

## Supporting information

# **High-efficiency and Versatile Approach to Fabricate Diverse Metal–Organic Frameworks Coatings on a Support Surface as Stationary Phases for Electrochromatographic Separation**

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## 1. Chemicals and Materials.

3-aminopropyltriethoxysilane (APTES), glutaraldehyde (25% aqueous solution), copper(II) nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ), zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ), terephthalic acid (BDC), 1,3,5-benzenetricarboxylic acid (BTC), 2-methylimidazole, cysteine (Cys), alanine (Ala), hydroquinone, resorcinol, catechol, p-phenylenediamine, m-phenylenediamine and o-phenylenediamine were purchased from Adamas Reagent Co., Ltd (Shanghai, China). Styrene, bromobenzene, chlorobenzene, o-dichlorobenzene and 1,2,4-trichlorobenzene were obtained from Macklin Reagent Co., Ltd (Shanghai, China). Zirconium chloride ( $\text{ZrCl}_4$ ), benzene, methylbenzene, ethylbenzene and allylbenzene were purchased from Aladdin Reagent Co., Ltd (Shanghai, China). Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), dimethyl sulfoxide (DMSO), methanol, ethanol, phosphoric acid, disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and other necessary reagents were obtained from KeLong Chemical Reagent Co., Ltd. (Chengdu, China).

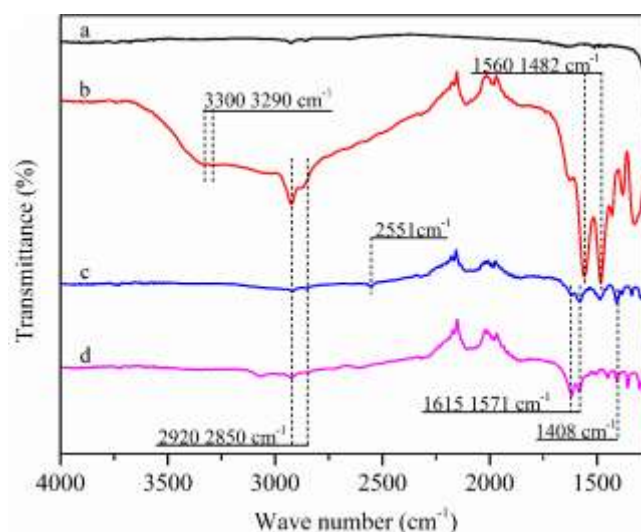
## 2. Preparation of MOFs-coated capillary columns

HKUST-1-coated capillary (Cys-HKUST-1@capillary) and MIL-100(Fe)-coated capillary (Cys-MIL-100(Fe)@capillary) were prepared using a similar process of Cys-ZIF-8@capillary. Briefly, the fresh ethanol solutions containing 10 mM metal ions ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) and 10 mM organic ligands (BTC) were respectively injected into the Cys-modified column and allowed to stand for 2 h at room temperature to form HKUST- and MIL-100(Fe) crystals in the capillary inner wall. Subsequently, the obtained Cys-HKUST-1@capillary and Cys-MIL-100(Fe)@capillary were washed with ethanol for 5 min and dried with nitrogen. The preparation process of UiO-66 modified column (Cys-UiO-66@capillary) was slightly different from that of Cys-ZIF-8@capillary. Briefly,  $\text{ZrCl}_4$  (8 mg, 0.0343 mmol) and BDC (5.7 mg, 0.0343 mmol) were dissolved in DMF (2 mL) at room temperature via ultrasonication to form a precursor solution. The prepared solution was filled into the Cys-modified column and incubated in an oven at 120 °C for 2h to grow UiO-66 crystals in the capillary inner wall. The fabricated column was flushed with methanol for 1 h to remove the residual reactant and DMF.

