Supporting Information

Continuous Flow fabrication of Metal Organic Framework Capillary Gas Chromatographic column

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Instruments. Gas Chromatograph (GC-9720$_{\mathrm{Plus}}$, Zhejiang Fuli Analytical Instruments Co., Ltd., China); Fourier Transform Infrared Spectrometer (FTIR-650S, Tianjin Gangdong Technology Co., Ltd., China); Powder X-ray Diffractometer (Bruker D8 Advance, Germany); Thermogravimetric Analyzer (Netzsch STA 449 F3, Germany); Automated Surface Area and Porosity Analyzer (Micromeritics ASAP 2460, USA); Flexible Quartz Capillary Columns (0.25 mm inner diameter, Yongnian Mengrui Instrument Technology Co., Ltd., Hebei, China).

Materials. Methanol, ethanol, sodium hydroxide, Glacial acetic acid, hydrochloric acid, 1,4-benzenedicarboxylic acid (BDC), 2-amino-1,4-benzenedicarboxylic acid (NH_2-BDC), N,N-Dimethylformamide (DMF), zirconium(IV) chloride ($ZrCl_4$), zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 2-methylimidazole, succinic anhydride, 3-aminopropyltriethoxysilane (APTES), copper(II) acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$), 1,3,5-benzenetricarboxylic acid (BTC), 2-imidazolecarboxaldehyde, iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), and cobalt(II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) were all of analytical grade and purchased from Titan Chemical Co., Ltd. (Shanghai, China). Alkane Mixture 1: C1–C5 (methane, ethane, propane, n-butane, and n-pentane, each at 5% concentration, balance N_2); Alkane Mixture 2: C3–C6 (propane: 1%, n-butane: 1%, iso-butane: 1%, n-pentane: 0.5%, iso-pentane: 0.5%, n-hexane: 1%, balance N_2) were obtained from Zhongce

Standards Technology Co., Ltd. (Chengdu, China). Hydrogen (fuel gas) and compressed air (support gas) for chromatographic analysis were supplied by a hydrogen generator and air generator, respectively.

Characterization of Fourier Transform Infrared Spectroscopy (FTIR). Samples were prepared via the KBr pellet method, with spectral acquisition spanning 400-4000 cm^{-1} at a resolution of 4 cm^{-1} and 32 cumulative scans.

Powder X-ray diffraction (PXRD). PXRD pattern was collected on Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 0.15406 nm) at a scanning rate of 1 °/min for 2Θ ranging of 5° to 50°.

Thermogravimetric analyses (TGA). TGA was carried out under a nitrogen atmosphere. The sample, pre-dried at 60 °C, was heated from 30 °C to 800 °C at a ramping rate of 10 °C/min.

Nitrogen adsorption-desorption characterization. The sample was degassed under vacuum at 120 °C for 6 hours prior to measurement. The nitrogen adsorption–desorption isotherm was recorded at -196 °C using a surface area and porosity analyzer.

Scanning Electron Microscope (SEM) characterization. The voltage is 15.0 kV and the working distance is 7.0 mm.

Synthesis of ZIF-8

In-column: During the preparation process, the capillary was placed in an ultrasonic bath and flushed at a high flow rate to dislodge ZIF-8 crystals formed on its inner surface.

Ex-column: ZIF-8 nanocrystals were synthesized following the method reported by Cravillon[1]. Specifically, 648.9 mg (7.904 mmol) of 2-methylimidazole and 293.3 mg (0.9859 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ were each dissolved in 20 mL of methanol. The two solutions were then combined in a round-bottom flask and magnetically stirred at room temperature for 1 hour, resulting in a milky suspension. The suspension was centrifuged at 10,000 rpm for 10 minutes, and the supernatant was discarded. The precipitate was washed three times with 10 mL of methanol to remove unreacted 2-methylimidazole. The final white product was dried at 60 °C.

Capillary column pretreatment

A bare fused-silica capillary column of predetermined length was initially activated by sequentially flushing with 1 mol/L NaOH solution for 2 h, rinsed thoroughly with distilled water until neutrality was achieved, subsequently flushed with 1 mol/L HCl solution for another 2 h, and again rinsed with distilled water to neutral pH. In preparation for subsequent modification, the capillary was then flushed with methanol and dried under nitrogen flow.

Capillary carboxylation

Succinic anhydride (122.8 mg, 1.227 mmol) and APTES (290 μL, 1.227 mmol) were reacted in 10 mL of DMF at 30 °C for 3 h. Subsequently, 100 μL of ultrapure water was added to the solution, which was then rapidly infused into pre-treated capillary columns. The capillary was sealed at both ends and allowed to react at 30 °C for 5 h. After completion of the reaction, the capillary was rinsed with methanol and dried under a nitrogen stream at 120 °C, resulting in carboxyl groups (–COOH) being grafted onto the inner surface of the capillaries.

The ZIF-8 capillary gas chromatography column was fabricated via the layer-by-layer growth method

Firstly, a 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution and a 0.2 M 2-methylimidazole methanol solution were prepared separately. The detailed procedure was as follows: Using a syringe pump at a flow rate of 50 μL/min, the $Zn(NO_3)_2 \cdot 6H_2O$ solution was injected into the carboxylated capillary, which was then sealed and reacted at 25 °C for 30 min. Subsequently, methanol was injected as a spacer fluid to separate the metal source and ligand solutions, followed by the injection of the 2-methylimidazole solution. The reaction continued under identical conditions for an additional 30 min. After one cycle, a ZIF-8 stationary phase layer was in situ formed on the capillary inner surface. To increase the coating thickness, multiple cycles were repeated. After flushing with methanol, the column was aged under the specified temperature program to finalize the preparation of the ZIF-8 capillary gas chromatographic column (10 m). The aging process was performed as follows: Initially, the temperature was maintained at 50 °C for 30 minutes. Subsequently, it was raised to 230 °C at a heating rate of 5 °C/min and held for 240 minutes. The temperature was then cooled back to 50 °C at a rate of 5 °C/min and stabilized for another 30 minutes. This entire thermal cycle was repeated once to complete the column aging procedure.

The ZIF-8 capillary gas chromatography column was fabricated via the in-situ growth method

Firstly, a 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution and a 0.2 M 2-methylimidazole methanol solution were prepared separately. The detailed procedure was as follows: The two solutions were thoroughly mixed, and the homogeneous mixture was rapidly infused into a carboxyl-functionalized capillary using a syringe pump at a flow rate of 50 μL/min. After filling the capillary, both ends were sealed, and the reaction proceeded at 25 °C for 8 h to allow in situ growth of the ZIF-8 stationary phase. Subsequently, the column underwent an aging treatment (the aging procedure was the same as above) to finalize the preparation of the ZIF-8 capillary gas chromatographic column (10 m).

The ZIF-8 capillary gas chromatography column was fabricated via the continuous flow technique

Firstly, a 0.1 M $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution and a 0.2 M 2-methylimidazole methanol solution were prepared separately. The two solutions were loaded into separate syringes mounted on a syringe pump.

These syringes were connected via a three-way connector and Peek tubing, with the outlet of the three-way connector linked to a carboxyl-functionalized capillary column (Scheme 1). By advancing the syringes at a controlled rate, the $Zn(NO_3)_2 \cdot 6H_2O$ and 2-methylimidazole solutions were mixed at the three-way junction and flowed into the carboxyl-functionalized capillary (flow rate: 60 μL/min). After continuously delivering at a flow rate of 0.3 mL/h for a specific period, the chromatographic column was subjected to thermal aging treatment (the aging procedure was the same as above) to complete the fabrication of the ZIF-8 capillary gas chromatographic column (10 m).

The ZIF-90 capillary gas chromatography column was fabricated via the continuous flow technique

Firstly, a 25 mM $Zn(NO_3)_2 \cdot 6H_2O$ methanol solution and a 50 mM 2-imidazolecarboxaldehyde solution were prepared separately. Subsequently, using a continuous-flow reaction system, the precursor solutions were co-delivered into a carboxyl-functionalized capillary at a flow rate of 60 μL/min until the capillary was completely filled. The flow rate was then adjusted to 0.3 mL/h, and the reaction was maintained at 25 °C for 6 h. Afterward, the column underwent an aging treatment (the aging procedure was the same as above) to complete the preparation of the 10 m-long ZIF-90 capillary gas chromatographic column.

