

Supporting Information

TpBD/UiO-66-NH₂ micro-mesoporous hybrid material as a stationary phase of open tubular capillary electrochromatography

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1. Experimental Methods:

1.1 Preparation and composition of ammonium acetate buffers

The ammonium acetate buffers are prepared by titrating equi-molar concentrations (20 mmol/L) of ammonium acetate, ammonia and acetic acid or adjusting with ammonia and acetic acid till a desired pH is reached.

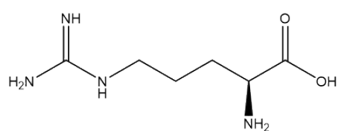
1.2 Preparation of samples solutions

Firstly, 25.0 mg of each standards (Glu, Asp, Ser, Ala, Val, Thr, Ile, Leu, Met, Trp, Phe, Arg and His; MHB, EHB, PHB and BHB; Mnz, Cpl, Tet and Ctc; SM1, SDM, SM2, SMZ, SIZ and ST) were accurately weighed, and then the standards were dissolved in a small amount of methanol or acetone solution, and then diluted with ultrapure water (18.2 M Ω /cm) to 5.0 mL to obtain their stock solutions with a concentration of 5.0 mg/mL. The work mixed solutions were obtained by mixing the corresponding stock solution of 1.00 mL of each analyte.

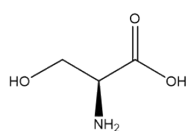
1.3 Preparation of TpBD- and UiO-66-NH₂-bonded OT-CEC column

TpBD- and UiO-66-NH₂-bonded OT-CEC column preparation followed three steps process: (i) pretreatment of the capillary column, (ii) activation of aldehyde groups, (iii) modification of TpBD or UiO-66-NH₂. The first and second steps are consistent with the preparation method of TpBD/UiO-66-NH₂. For the immobilization of TpBD COF on the inner wall of the capillary column by TpBD-bonded OT-CEC column, the aldehyde-coated capillary was filled with a 1:1.5 molar ratio mixture of Tp (12.0 mg) and BD (16.0 mg) as the monomers, and kept for 12 h in a water bath at 80 °C with sealing at both ends^[1]. The reaction principle of UiO-66-NH₂ bonded open tubular column is the same as that of TpBD bonded open tubular column. In order to fix UiO-66-NH₂ on the inner wall of the capillary column of UiO-66-NH₂-bonded OT-CEC column, the aldehyde-coated capillary was filled with UiO-66-NH₂ (38.8 mg), and kept in a water bath at 80 °C for 24 h, both ends sealed. Both processes were repeated twice. The inner diameter, outer diameter and effective length of TpBD- and UiO-66-NH₂-bonded OT-CEC columns were the same as those of TpBD/UiO-66-NH₂ bonded OT-CEC column.

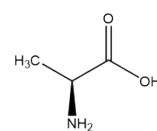
2. Supporting Figures:



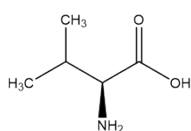
Arginine (Arg)



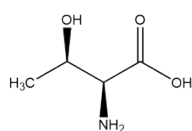
Serine (Ser)



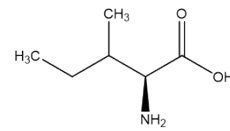
Alanine (Ala)



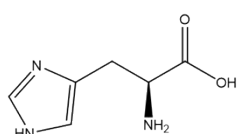
Valine (Val)



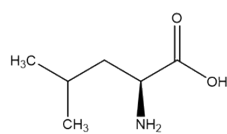
Threonine (Thr)



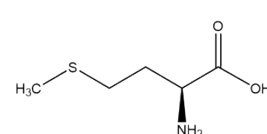
Isoleucine (Ile)



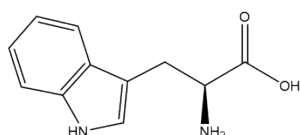
Histidine (His)



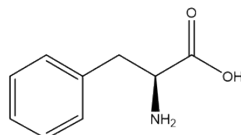
Leucine (Leu)



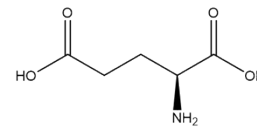
Methionine (Met)