### 3. Operational conditions for CEC.

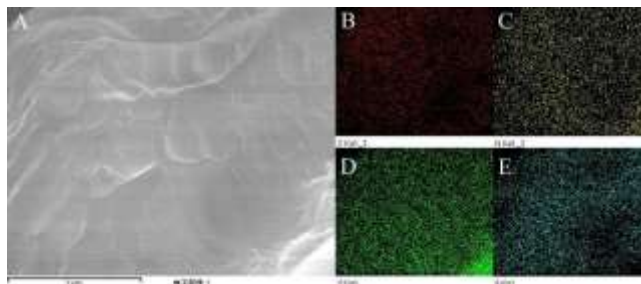
The phosphate buffers with different concentrations were obtained by dissolving the appropriate amount of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  in ultrapure water and the pH values were adjusted using NaOH or phosphoric acid. The running buffers were prepared by mixing the phosphate buffer with a suitable amount of acetonitrile. The standard stock solutions of model analytes were prepared in acetonitrile and stored in a refrigerator at 4 °C. All solutions were filtered through a 0.45  $\mu\text{m}$  membrane filter and degassed by sonication before use. At the start of CE operation each day, the coated capillary was rinsed with ultrapure water and running buffer for 10 min, respectively. Between two runs, the column was flushed using ultrapure water and running buffer for 2 min. After daily electrophoresis experiment, the column was filled with ultrapure water containing 10% acetonitrile and stored at room temperature. The CEC separations were conducted utilizing the desired voltage at 20 °C with the prepared columns. All samples were detected at 200 nm and injected by pressure-driven for 35 mbar  $\times$  5 s.

### 4. ATR-FT-IR spectra

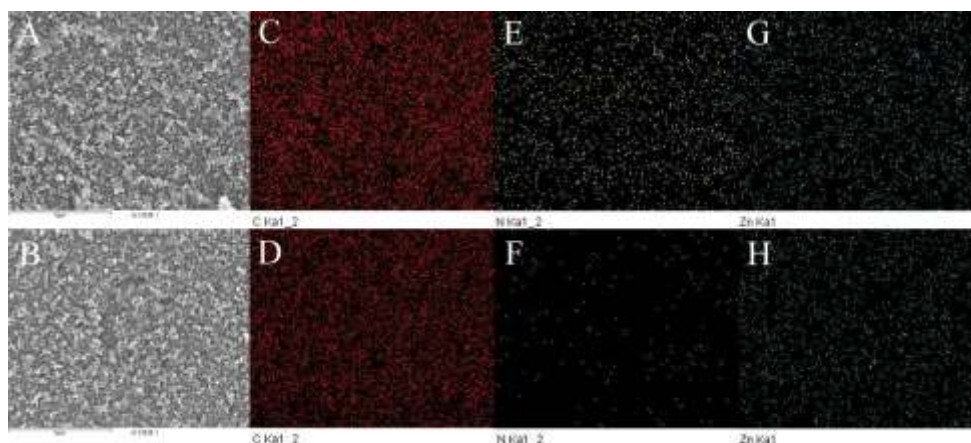


**Figure S1.** ATR-FTIR spectra of unmodified (a), APTES-coated (b), Cys-coated (c) and Ala-coated (d) quartz sheets.

## 5. Energy dispersive X-ray spectroscopy (EDS) element mapping images

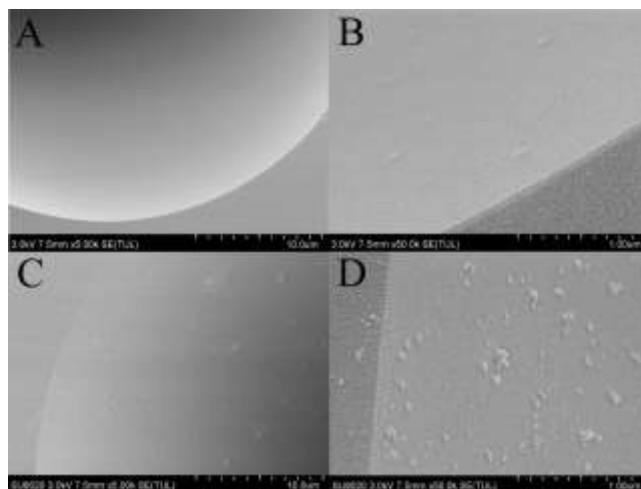


**Figure S2.** Energy dispersive X-ray spectroscopy (EDS) element mapping images of the inner wall of Cys modified capillary. C, N, O and S element mapping (B, C, D, E) for the Cys modified capillary column (A).

