Supplementary Material

Supporting Figures

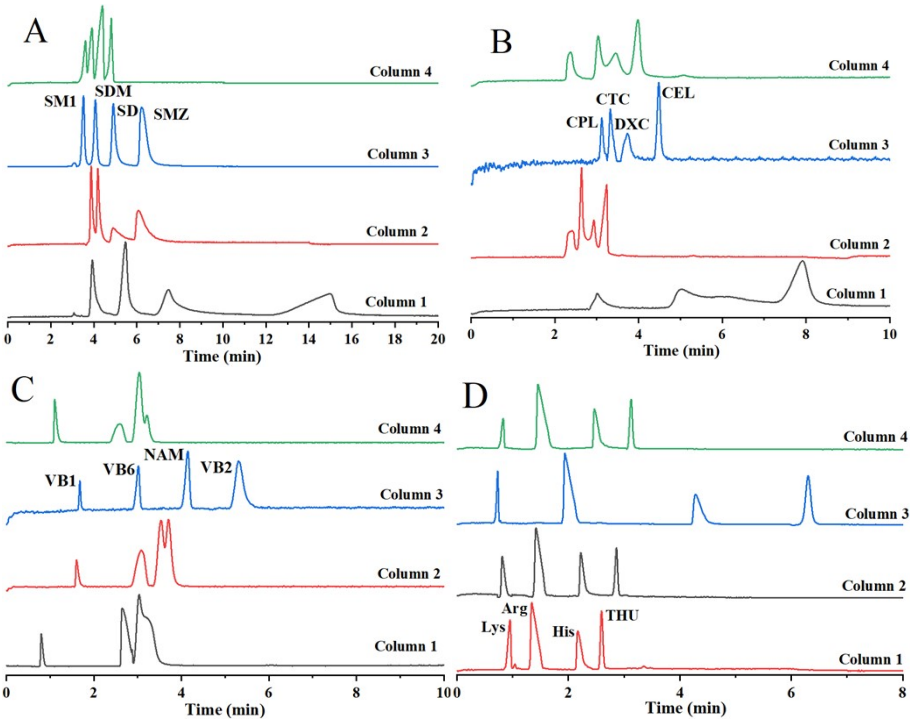

Fig. S1 The effects of ligand amounts on the separation performance of the ZIF-93/TpBD-coated OT column (A) four sulfonamide antibiotics, (B) four acidic antibiotics, (C) four vitamin B compounds, (D) three alkaline amino acids and THU (Experimental conditions: pH=6.0, 7.0, 5.0, 6.0, respectively; 20 mmol/L of phosphate buffer solution; separation voltage, 15 kV)

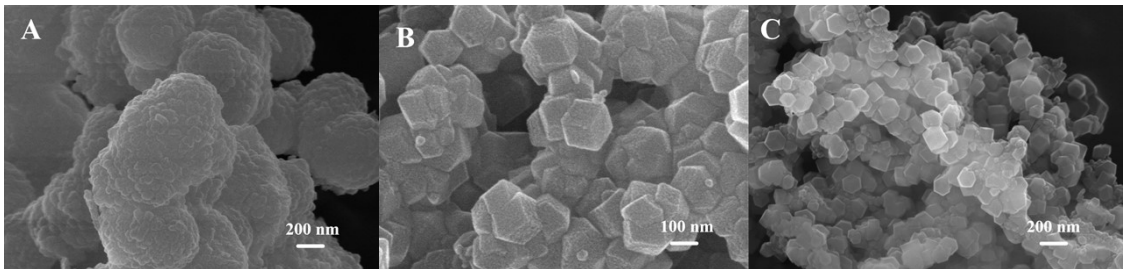

Fig. S2 SEM images of TpBD (A), ZIF-93 (B) and the ZIF-93/TpBD hybrid stationary phase (C)