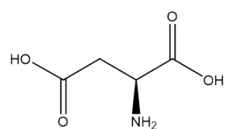
Tryptophan (Trp)



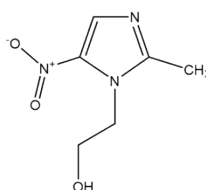
Phenylalanine (Phe)



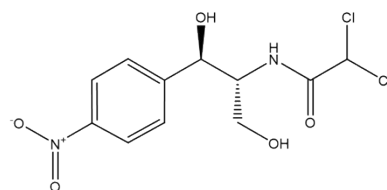
Glutamic acid (Glu)



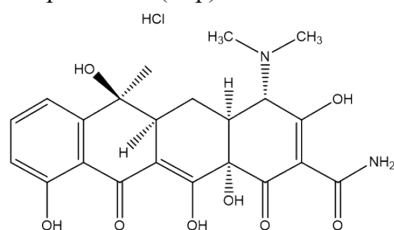
Aspartic acid (Asp)



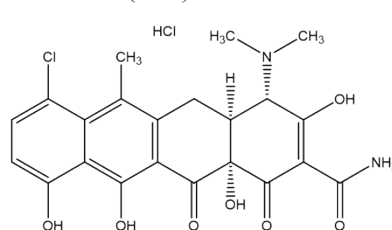
Metronidazole (Mnz)



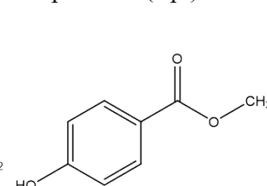
Chloramphenicol (Cpl)



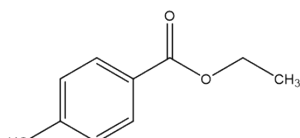
Tetracycline hydrochloride (Tet)



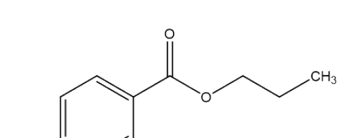
Chlortetracycline hydrochloride (Ctc)



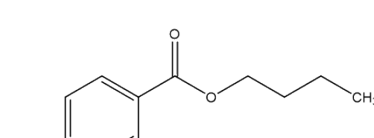
Methyl 4-hydroxybenzoate (MHB)



Ethyl 4-hydroxybenzoate (EHB)



Propyl 4-hydroxybenzoate (PHB)



Butyl 4-hydroxybenzoate (BHB)