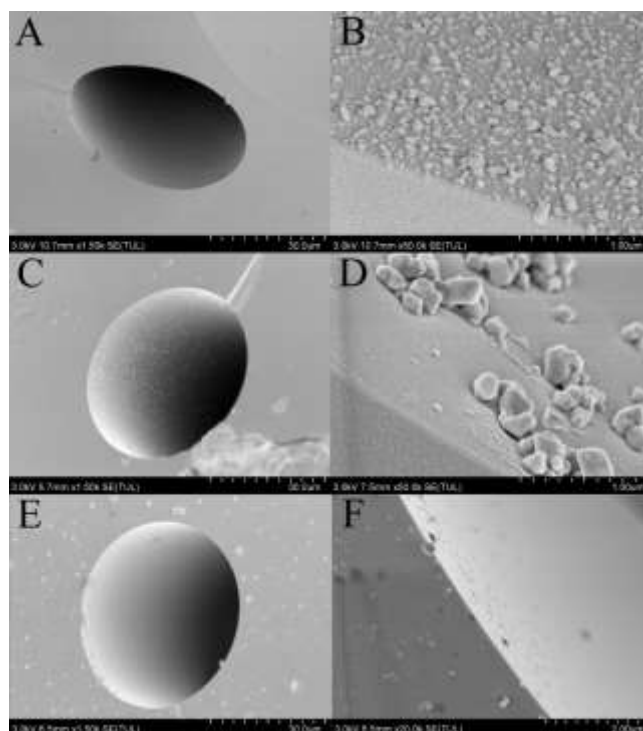


**Figure S3.** Energy dispersive X-ray spectroscopy (EDS) element mapping images of the surface of Cys-ZIF-8@plate and Ala-ZIF-8@plate. (C, E, G) C, N and Zn element mapping for the Cys-ZIF-8@plate (A); (D, F, H) C, N and Zn element mapping for the Ala-ZIF-8@plate (B).

## 6. SEM images

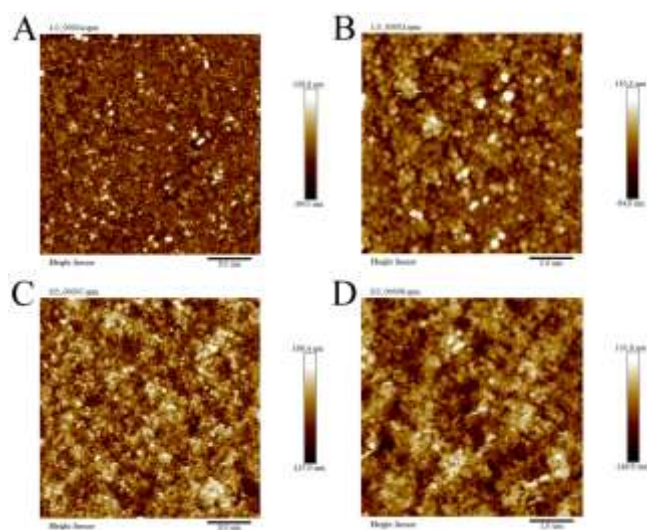


**Figure S4.** SEM images of APTES-ZIF-8@capillary (A, B), Cys-ZIF-8@capillary after CE separation (C, D).



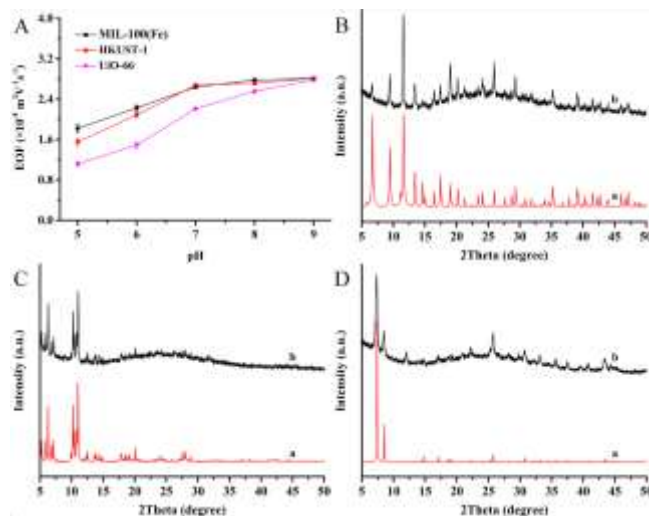
**Figure S5.** SEM images of Cys-UiO-66@capillary (A, B), Cys-HKUST-1@capillary (C, D) and Cys-MIL-100(Fe)@capillary (E, F).