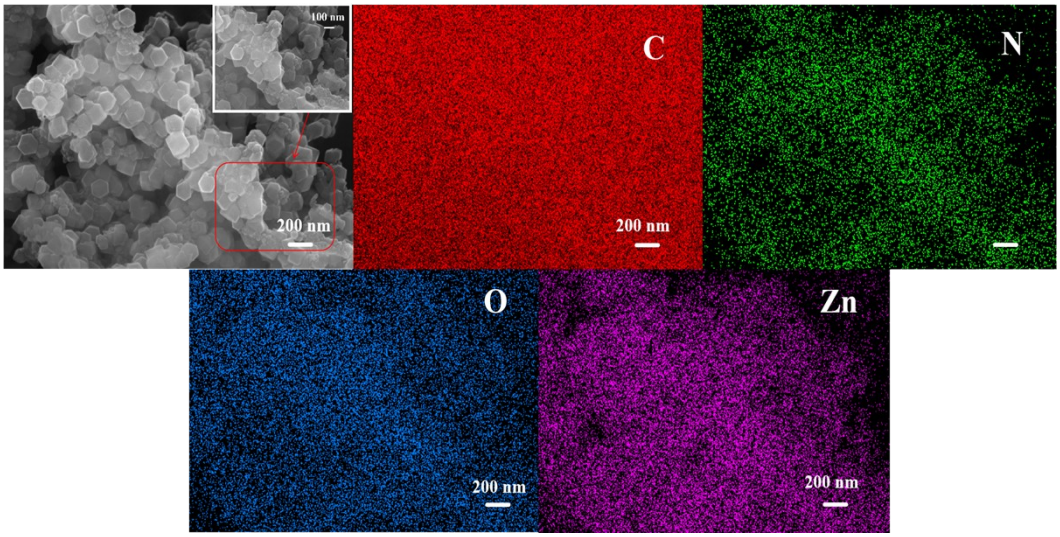

Fig. S3 EDS mapping of the ZIF-93/TpBD hybrid stationary

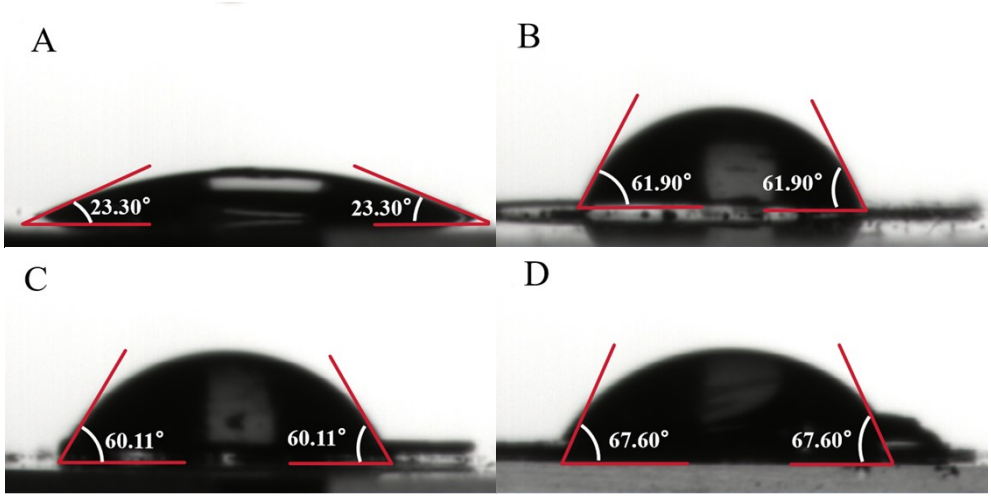

Fig. S4 Contact angle test diagram of (A) bare capillary column, (B) TpBD, (C) ZIF-93 and (D) the ZIF-93/TpBD hybrid stationary phase