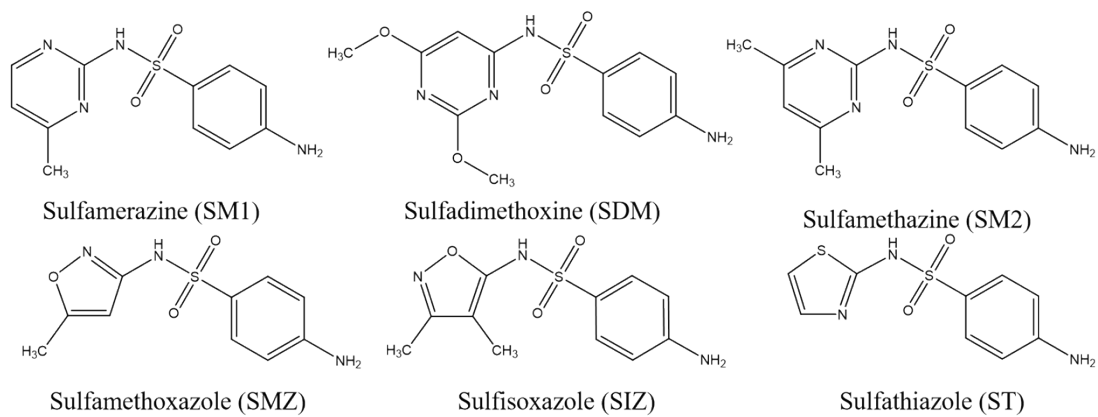


Fig. S1 Chemical structures of the analytes investigated

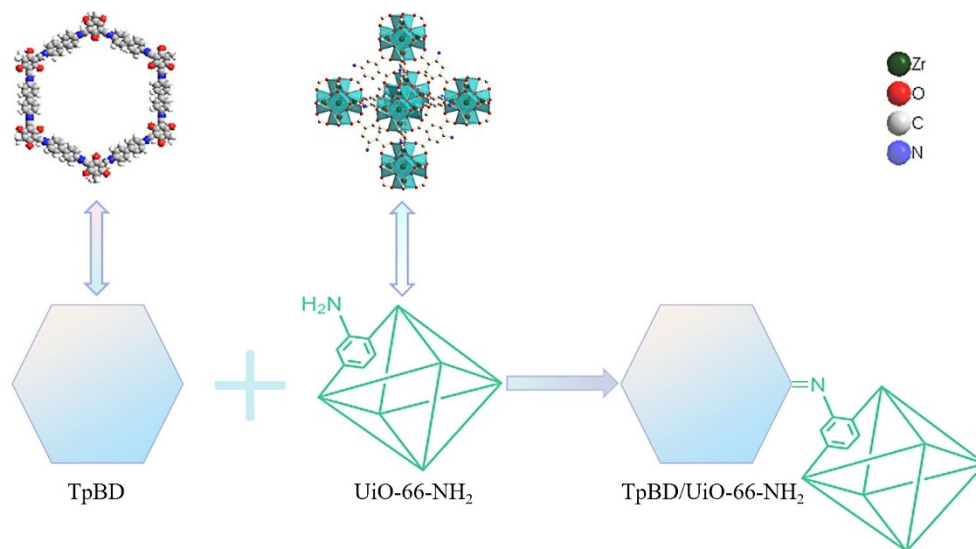


Fig. S2 Schematic illustration of TpBD/Uio-66-NH₂ synthesis

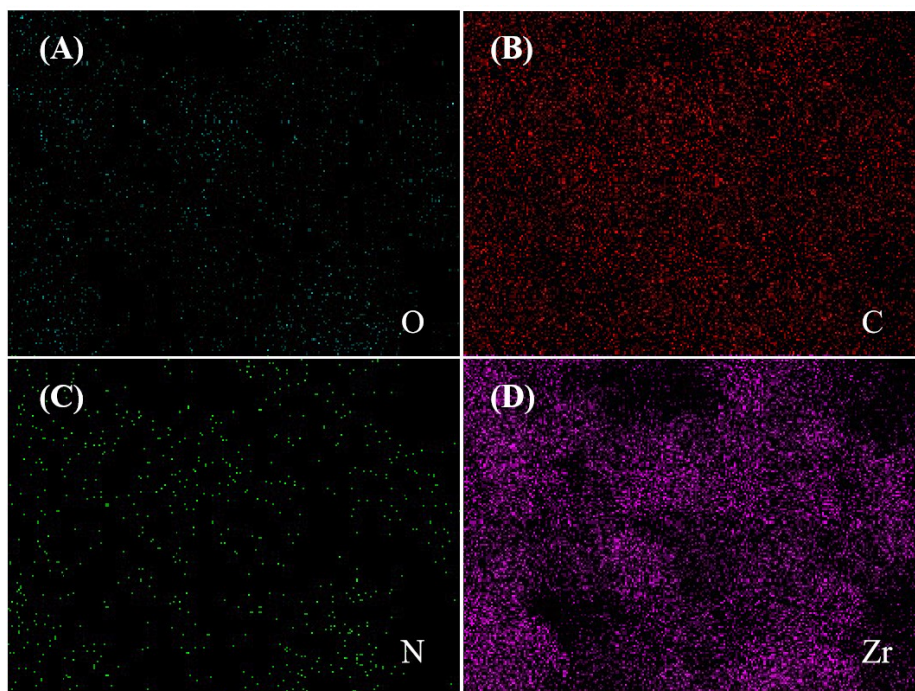


Fig. S3 EDS mapping (A-D) of TpBD/UiO-66-NH₂.