## 7. AFM images

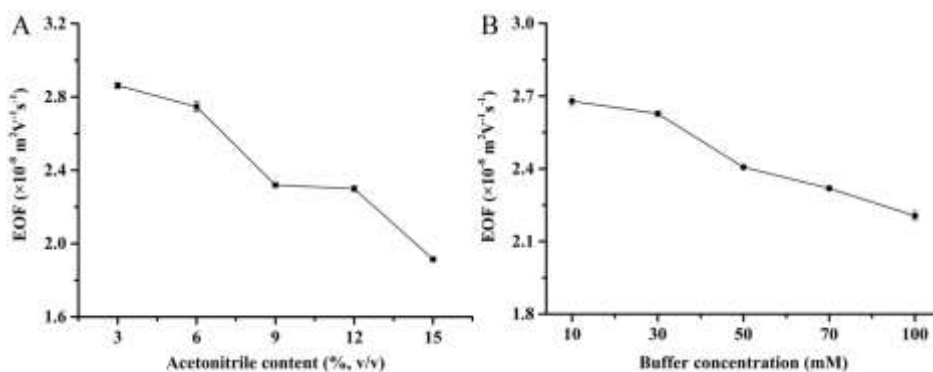


**Figure S6.** AFM images of Cys-ZIF-8@plate (A, B), Ala-ZIF-8@plate (C, D).

## 8. XRD measurement and EOF mobility



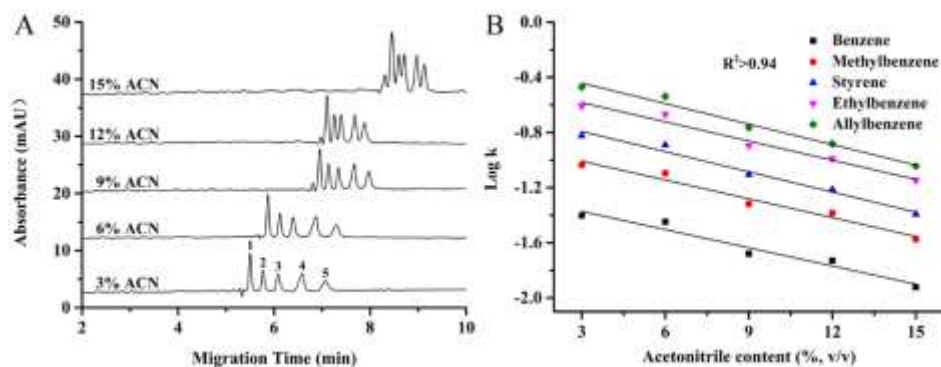
**Figure S7.** (A) The EOF mobilities of other three MOFs coated capillary at different pH values (the CE experimental conditions are the same as Figure 3B); (B) XRD patterns of the simulated HKUST-1 and Cys-HKUST-1@plate; (C) XRD patterns of the simulated MIL-100(Fe) and Cys-MIL-100(Fe)@plate; (D) XRD patterns of the simulated UiO-66 and Cys-UiO-66@plate.



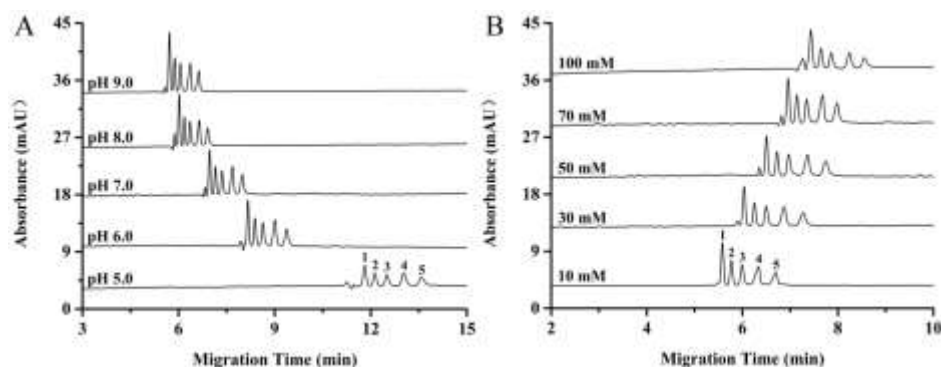
**Figure S8.** The EOF mobility of Cys-ZIF-8@capillary with different concentration of acetonitrile (A) and phosphate buffer (B). Background electrolyte, 70 mM phosphate buffer (pH 7.0) for (A) and phosphate buffer (pH 7.0) containing 9% acetonitrile for (B). The other CE experimental conditions are the same as Figure 3B.