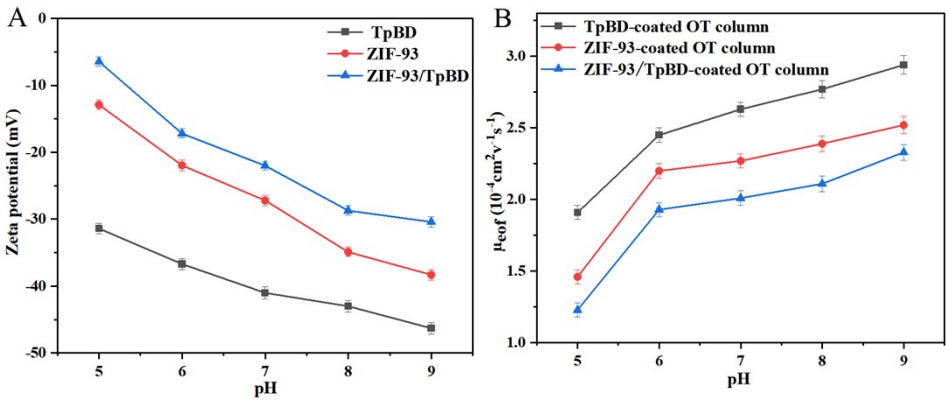

Fig. S5 Effect of buffer pH on ZP (A) and EOF (B) (Experimental conditions: 20 mmol/L of phosphate buffer solution; separation voltage, 15 kV)

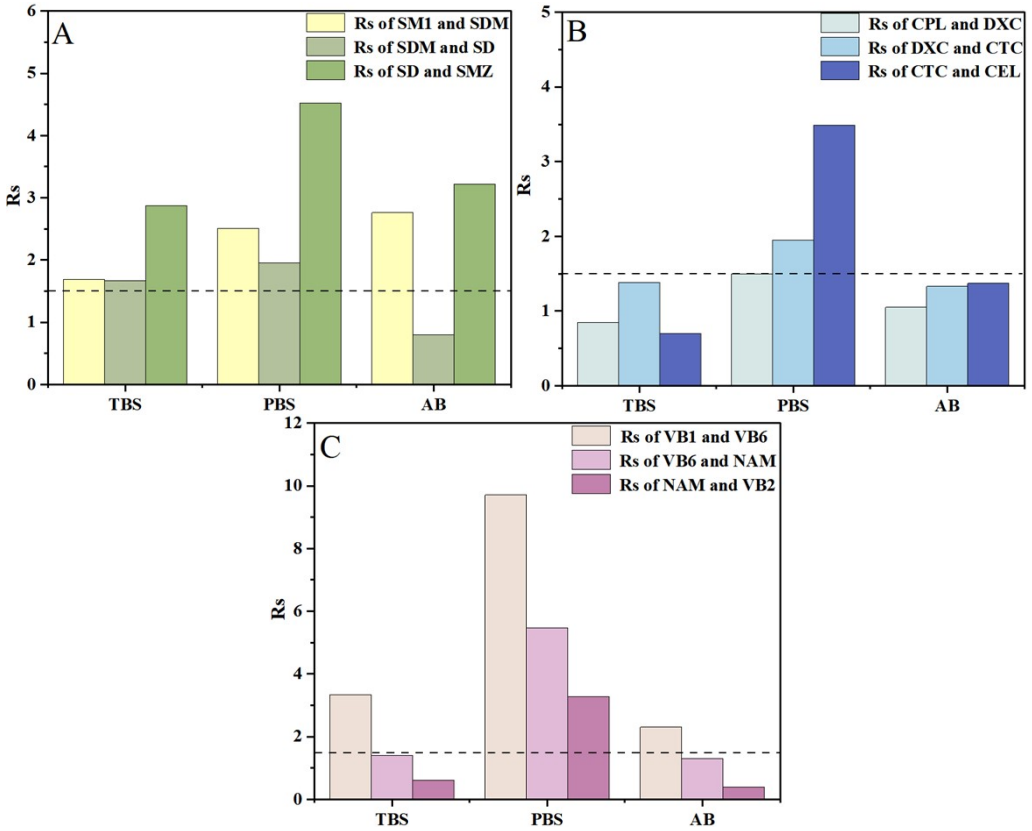

Fig. S6 Effect of buffer salt types on the separation performance of the ZIF-93/TpBD-coated OT column (A. four sulfonamide antibiotics, B. four acidic antibiotics, C. four vitamin B compounds) (Experimental conditions: pH=6.0, 7.0, 5.0, respectively; 20 mmol/L buffer solution; separation voltage, 15 kV)