The ZIF-67 capillary gas chromatography column was fabricated via

the flow chemistry method

Firstly, a 0.1 M $Co(NO_3)_2 \cdot 6H_2O$ methanol solution and a 0.2 M 2-methylimidazole solution were prepared separately. Subsequently, using a continuous-flow reaction system, the precursor solutions were co-delivered into a carboxyl-functionalized capillary at a flow rate of 60 μL/min until the capillary was completely filled. The flow rate was then adjusted to 0.3 mL/h, and the reaction was maintained at 25 °C for 6 h. Afterward, the column underwent an aging treatment (the aging procedure was the same as above) to complete the preparation of the 10 m-long ZIF-67 capillary gas chromatographic column.

The MIL-100 capillary gas chromatography column was fabricated via the flow chemistry method

Firstly, a 20 mM $FeCl_3 \cdot 6H_2O$ ethanol solution and a 20 mM BTC ethanol solution were prepared separately. Subsequently, using a continuous-flow reaction system, the precursor solutions were co-delivered into a carboxyl-functionalized capillary at a flow rate of 60 μL/min until the capillary was completely filled. The flow rate was then adjusted to 0.3 mL/h, and the reaction was maintained at 70 °C for 6 h. Afterward, the column underwent an aging treatment (the aging procedure was the same as above) to complete the preparation of the 10 m-long MIL-100 capillary gas chromatographic column.

The Cu-BTC capillary gas chromatography column was fabricated via

the flow chemistry method

Firstly, A 30 mM $Cu(CH_3COO)_2 \cdot H_2O$ ethanol solution and a 30 mM BTC ethanol solution were prepared separately. Subsequently, using a continuous-flow reaction system, the precursor solutions were co-delivered into a carboxyl-functionalized capillary at a flow rate of 60 μL/min until the capillary was completely filled. The flow rate was then adjusted to 0.3 mL/h, and the reaction was maintained at 25 °C for 6 h. Afterward, the column underwent an aging treatment (the aging procedure was the same as above) to complete the preparation of the 10 m-long Cu-BTC capillary gas chromatographic column.

The UiO-66 and UiO-66-NH_2 capillary gas chromatography columns were fabricated via the flow chemistry method

Firstly, $ZrCl_4$ (18.0 mg, 0.0772 mmol) and BDC (13.0 mg, 0.0783 mmol) were separately dissolved in 6.00 mL DMF each, with each solution supplemented with 1 μL deionized water and 2.3 mL glacial acetic acid as modulators. Subsequently, using a continuous-flow reaction system, the precursor solutions were co-delivered into a carboxyl-functionalized capillary at a flow rate of 60 μL/min until the capillary was completely filled. The flow rate was then adjusted to 0.3 mL/h, and the reaction was maintained at 120 °C for 6 h. Afterward, the column underwent an aging treatment (the aging procedure was the same as above) to complete the preparation of the 10 m-long UiO-66 capillary gas chromatographic column.

The UiO-66-NH_2 capillary (10 m) chromatographic column was prepared following the identical procedure described above, with the organic ligand BDC replaced by NH_2-BDC.

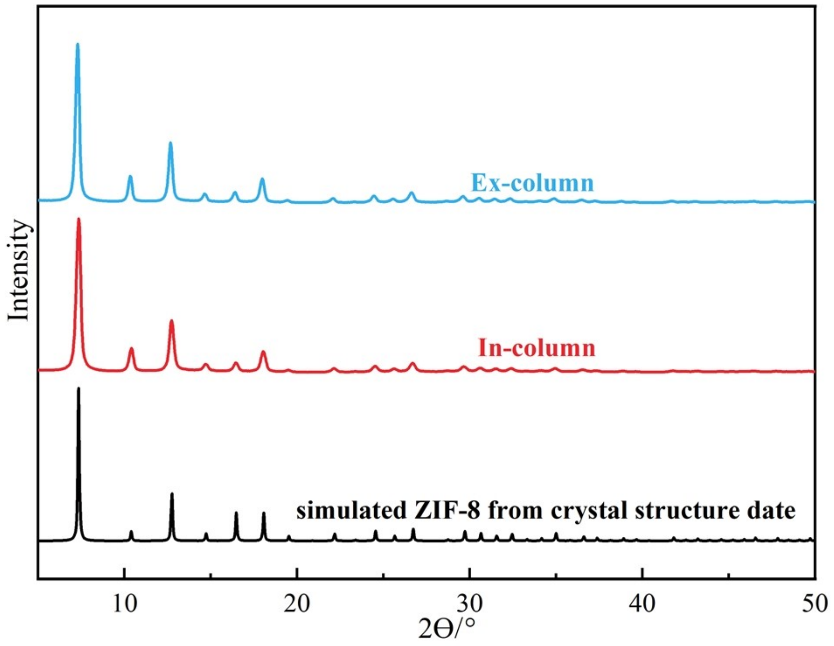


Figure S1 The PXRD pattern of ZIF-8.

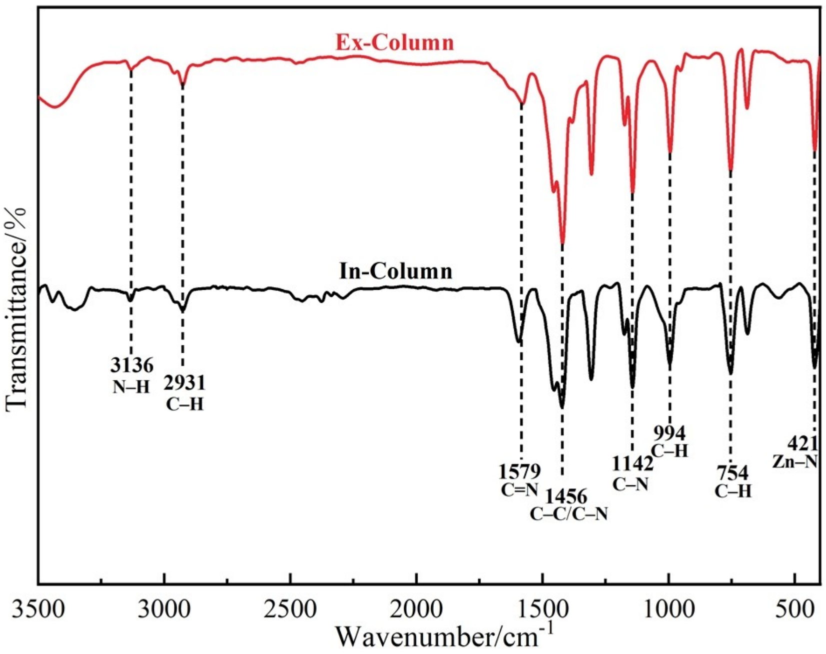


Figure S2 The FTIR spectra of ZIF-8.

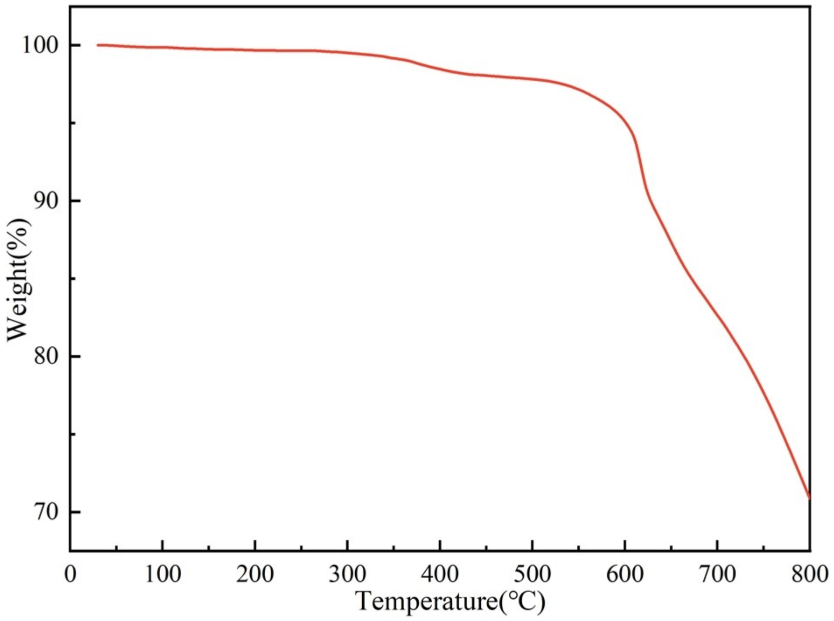


Figure S3 The TGA curve of ZIF-8 in N_2 atmosphere.

