹ acetylene and 9.4 L min⁻¹ air) were employed according to standard recommendations. Fourier transform infrared (FT-IR) spectra (4000-400 cm⁻¹) in KBr were recorded on a Magna-560 spectrometer (Nicolet, Madison, WI, USA).

The Synthesis of ZIF-7 Nano-crystals. The ZIF-7 nanocrystals was prepared according to Li *et al.*¹ A solution of Zn(NO₃)₂·6H₂O (0.610 g, 2.054 mmol) dissolved in 100 mL DMF was added into a solution of benzimidazole (1.540 g, 13.05 mmol) dissolved in 100 mL DMF under stirring with a magnetic bar. After keeping at room temperature for 60 h, the ZIF-7 nanocrystals were obtained. The ZIF-7 nano-crystals were separated by centrifugation at 10000 rpm for 10 min and washed with methanol for 3 times. The obtained white solid was dried at 90 °C for 12 h and grinded with an agate mortar for 15 min to get well-distributed size ZIF-7 nano-crystals.

Synthesis of ZIF-7-M by PSE. ZIF-7-M was synthesized as follows. 8 mL DMF, or methanol solution with different benzotriazole concentrations (0.5, 1.0, 5.0 mg mL⁻¹) was placed in 10 mL centrifugal tube. 20 mg ZIF-7 nanocrystals were immersed in the resulting solution. The centrifugal tube was capped and placed in thermostat water bath at 30 or 50 °C for 1, 3 or 10 days. The solution was replaced with a fresh solution

of the same concentration of benzotriazole as the original every 24 h. The progress of the linker exchange reaction was monitored by ^1H NMR (the solid was washed with methanol for 10 times before measurement).

NMR of ZIF-7-M. Approximately 3.5 mg of ZIF-7-M was placed in a 1.5 dram vial and dissolved in 0.5 mL $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ (1/9, v/v) solution by sonication. As a homogeneous solution was obtained, the solution was transferred to an NMR tube, and the sample was locked to D_2O during the measurement.

HPLC Experiments. 50 mg ZIF-7 nanocrystals were immersed in the 20 mL benzotriazole (5 mg mL^{-1}) methanol solution in 50 mL centrifugal tube. The centrifugal tube was capped and placed in thermostat water bath at $30 \text{ }^\circ\text{C}$. The solution was replaced with a fresh solution of the same concentration of benzotriazole as the original every 24 h. The concentration of exchanged benzimidazole in the supernatant for different time was measured by HPLC.

Adsorption of Cd^{2+} Solutions. To study the adsorption kinetics, 6 mL of Cd^{2+} solution (0.5 mg L^{-1}) was added into a 10 mL centrifugal tube containing 5.0 mg ZIF-7 or ZIF-7-M at $25 \text{ }^\circ\text{C}$. After adsorption for a pre-determined time (from 1 to 60 min), the mixture was filtered with $0.22 \text{ }\mu\text{m}$ Millipore cellulose membrane, and the filtrate was sampled for flame atomic absorption spectrometry analysis. To study the adsorption isotherm, 6 mL of Cd^{2+} solution ($0.1\text{-}4 \text{ mg L}^{-1}$) was added into a 10 mL centrifugal tube containing 5.0 mg ZIF-7 or ZIF-7-M at $25 \text{ }^\circ\text{C}$ for 2 h. The mixture was filtered with $0.22 \text{ }\mu\text{m}$ Millipore cellulose membrane, and the filtrate was sampled for flame atomic absorption spectrometry analysis.

Preparation of ZIF-7 and ZIF-7-M Coated Capillary Columns. The capillary was treated with following recipe:² 1 M NaOH for 2 h, water for 30 min, 0.1 M HCl for 2 h, water until the outflow reach pH 7.0, and methanol for 15 min. The capillary was dried with nitrogen at 120 °C for 6 h.

ZIF-7 and ZIF-7-M coated capillary columns were prepared by the following dynamic coating method:² 0.5 mL ZIF-7 or ZIF-7-M (0.5 mg mL⁻¹) DMF suspension was filled into the capillary column (20 m long × 0.25 mm i.d.), then it was pushed through the column at a velocity of 40 cm min⁻¹. To avoid acceleration of the solution plug near the end of the column, a 1 m long buffer tube was attached to the column end as a restrictor. After coating, the capillary column settled for 2 h under nitrogen and was carried out using a temperature program: 30 °C for 10 min, ramp from 30 °C to 320 °C at a rate of 2 °C min⁻¹, and 320 °C for 30 min. The temperature program was repeated 3 times.