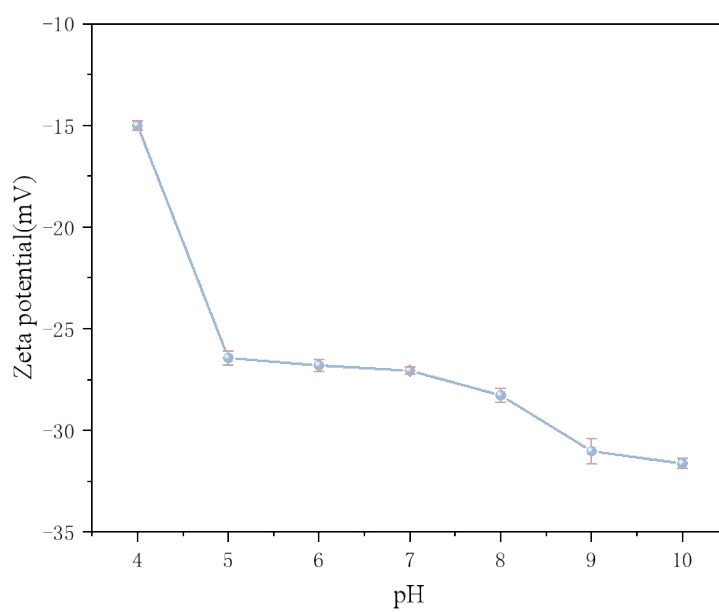


Fig. S4 Zeta potential curve of TpBD/UiO-66-NH₂. (Experimental conditions: 0.2 mg/mL of TpBD/UiO-66-NH₂, 20 mmol/L ammonium acetate buffer, 25°C.) (n=3)

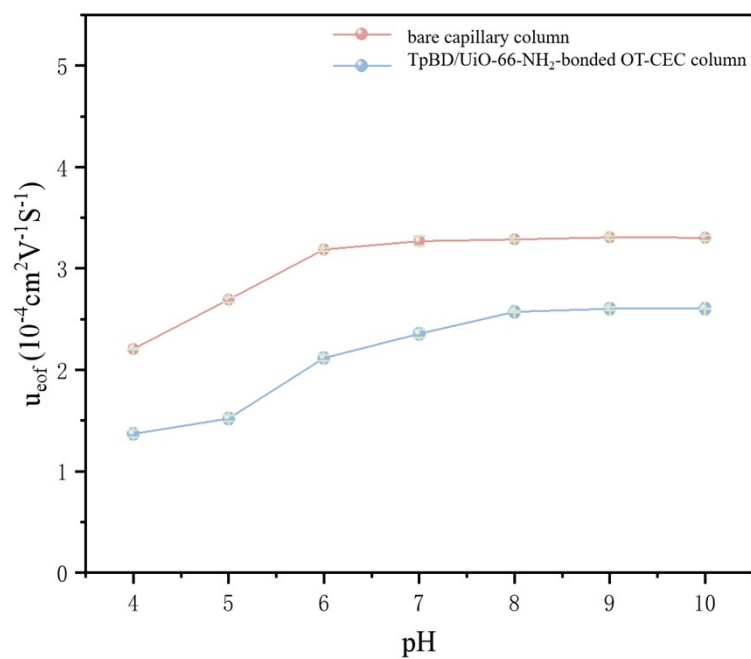


Fig. S5 Effect of buffer pH on EOF. (Experimental conditions: sample, 1.0 mg/mL thiourea; 20 mmol/L of ammonium acetate buffer solution; operating voltage, 15 kV.) (n=3)

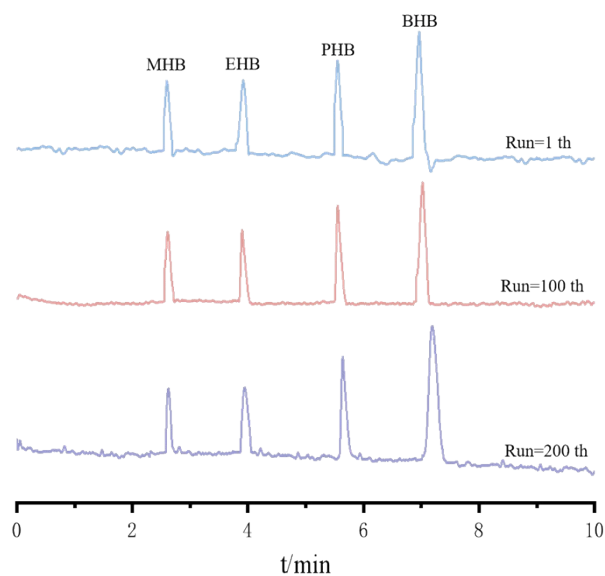


Fig. S6 Separation chromatogram of MHB, EHB, PHB and BHB with different runs. (Experimental conditions: sample, 5 mg/mL the mixture of MHB, EHB, PHB and BHB; 20 mmol/L of ammonium acetate buffer, pH=9; operating voltage, 15 kV; detection wavelength, 254 nm.)