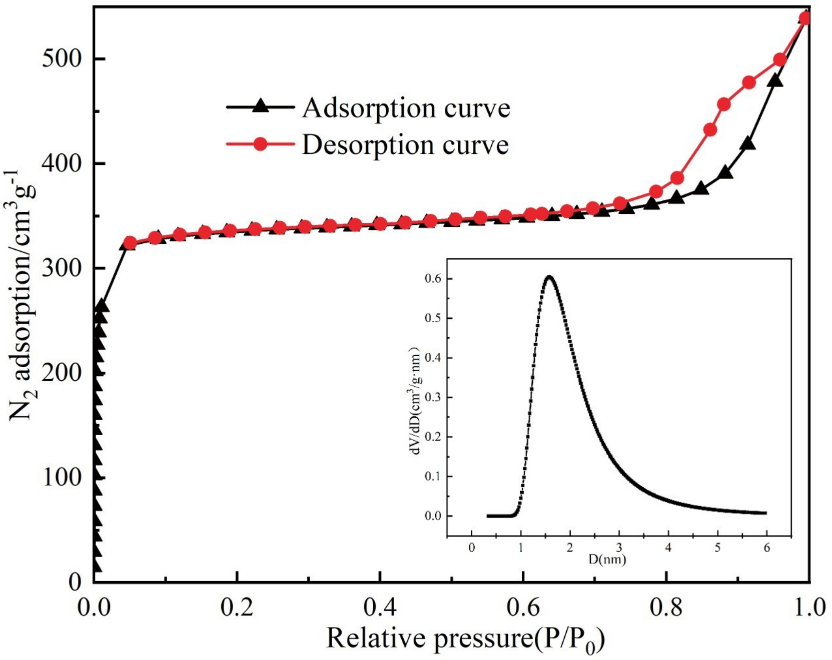


Figure S4 N_2 adsorption-desorption curve and pore size distribution of ZIF-8.

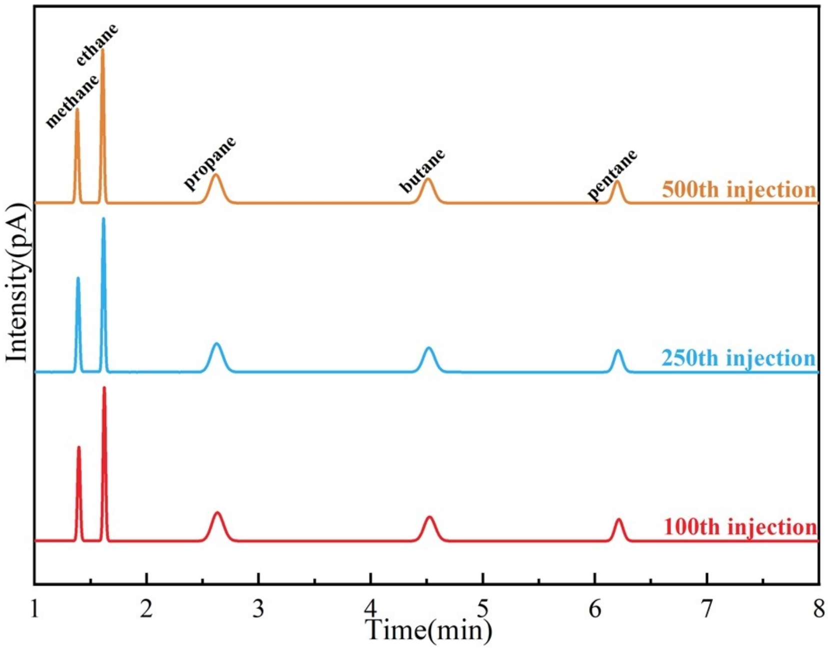


Figure S5 Stability evaluation of the ZIF-8 capillary column fabricated under optimized preparation protocol. **Chromatographic conditions:** flow rate of 15 cm/s; column temperature held at 35 °C for 1.5 min, then increased to 200 °C at a rate of 30 °C/min.

Table 1. RSDs of retention time and peak area for C1-C5 at 100th, 250th, and 500th injection cycles.

Analytes	Retention time		Peak area	
	AVG	RSD (%)	AVG	RSD (%)
C1	1.35	0.33	8546	1.36
C2	1.60	0.41	16843	1.75
C3	2.62	0.46	24756	2.16
C4	4.54	0.22	23462	2.68
C5	6.23	0.16	14946	2.95

Table S2 RSDs of retention times and peak areas for C1-C5 separation across five replicate ZIF-8 capillary columns fabricated via optimized protocol. **Chromatographic conditions:** flow rate of 15 cm/s; column temperature held at 35 °C for 1.5 min, then increased to 200 °C at a rate of 30 °C/min.

Analytes	Retention time		Peak area	
	AVG	RSD (%)	AVG	RSD (%)
C1	1.35	0.31	8679	1.24
C2	1.60	0.27	16688	2.75
C3	2.63	0.21	24424	1.26
C4	4.55	0.16	23355	2.17
C5	6.24	0.09	14289	2.65

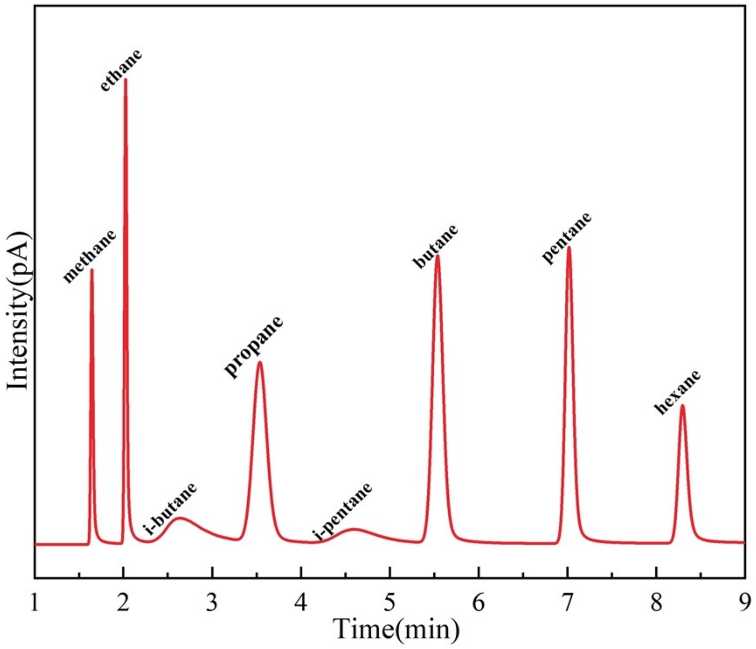


Figure S6 Chromatographic profile of C1-C6+ alkane mixture separated on ZIF-8 capillary column fabricated via optimized protocol.

Chromatographic conditions: flow rate of 12 cm/s; column temperature held at 35 °C for 2 min, then increased to 200 °C at a rate of 30 °C/min.