## 9. Effect of CEC conditions on the separation

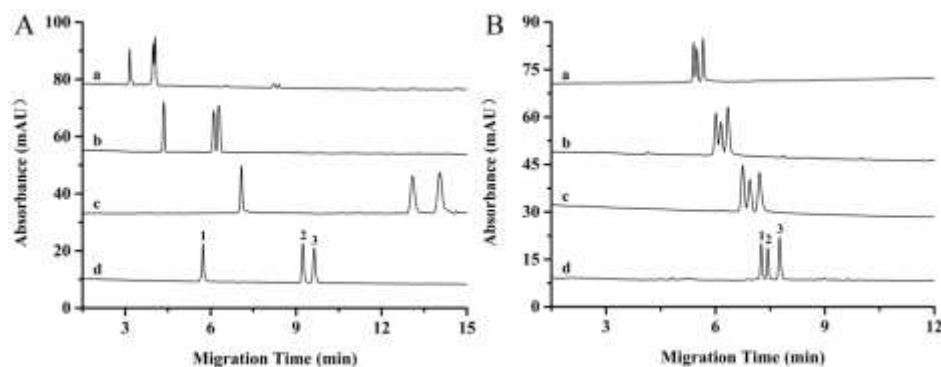


**Figure S9.** (A) Electropherograms of substituted benzenes on Cys-ZIF-8@capillary at different acetonitrile content. (1) benzene, (2) methylbenzene, (3) styrene, (4) ethylbenzene, (5) allylbenzene. (B) The relationship between acetonitrile content and retention factors of analytes on Cys-ZIF-8@capillary. Background electrolyte, pH 7.0, 3% to 15% acetonitrile (v/v). Other CE conditions are the same as Figure 3B.

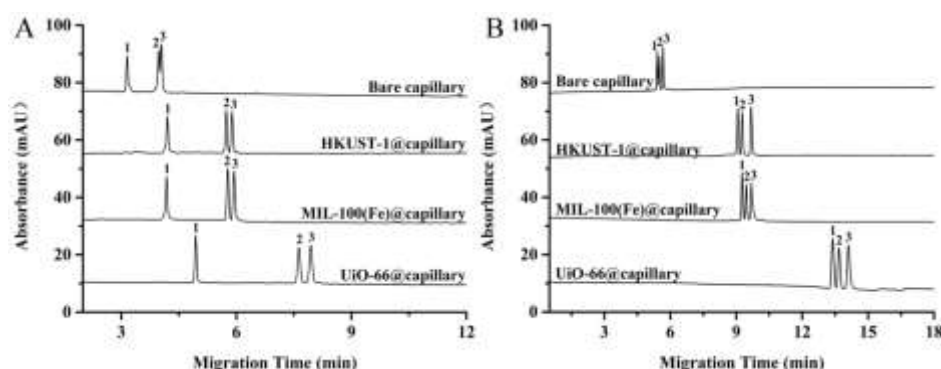


**Figure S10.** Electropherograms of five substituted benzenes on Cys-ZIF-8@capillary at different buffer pH values (A) and buffer concentrations (B). (1) benzene, (2) methylbenzene, (3) styrene, (4) ethylbenzene, (5) allylbenzene. Background electrolyte, 70 mM phosphate buffer containing 9% acetonitrile for (A) and phosphate buffer (pH 7.0, 9% acetonitrile) for (B). The other CE experimental conditions are the same as Figure 3B.

## 10. Separation of charged compounds

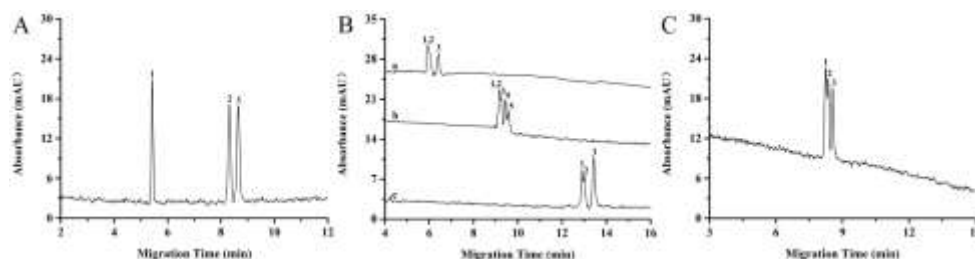


**Figure S11.** Electropherograms of two types of charged analytes on bare capillary (a), ZIF-8@capillary (b), Ala-ZIF-8@capillary (c) and Cys-ZIF-8@capillary (d). (A) diamine isomers: (1) p-, (2) m- (3) o-phenylenediamine; (B) diphenol isomers: (1) hydroquinone, (2) resorcinol, (3) catechol. Background electrolyte, phosphate buffer (pH 6.0, 10% acetonitrile) for (A) and phosphate buffer (pH 8.0, 50% acetonitrile) for (B). The other CE experimental conditions are the same as Figure 3B.