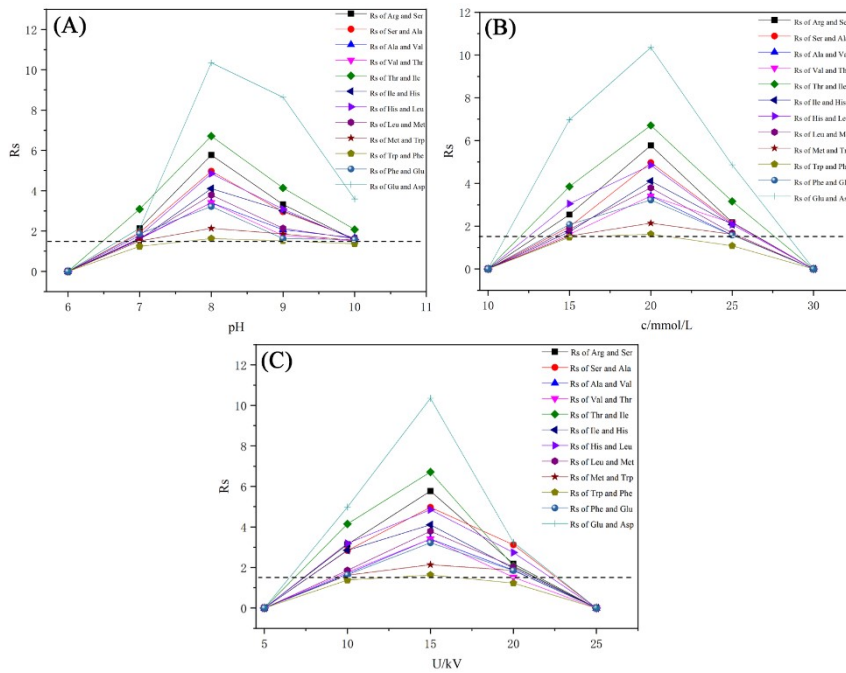


Fig. S7 Effects of buffer solution pH under the conditions of 20 mmol/L of ammonium acetate buffer and operating voltage of 15 kV (A), buffer concentration (pH=8) at operating voltage of 15 kV (B) and separation voltage with 20 mmol/L of ammonium acetate buffer (pH=8) (C) on resolution of 13 amino acids on TpBD/UiO-66-NH₂-bonded OT-CEC column. (Detection wavelength, 214 nm. Rs of all the analytes under the different experimental conditions was the average of three determinations (n=3).)