The Adsorption Enthalpy of Targets on Stationary Phase. All separations were performed on an Agilent 7890A gas chromatographic system with a flame ionization detector (FID) with the ChemStation software to control the data acquisition and processing. The inlet temperature of gas chromatograph was set at 250 °C. The split ratio was 100:1. The temperature of FID was set to 250 °C. A 10 µL analytes was introduced to a 125 mL gastight sealed glass vial for injection. The adsorption enthalpy for the interaction between the analyte and stationary phase was calculated from the slope of the van't Hoff plots with a temperature range of 30-90 °C.³⁻⁵

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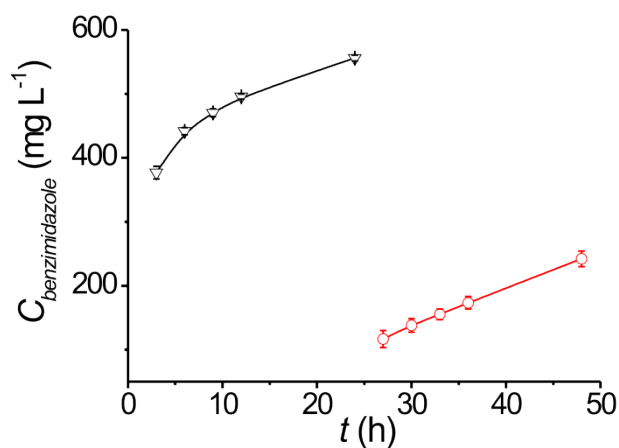


Fig. S1 The concentration of benzimidazole in the supernatant of PSE reaction for different time. The black curve shows the concentration of benzimidazole in the supernatant of the first aliquot of benzotriazole methanolic solution (20 mL) increased with time during the first 24-h PSE. After 24-h exchange, the first aliquot of benzotriazole methanolic solution was replaced with the second fresh aliquot of benzotriazole methanolic solution for next 24-h exchange. So, the red curve shows the concentration of benzimidazole in the supernatant of the second aliquot of methanolic solution (20 mL) during the second 24-h exchange increased with time for PSE.

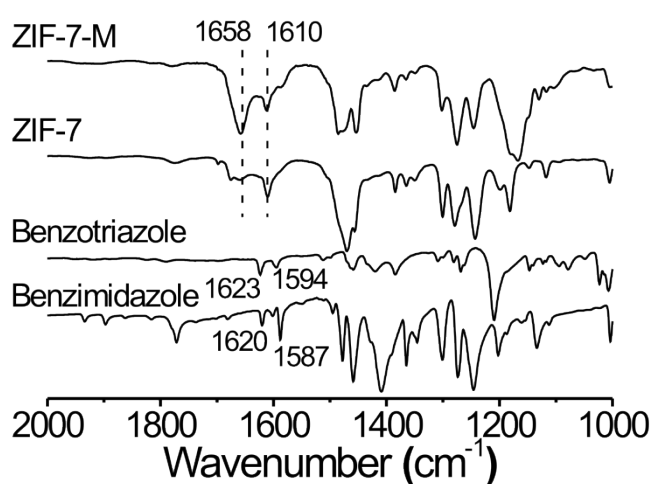


Fig. S2 Fourier transform infrared spectra of ZIF-7 and ZIF-7-M.

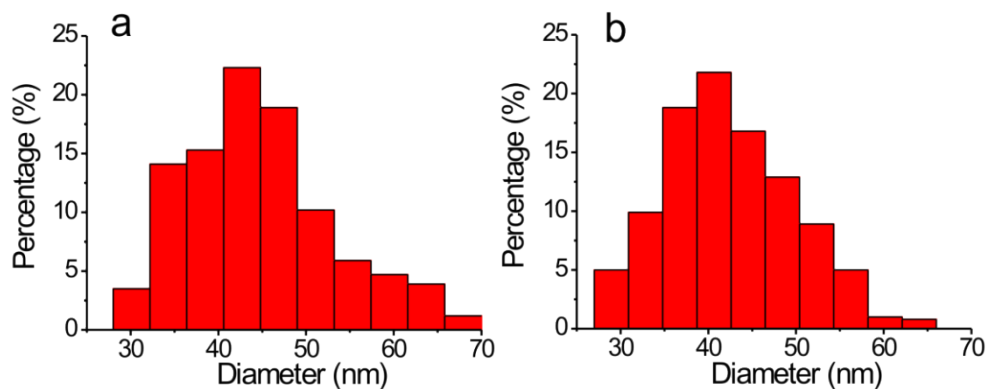


Fig. S3 The statistics of diameter of the synthesized ZIF-7 (a) and ZIF-7-M (b).