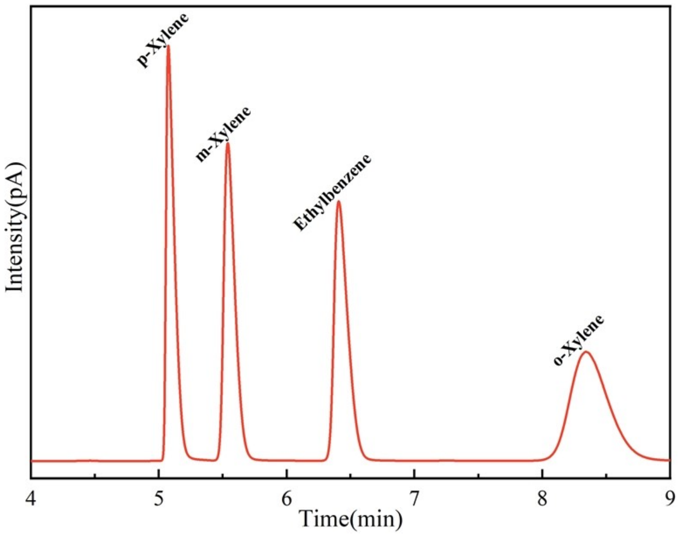


Figure S7 Chromatographic profile of xylene isomers separated on UiO-66 capillary column. **Chromatographic conditions:** flow rate of 30 cm/s; column temperature held at 100 °C for 1 min, then increased to 200 °C at a rate of 30 °C/min.

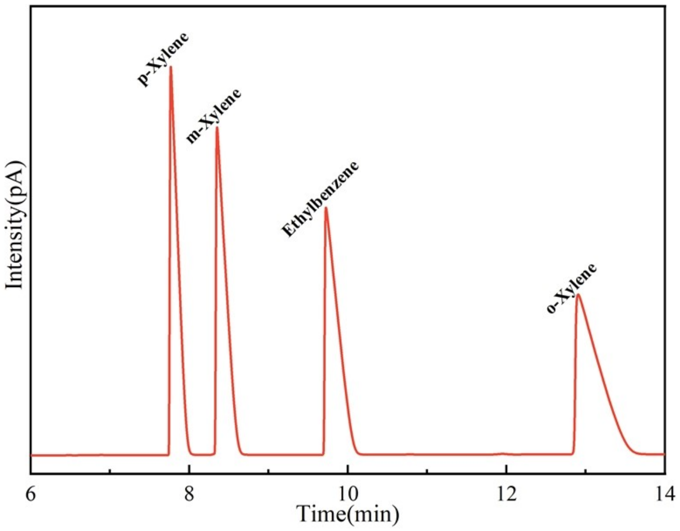


Figure S8 Chromatographic profile of xylene isomers separated on UiO-66-NH_2 capillary column. **Chromatographic conditions:** flow rate of 30 cm/s; column temperature held at 100 °C for 1 min, then increased to 200 °C at a rate of 30 °C/min.

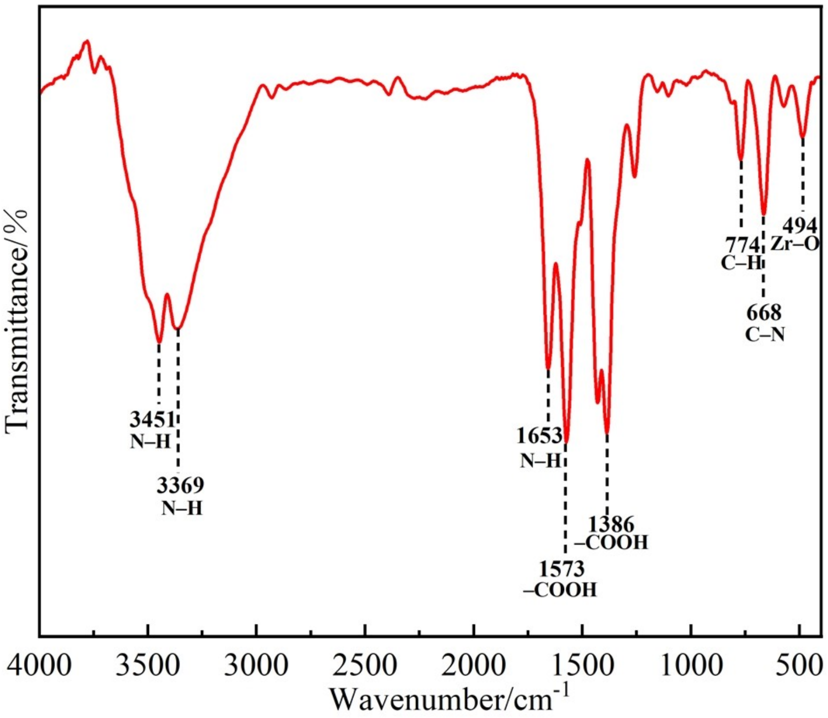


Figure S9 The FTIR spectra of UiO-66-NH_2.

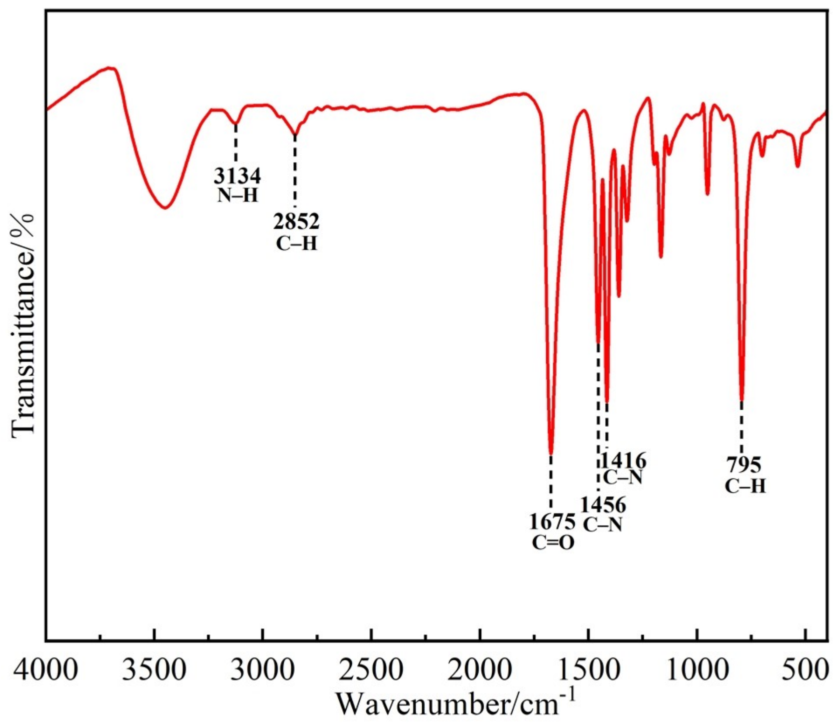


Figure S10 The FTIR spectra of ZIF-90 (The strong absorption peak observed around 3500 cm^{-1} is attributed to residual methanol in the sample).

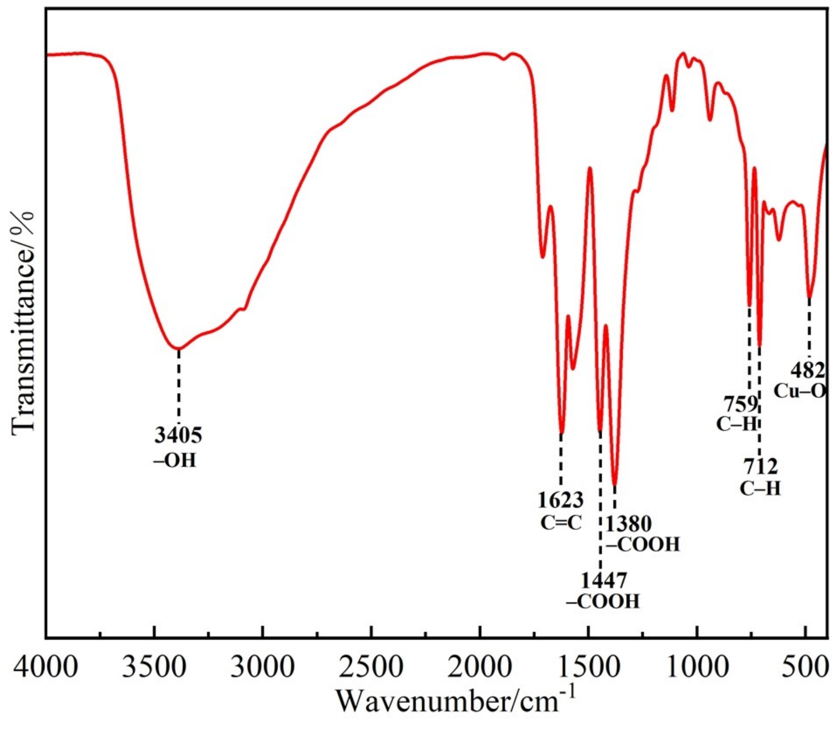


Figure S11 The FTIR spectra of Cu-BTC.