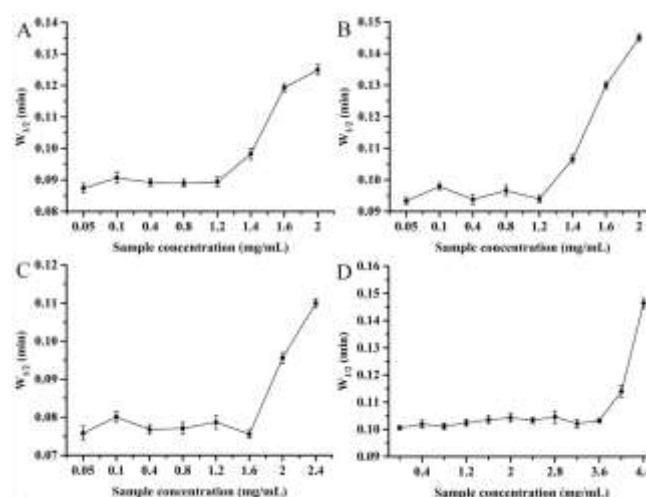
**Figure S12.** Electropherograms of two types of charged analytes on bare and other three MOFs coated columns. (A) diamine isomers: (1) p-, (2) m- (3) o-phenylenediamine; (B) diphenol isomers: (1) hydroquinone, (2) resorcinol, (3) catechol. The CE experimental conditions are the same as Figure S5.

## 11. CE separation on APTES-ZIF-8@capillary



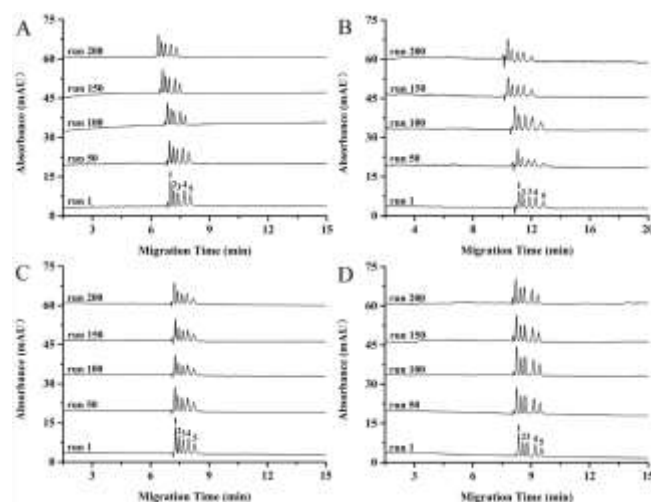
**Figure S13.** Electropherograms of five types of analytes on APTES-ZIF-8@capillary. (A) diamine isomers; (B) halogenated benzenes (a), substituted benzenes (b) and chlorobenzenes (c); (C) diphenol isomers. The CE conditions and peak identification for the five types of analytes were same as corresponding separation conditions on Cys-ZIF-8@capillary.

## 12. Column loadability



**Figure S14.** Column loadability test on Cys-ZIF-8@capillary (A), Cys-UiO-66@capillary (B), Cys-HKUST-1@capillary (C) and Cys-MIL-100(Fe)@capillary (D) using methylbenzene as the analyte and 70 mM phosphate buffer containing 20% acetonitrile as the mobile phase. The other CE experimental conditions are the same as Figure 3B.

### 13. Continuous electrophoresis operation tests



**Figure S15.** Electropherograms of five substituted benzenes after 200 consecutive runs on Cys-ZIF-8@capillary (A), Cys-UiO-66@capillary (B), Cys-HKUST-1@capillary (C) and Cys-MIL-100(Fe)@capillary (D). The peak identification for the substituted benzenes were same as Figure 5B. The CE conditions of four MOFs coated columns were same as corresponding separation conditions.