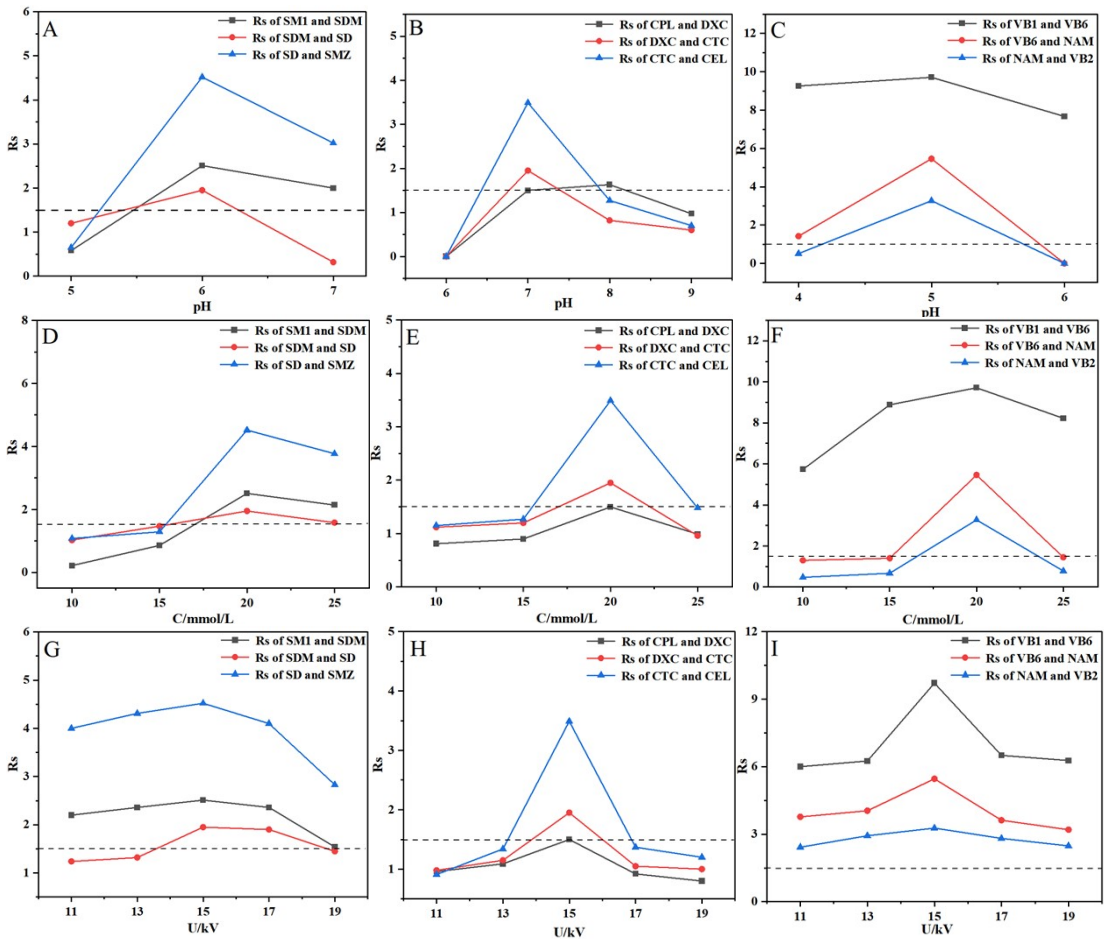

Fig. S7 Effect of pH (A~C), buffer solution concentration (D~F) and separation voltage (G~I) on Rs of three groups of structural analogs