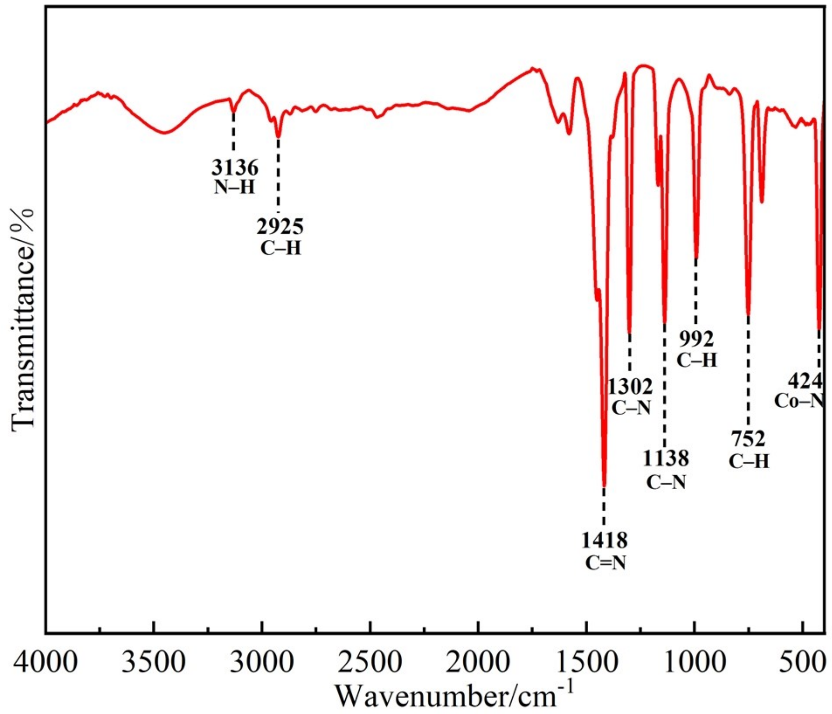


Figure S12 The FTIR spectra of ZIF-67.

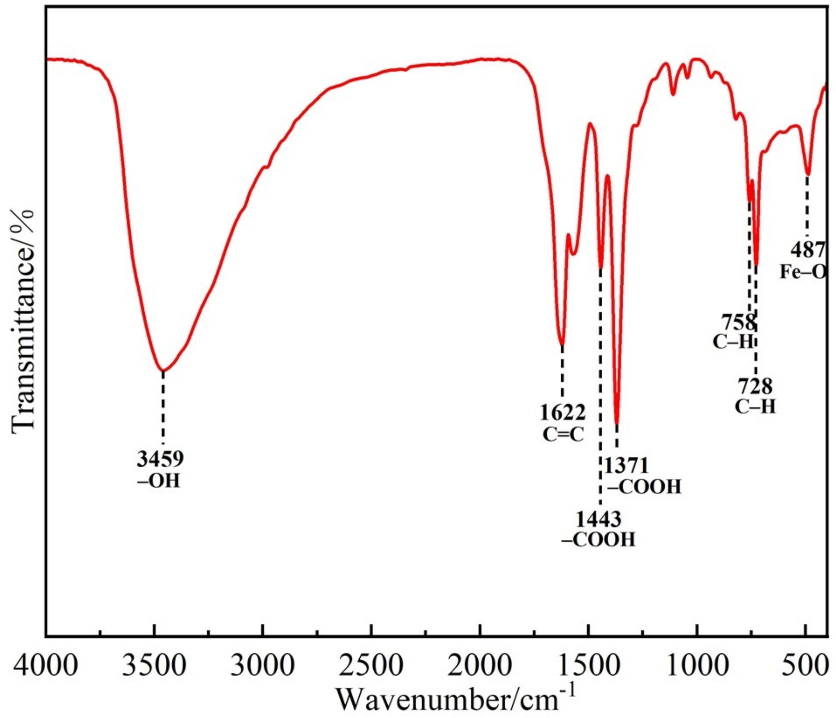


Figure S13 The FTIR spectra of MIL-100.

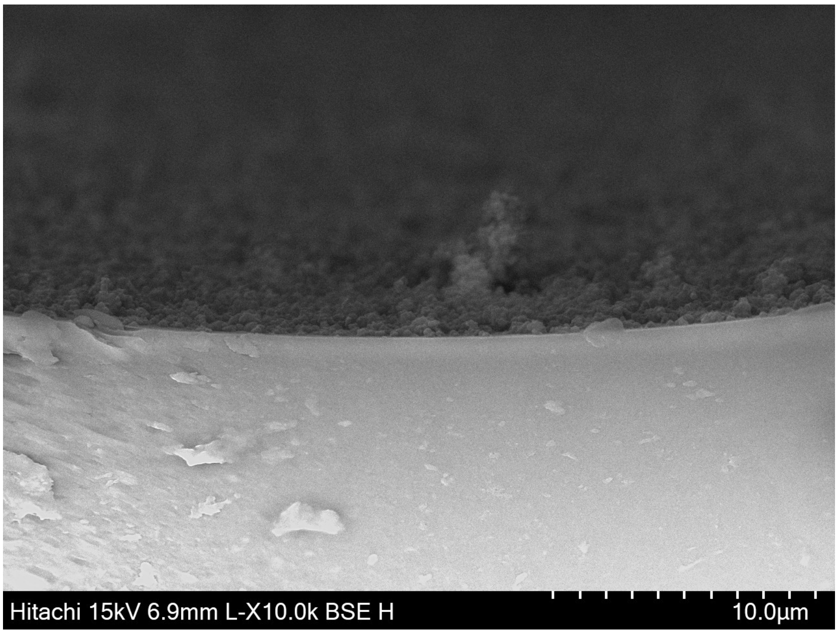


Figure S14 The cross-sectional SEM image of ZIF-90 capillary column.

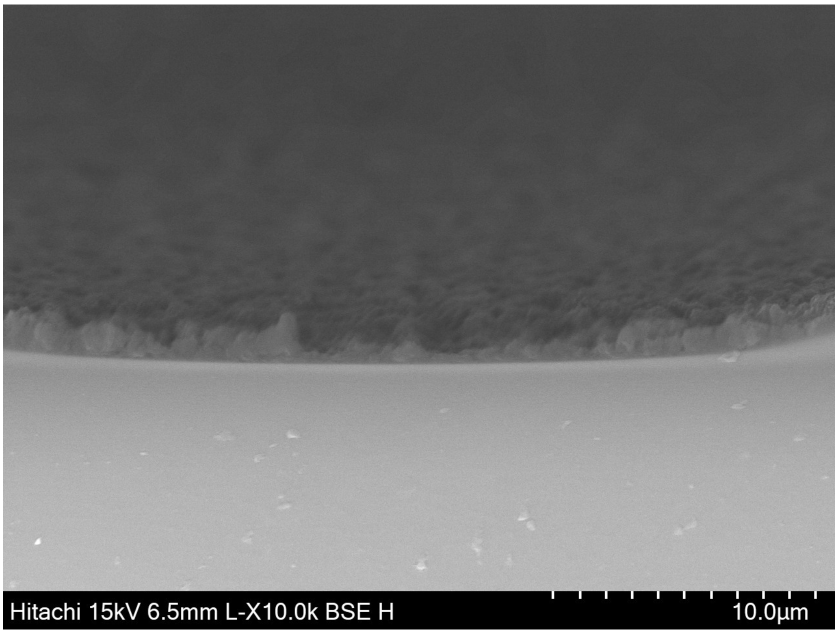


Figure S15 The cross-sectional SEM image of Cu-BTC capillary column.