#### 14. The areal loading of ZIF-8

**Table S1.** The areal loading of ZIF-8 on the surface modified with different amino acids.

Functionalized quartz plate	Average weight (mg, $n=3$ )	
	Ala modified plate	Cys modified plate
Before coating	143.72	146.23
After coating	143.95	146.51
ZIF-coating	0.17	0.28

#### 15. The leaching amount of $\text{Zn}^{2+}$

**Table S2.** The leaching amount of  $\text{Zn}^{2+}$  from ZIF-8 coating.

leaching time	Leaching amount of $\text{Zn}^{2+}$ (ng/mL)	Leaching content (%)
2 h	64.55	0.08
8 h	157.52	0.19
24 h	668.53	0.84

## 16. Comparison with other methods

**Table S3.** Comparison with other previously reported methods for preparing supported MOFs coating-based stationary phases.

MOF materials	Preparing methods	Analytes	N <sub>max</sub> (plates/m)	Ref.
MOF-5	liquid-phase epitaxy	substituted benzenes	76383	1
HKUST-1	liquid-phase epitaxy	halogenated benzenes	29245	2
MIL-100(Fe)	layer-by-layer self-assembly	pyridine and alkylbenzenes	57868	3
ZIF-8	polydopamine-assisted in situ growth	benzene series, PAHs and chlorobenzenes	-	4
Bio-MOF-1	polydopamine-assisted in situ growth	substituted benzenes	72000	5
		chlorobenzenes	54000	
UiO-66-NH <sub>2</sub>	in situ growth	chlorobenzenes	-	6
ZIF-90	post-synthetic modification	xylene isomers	65456	7
		dichlorobenzene isomers	49251	
		chlorotoluene isomers	25639	
MOF-180	in situ growth	chlorobenzenes	43754	8

## 17. Separation performance of three MOFs modified columns for substituted benzenes

**Table S4.** The separation performance for substituted benzenes of Cys-UiO-66@capillary, Cys-HKUST-1@capillary and Cys-MIL-100(Fe)@capillary.

Columns	UiO-66		MIL-100(Fe)		HKUST-1	
Analytes	Rs	N (plates/m)	Rs	N (plates/m)	Rs	N (plates/m)
Benzene	-	80600	-	91467	-	73157
Methylbenzene	1.57	80400	2.09	99162	1.50	64867
Styrene	1.83	52953	1.88	89397	1.72	46743
Ethylbenzene	1.79	44012	3.19	75548	1.75	30128
Allylbenzene	1.79	40174	2.18	59336	1.59	25389

**Table S5.** The BET surface area ( $S_{\text{BET}}$ ) and column loadability normalized by  $S_{\text{BET}}$  of ZIF-8 Modified Column.

Modified columns	Column loadability (mg/mL)	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Column loadability normalized by $S_{\text{BET}}$	Pore diameter (nm)
ZIF-8	1.2	0.2945	1.2	0.34, 1.16
UiO-66	1.2	0.3156	1.12	0.6, 1.1
HKUST-1	1.6	0.5909	0.8	0.6, 0.9
MIL-100(Fe)	3.6	0.5029	2.11	0.55-0.86, 2.5-2.9

## 18. Repeatability of three MOFs modified columns

**Table S6.** The intra-day repeatability.

Analytes	Intra-day ( $n=5$ )/Migration time (RSD%)		
	UiO-66@column	HKUST-1@column	MIL-100(Fe)@column
Benzene	1.92	1.88	1.10
Methylbenzene	1.32	1.68	1.37
Styrene	1.76	1.52	1.44
Ethylbenzene	1.25	1.84	2.88
Allylbenzene	2.35	1.42	3.24

**Table S7.** The column-to-column repeatability.

Analytes	Column-to-column ( $n=3$ )/Migration time (RSD%)		
	UiO-66@column	HKUST-1@column	MIL-100(Fe)@column
Benzene	3.35	4.45	4.15
Methylbenzene	4.30	4.41	4.14
Styrene	4.88	2.24	4.10
Ethylbenzene	4.81	4.22	4.13
Allylbenzene	5.25	5.21	3.97

**Table S8.** The column-to-column repeatability.

Analytes	Column-to-column ( $n=3$ )/Migration time (RSD%)		
	UiO-66@column	HKUST-1@column	MIL-100(Fe)@column
Benzene	3.35	4.45	4.15
Methylbenzene	4.30	4.41	4.14
Styrene	4.88	2.24	4.10
Ethylbenzene	4.81	4.22	4.13
Allylbenzene	5.25	5.21	3.97



## 19. References

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