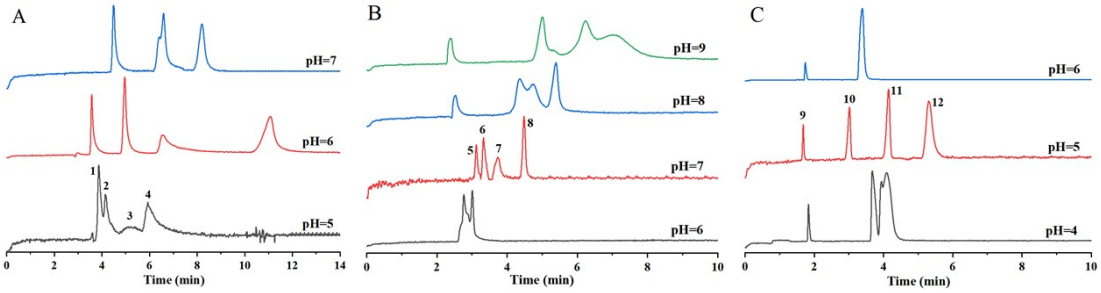

Fig. S8 Effect of different pH content on the ZIF-93/TpBD-coated OT column separation of sulfonamide antibiotics (A), acidic antibiotics (B) and vitamin B (C) (1. SM1, 2. SDM, 3. SD, 4. SMZ, 5. CPL, 6. CTC, 7. DXC, 8. CEL, 9. VB1, 10. VB6, 11. NAM, 12. VB6) (Experimental conditions: 20 mmol/L of phosphate buffer solution; separation voltage, 15 kV)

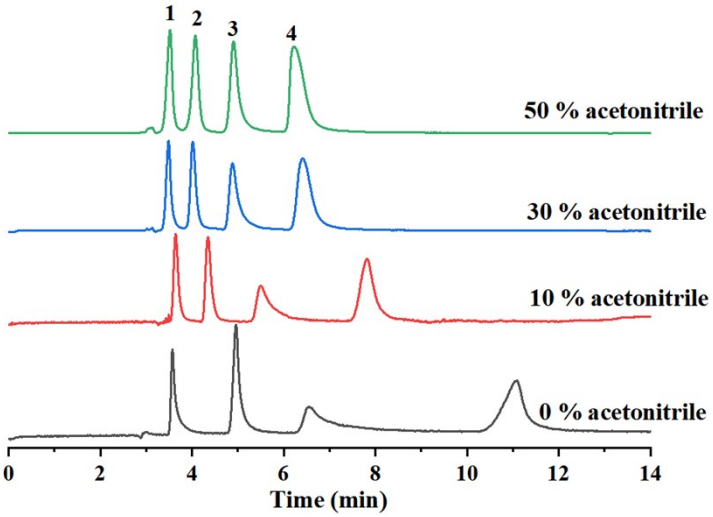

Fig. S9 Effect of different acetonitrile content on the ZIF-93/TpBD-coated OT column separation of sulfonamide antibiotics (1. SM1, 2. SDM, 3. SD, 4. SMZ) (Experimental conditions: pH=6.0, 20 mmol/L of phosphate buffer solution; separation voltage, 15 kV)

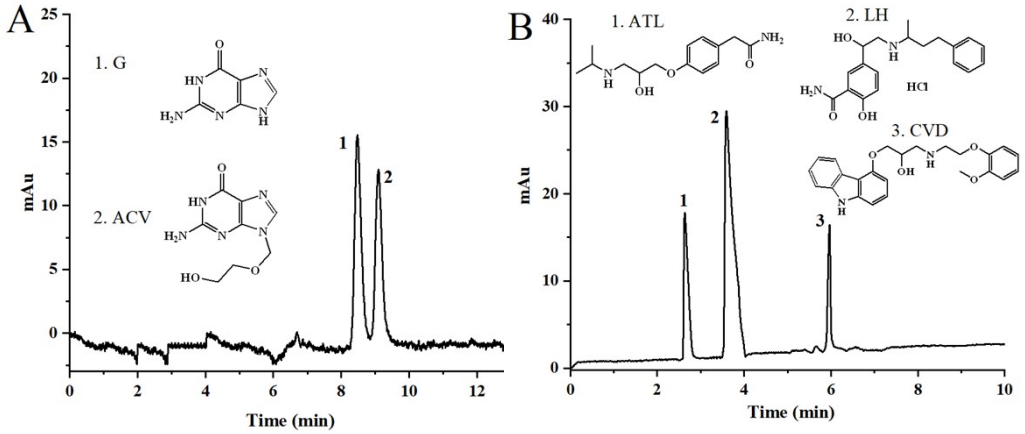

Fig. S10 Separation chromatograms of two G and ACV (A), and three β blockers (B) on ZIF-93/TpBD-coated OT column under the optimal separation conditions (Experimental conditions: pH=8.0, 7.0, respectively; 20 mmol/L phosphate buffer solution; separation voltage, 15 kV)