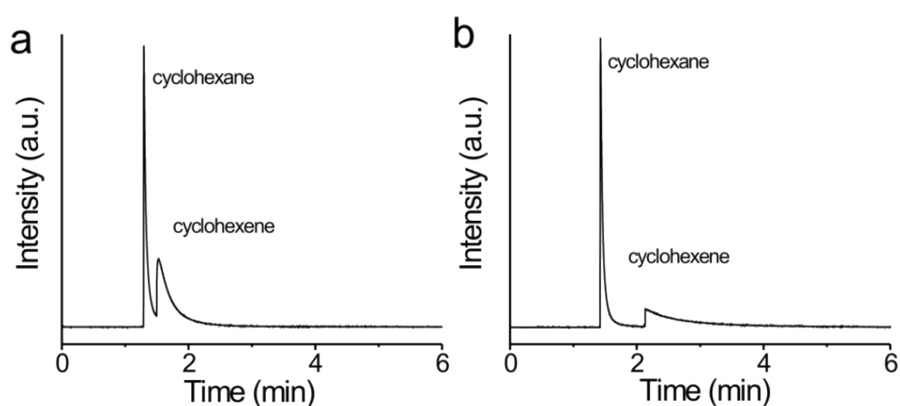


Fig. S4 Gas chromatograms of cyclohexane and cyclohexene obtained by (a) ZIF-7 and (b) ZIF-7-M coated capillary column under 50 °C.

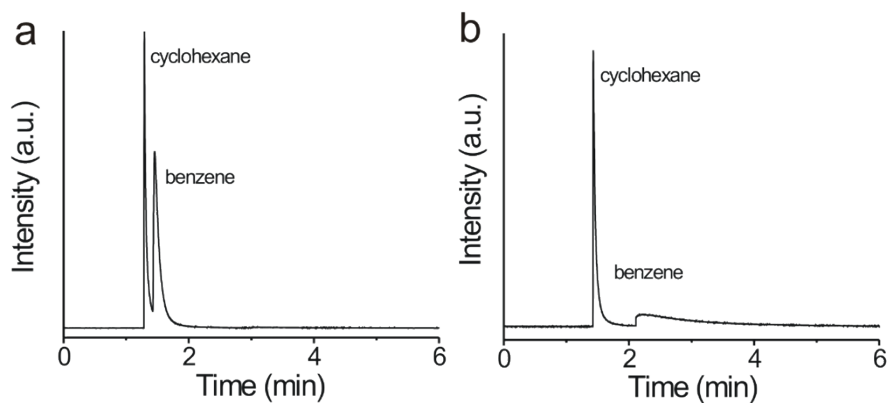


Fig. S5 Gas chromatograms of cyclohexane and benzene obtained by (a) ZIF-7 and (b) ZIF-7-M coated capillary column under 50 °C.

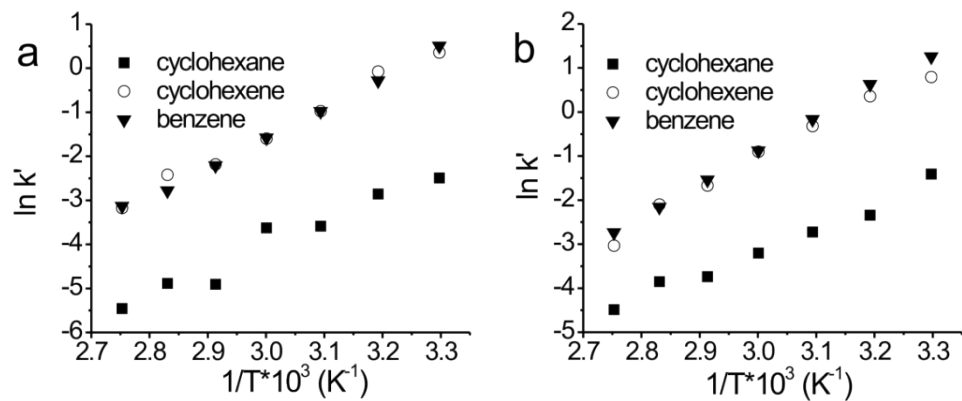


Fig. S6 The van't Hoff plots for cyclohexane, cyclohexene and benzene on the (a) ZIF-7 and (b) ZIF-7-M coated capillary column.

Table S1. BET surface areas of ZIF-7 and ZIF-7-M characterized with CO_2

MOF	BET surface area ($\text{m}^2 \text{ g}^{-1}$)
ZIF-7	351
ZIF-7-M	207