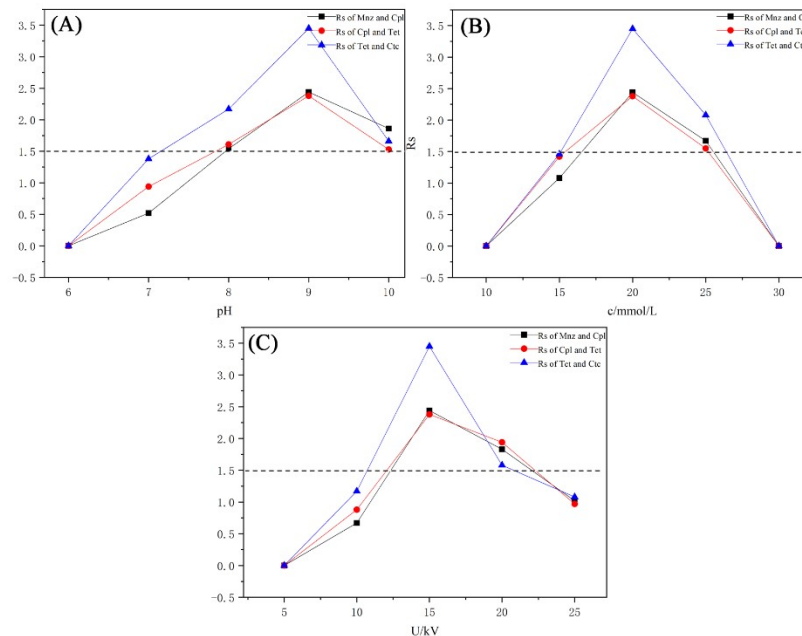


Fig. S8 Effects of buffer solution pH under the conditions of 20 mmol/L of ammonium acetate buffer and operating voltage of 15 kV (A), concentration (pH=9) at operating voltage of 15 kV (B) and separation voltage with 20 mmol/L of ammonium acetate buffer (pH=9) (C) on resolution of four antibiotics on TpBD/UiO-66-NH₂-bonded OT-CEC column (Detection wavelength, 270 nm. (n=3)).

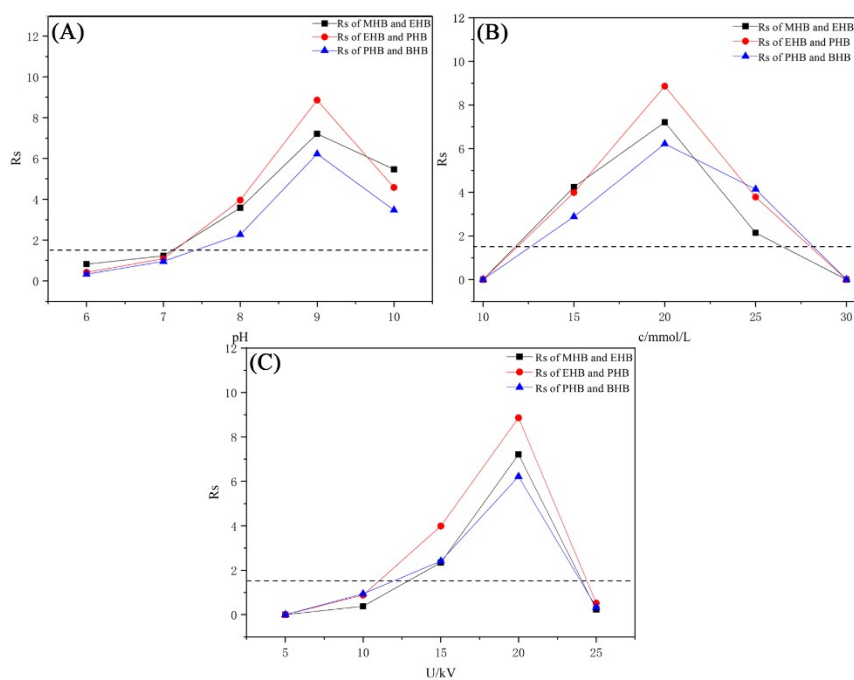


Fig. S9 Effects of buffer solution pH under the conditions of 20 mmol/L of ammonium acetate buffer and operating voltage of 20 kV (A), concentration (pH=9) at operating voltage of 20 kV (B) and separation voltage with 20 mmol/L of ammonium acetate buffer (pH=9) (C) on resolution of four preservatives on TpBD/UiO-66-NH₂-bonded OT-CEC column (Detection wavelength, 270 nm. (n=3)).