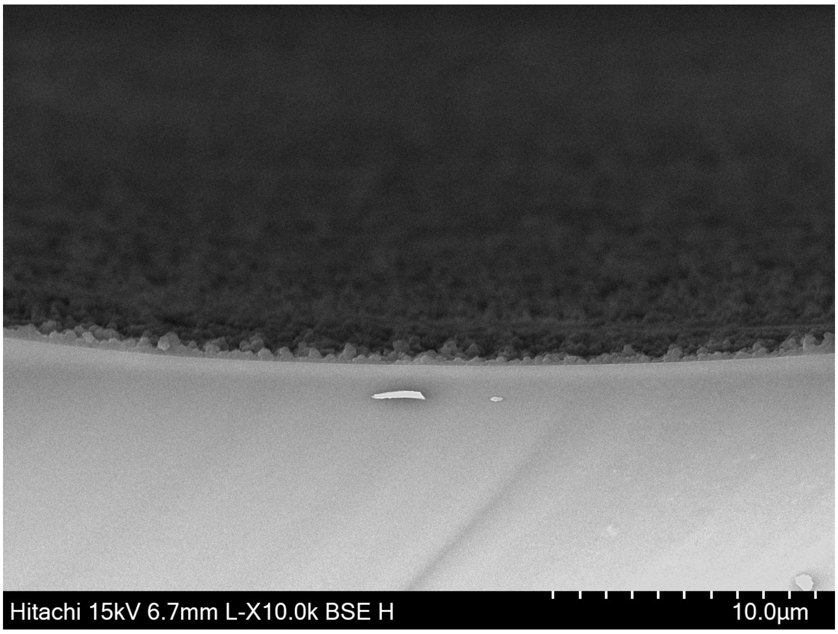


Figure S16 The cross-sectional SEM image of ZIF-67 capillary column.

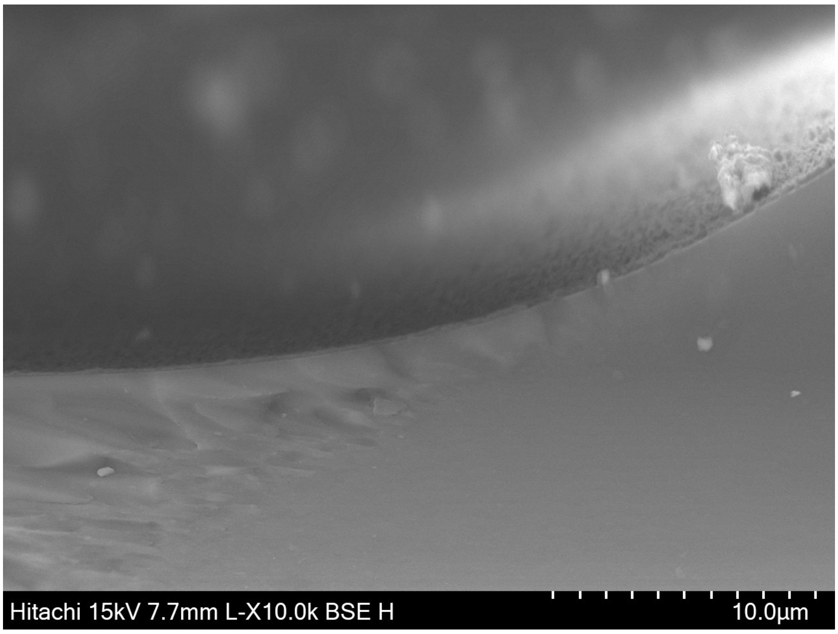


Figure S17 The cross-sectional SEM image of MIL-100 capillary column.

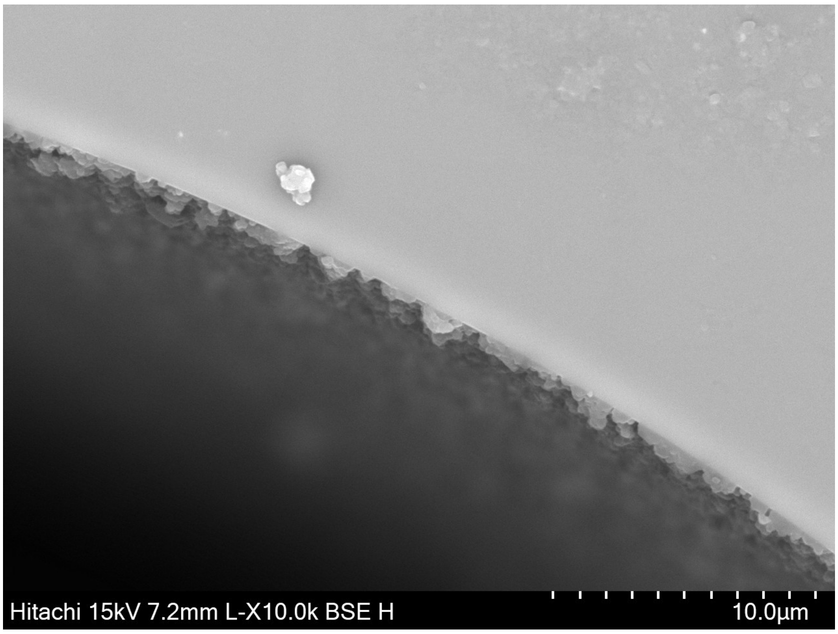


Figure S18 The cross-sectional SEM image of UiO-66 capillary column.

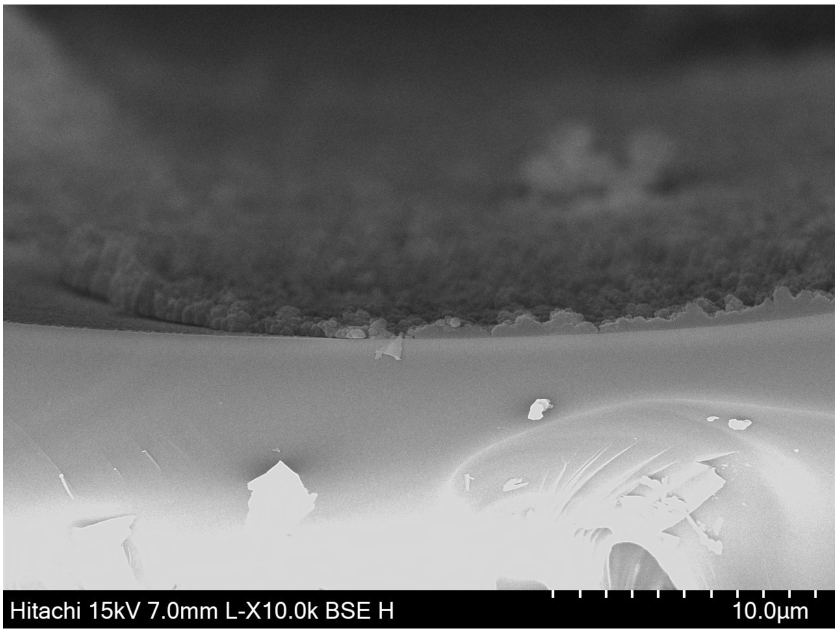


Figure S19 The cross-sectional SEM image of UiO-66-NH_2 capillary column.