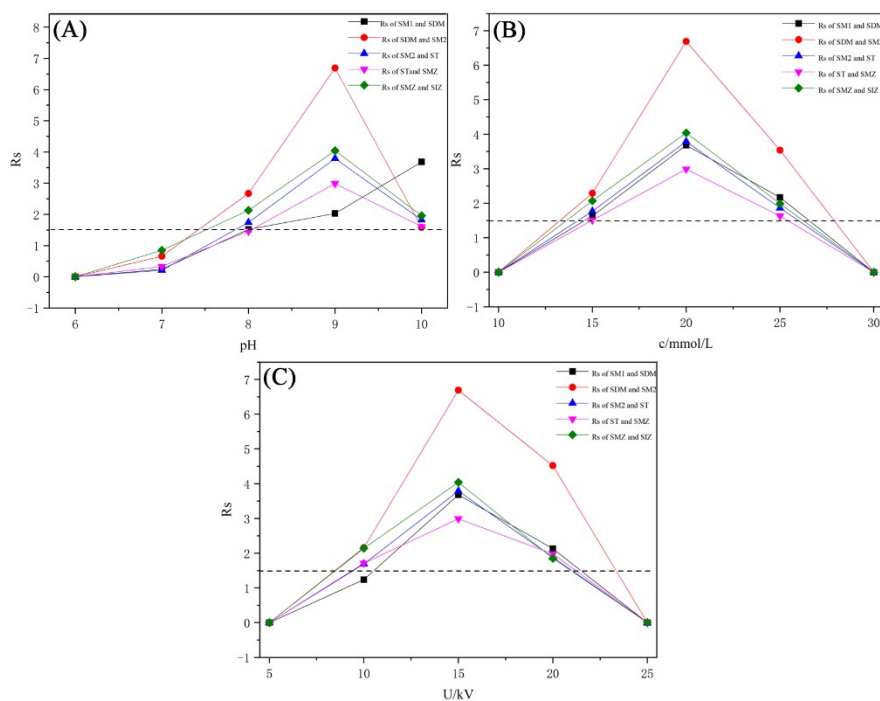


Fig. S10 Effects of buffer solution pH under the conditions of 20 mmol/L of ammonium acetate buffer and operating voltage of 15 kV (A), concentration (pH=9) at operating voltage of 15 kV (B) and separation voltage with 20 mmol/L of ammonium acetate buffer (pH=9) (C) on resolution of six sulfonamides on TpBD/UiO-66-NH₂-bonded OT-CEC column. (Detection wavelength, 254 nm.

(n=3).

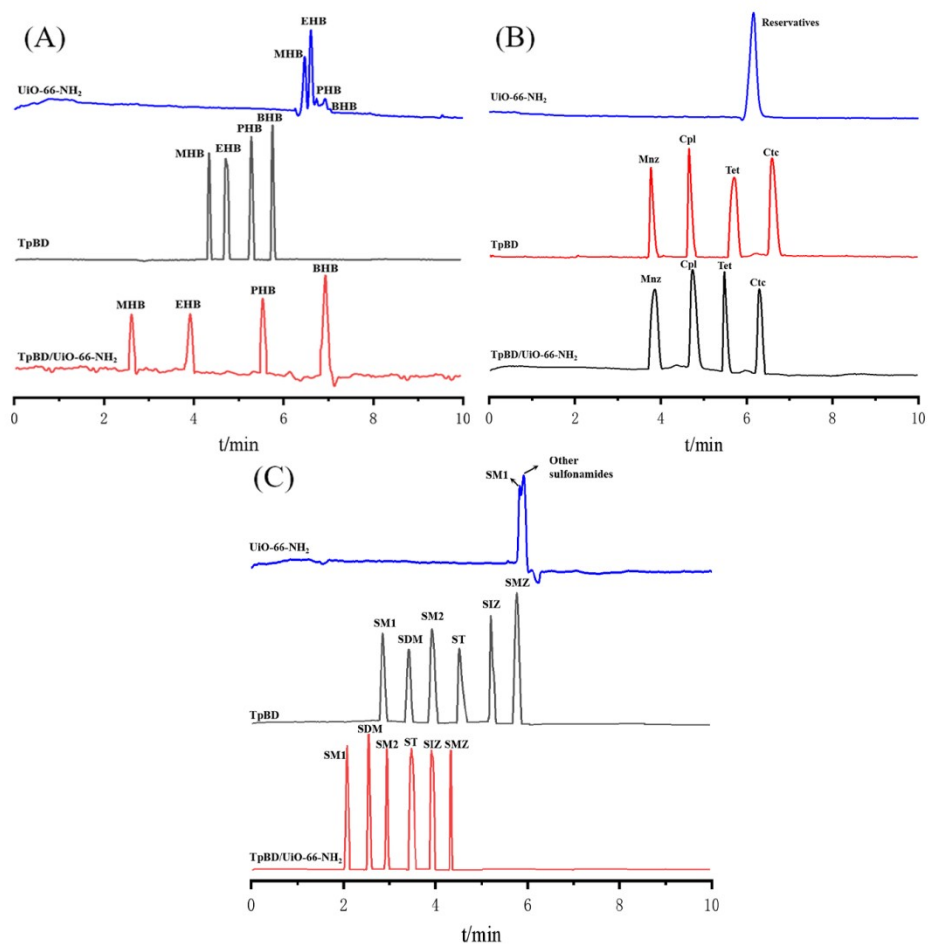


Fig. S11 Separation diagrams of four antibiotics (A), four preservatives (B) and six sulfonamides (C) on three open-tubular columns. (Experimental conditions: 20 mmol/L of ammonium acetate buffer; pH=9; operating voltage, 15 kV; detection wavelength, sulfonamides at 254 nm, antibiotics and preservatives at 270 nm.)

3. Supporting Tables:

Table S1 XPS data of TpBD/UiO-66-NH₂ hybrid material

Elements	Peak BE	Atomic%
C1s	283.48	60.45
O1s	530.28	29.03
N1s	182.19	4.81
Zr3d	398.34	5.72

Table S2 Pore structure parameters of UiO-66-NH₂, TpBD, TpBD/UiO-66-NH₂

Samples	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
UiO-66-NH ₂ ^[32]	897.78	0.31	1.232
TpBD ^[33]	524.38	0.84	3.50-7.80
TpBD/UiO-66-NH ₂	340.04	0.21	1.18-2.65

Table S3 Reproducibility and stability of the TpBD/UiO-66-NH₂ bonded OT-CEC column.

Types and numbers (n)	RSDs (%) of migration time				RSDs (%) of resolution		
	MHB	EHB	PHB	BHB	MHB-EHB	EHB-PHB	PHB-BHB
Run to run (n=9)	1.24	1.17	1.62	1.55	1.85	1.79	1.94
Day to day (n=9)	1.63	1.74	1.71	1.83	2.14	1.86	1.99
Column to column (n=3)	2.99	3.12	3.20	3.17	4.01	3.23	3.94
Runs (n=200)	3.54	3.46	3.93	3.69	3.77	3.72	4.31

Table S4 Separation results of the analytes by three types of bonded-OT column

Stationary phase	Analytes	Migration time (t /min)	Column efficiency (plates/m)	Rs	α
TpBD	MHB	4.34	43460	-	-
	EHB	4.71	33023	2.55	1.09
	PHB	5.29	14355	3.79	1.12
	BHB	5.77	21785	3.60	1.09
	Mnz	3.76	8155	-	-
	Cpl	4.65	11979	3.52	1.24
	Tet	5.71	5607	3.68	1.23
	Ctc	6.61	9110	2.58	1.16
	SM1	2.85	4500	-	-
	SDM	3.41	6423	3.08	1.20
	SM2	3.93	5304	2.45	1.15
	ST	4.52	8412	2.51	1.15
	SIZ	5.21	16317	3.36	1.15
	SMZ	5.77	9823	2.79	1.11
UiO-66-NH ₂	MHB	6.47	30636	-	-
	EHB	6.61	37820	0.74	1.02
	PHB	6.73	17400	1.05	1.02
	BHB	6.93	6033	1.32	1.03
	Mnz				
	Cpl	6.17	6809	-	-
	Tet				
	Ctc				
	SM1	5.89	7143	-	-
	SDM				
	SM2				
	ST	5.92	7394	0.14	1.00
	SIZ				
	SMZ				
TpBD/UiO-66-NH ₂	MHB	2.59	3315	-	-
	EHB	2.91	3682	7.21	1.52
	PHB	5.55	14888	8.86	1.41
	BHB	6.97	16672	6.22	1.25
	Mnz	3.85	2651	-	-
	Cpl	4.73	5295	2.44	1.32
	Tet	5.48	20540	2.38	1.16
	Ctc	6.29	12968	2.45	1.15
	SM1	2.07	4858	-	-
	SDM	2.55	9998	3.68	1.23
	SM2	2.95	30092	6.69	1.16
	ST	3.47	5833	3.79	1.18
	SIZ	3.02	8866	2.99	1.12
	SMZ	4.34	64903	4.04	1.11