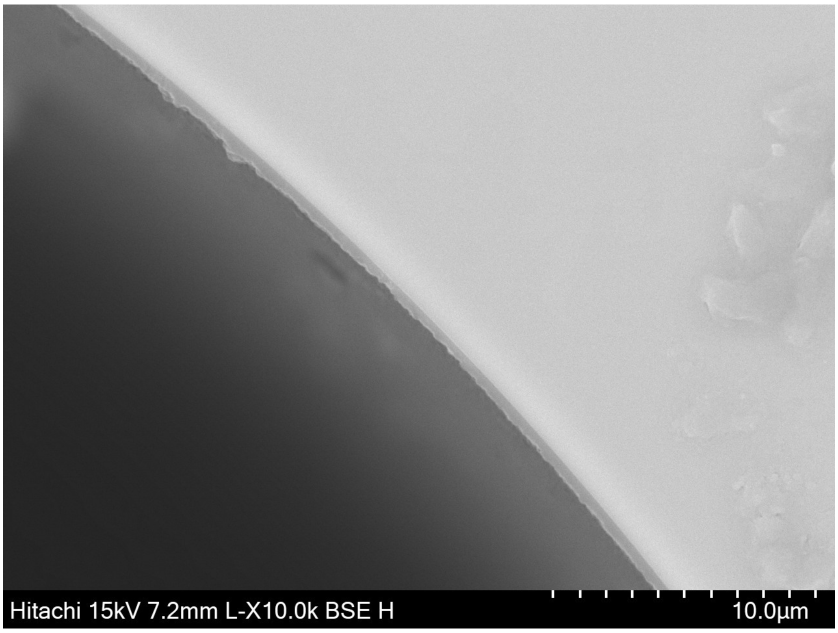


Figure S20 The cross-sectional SEM image of ZIF-8 capillary column (LBL 60 times).

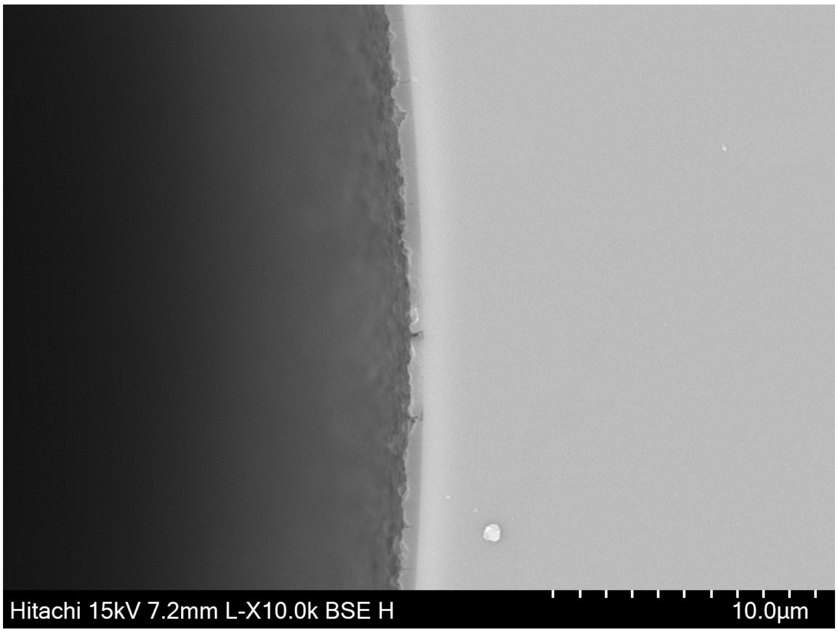


Figure S21 Cross-sectional SEM image of ZIF-8 capillary column (LBL 120 times).

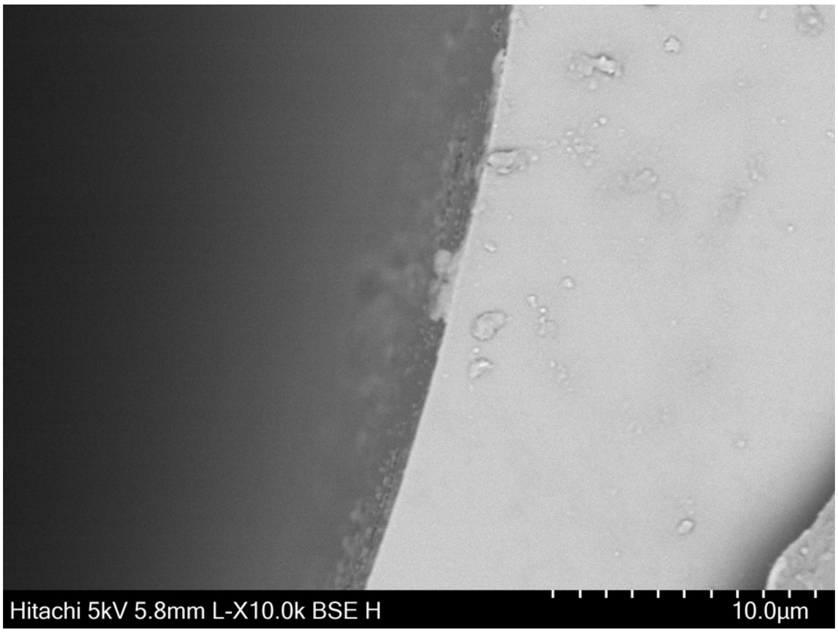


Figure S22 The cross-sectional SEM image of ZIF-8 capillary column (In-situ growth).

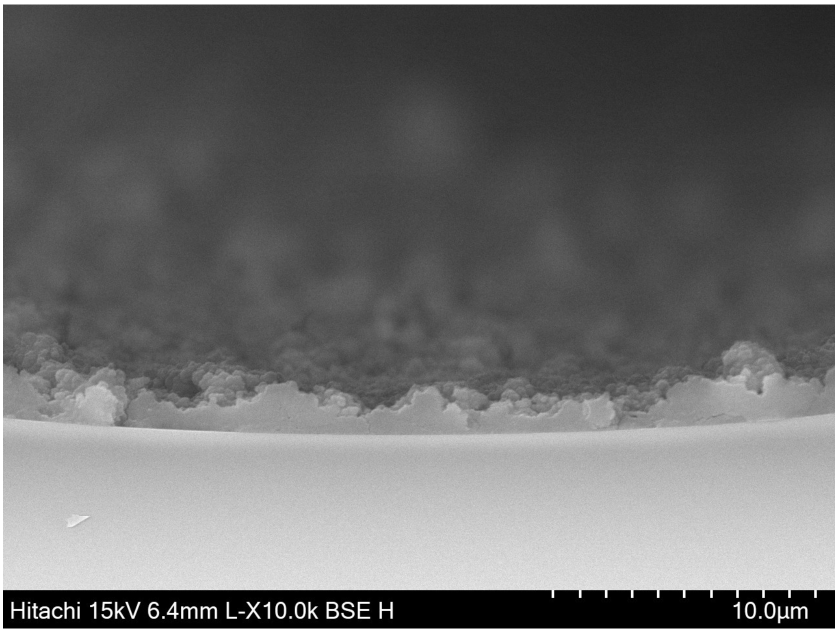


Figure S23 The cross-sectional SEM image of ZIF-8 capillary column (Continuous flow preparation, Zn(II) 0.1 M and 2-IM 0.2 M, 8 h).

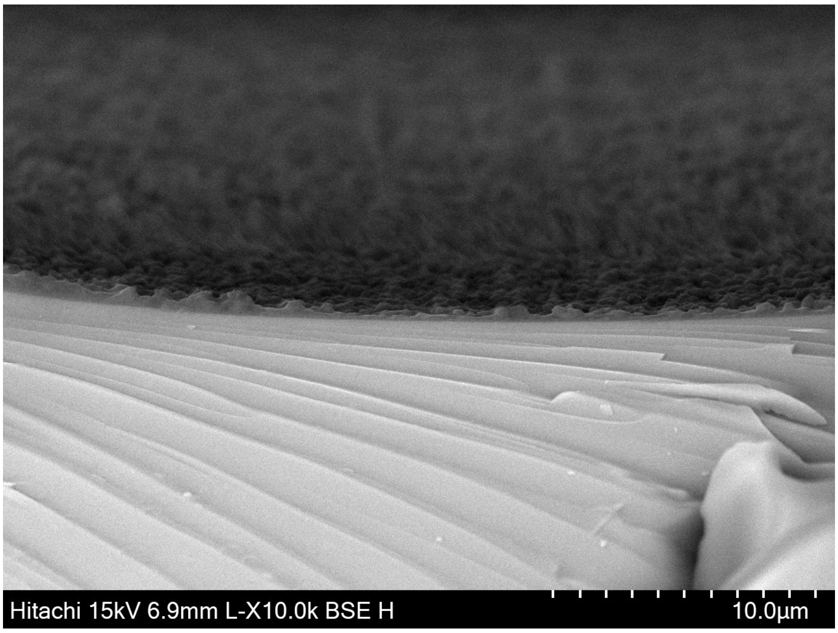


Figure S24 The cross-sectional SEM image of ZIF-8 capillary column (Continuous flow preparation, Zn(II) 0.1 M and 2-IM 0.2 M, 2 h).

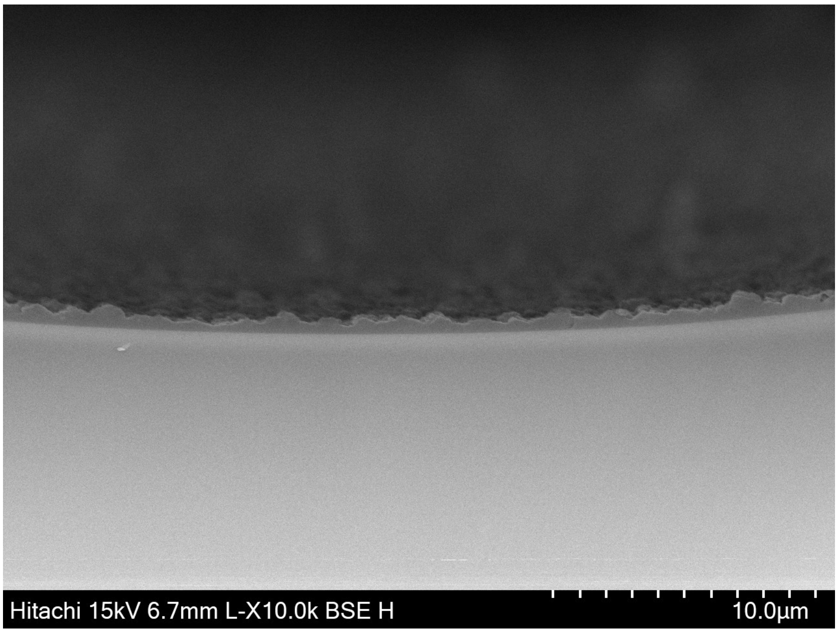


Figure S25 The cross-sectional SEM image of ZIF-8 capillary column (Continuous flow preparation, Zn(II) 0.1 M and 2-IM 0.2 M, 4 h).

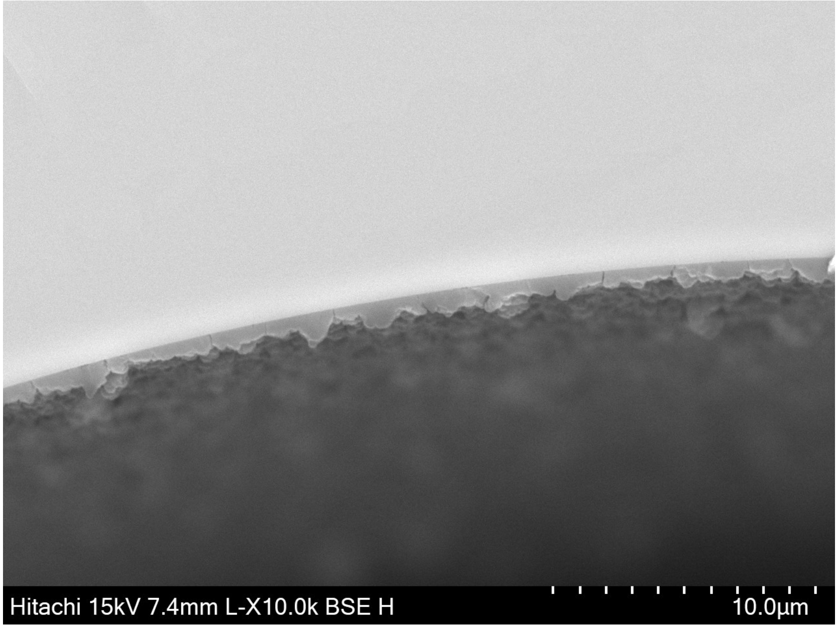


Figure S26 The cross-sectional SEM image of ZIF-8 capillary column (Continuous flow preparation, Zn(II) 0.1 M and 2-IM 0.2 M, 6 h).

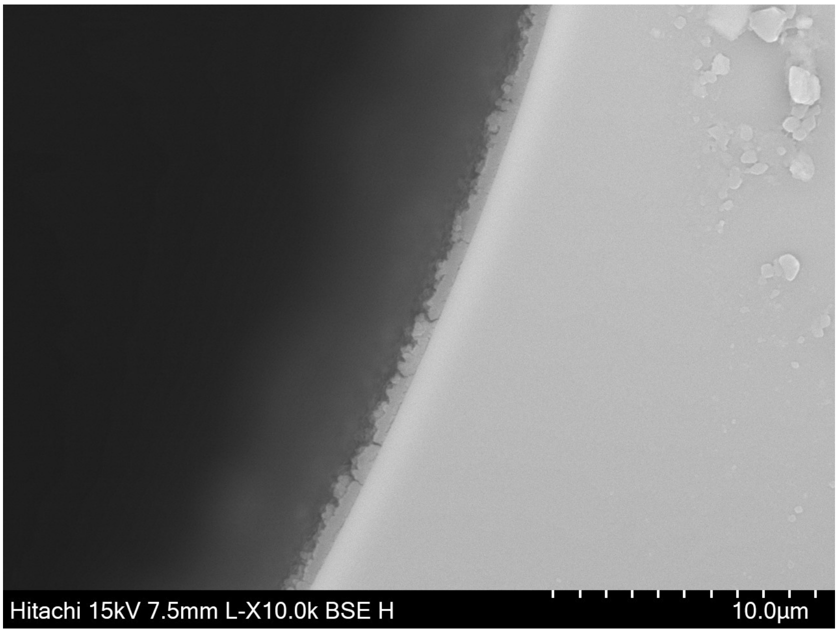
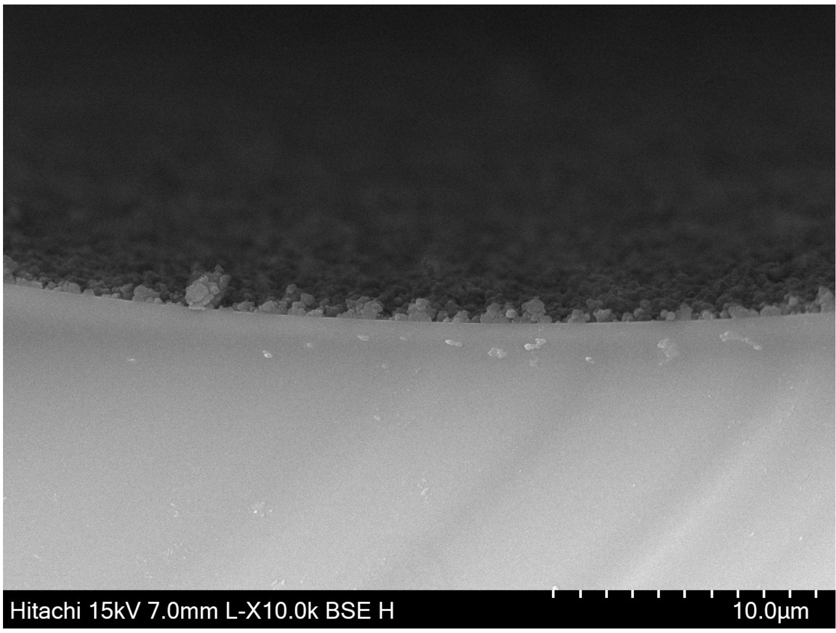


Figure S27 The cross-sectional SEM image of ZIF-8 capillary column (Continuous flow preparation, Zn(II) 0.025 M and 2-IM 0.05 M, 6 h).



h)

Figure S28 Cross-sectional SEM image of ZIF-8 capillary column (Continuous flow preparation, Zn(II) 0.05 M and 2-IM 0.1 M, 6 h).

Notes and References

1. J. Cravillon, S. Münzer, S. J. Lohmeier, A. Feldhoff, K. Huber and M. Wiebcke, *Chem. Mat.*, 2009, **21**, 1410-1412.