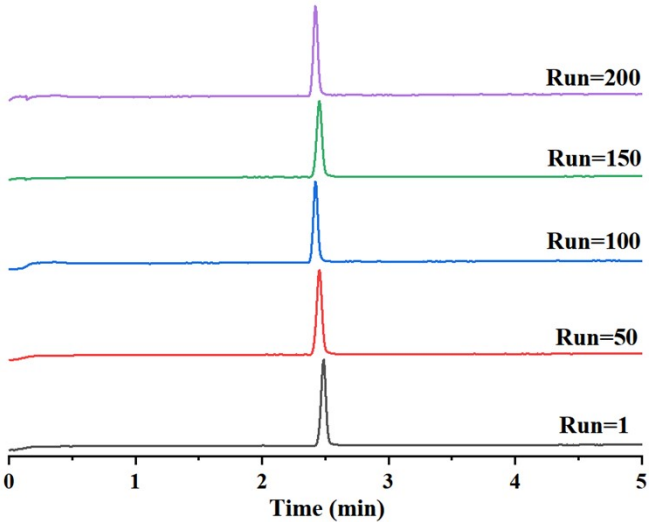

Fig. S11 Electrochromatograms of THU with different runs (Experimental conditions:pH=6.0; 20 mmol/L of phosphate buffer solution; separation voltage, 15 kV)

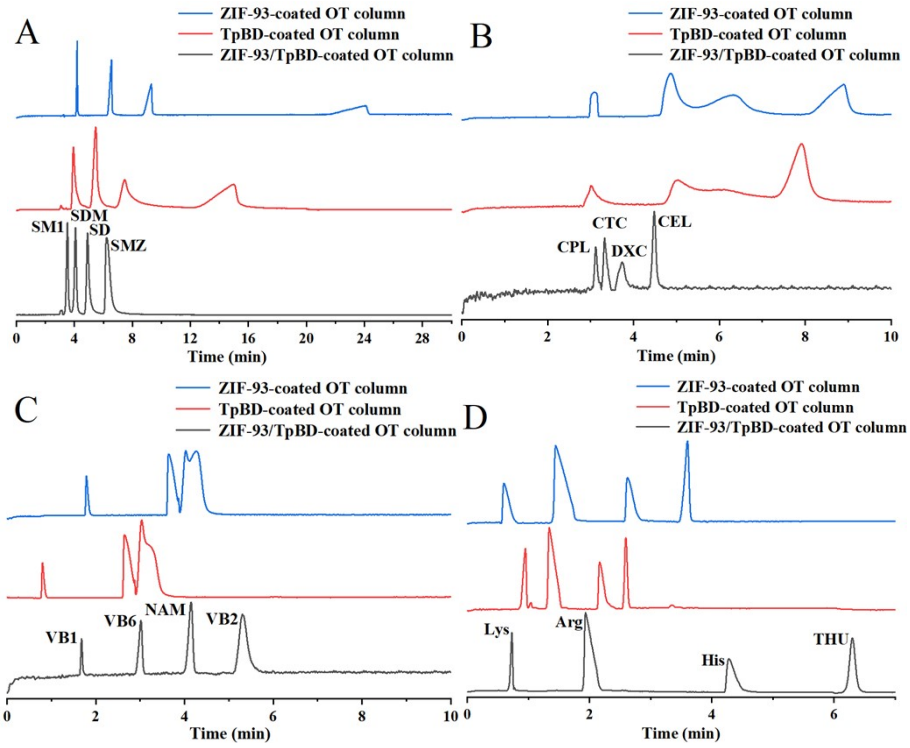

Fig. S12 Separation of (A) four sulfonamide antibiotics, (B) four acidic antibiotics, (C) four vitamin B compounds, (D) three alkaline amino acids and THU by ZIF-93/TpBD-coated OT column, ZIF-93-coated OT column and TpBD-coated OT column (Experimental conditions: pH=6.0, 7.0, 5.0, 6.0, respectively; 20 mmol/L of phosphate buffer solution; separation voltage, 15 kV)

Supporting Tables

Tab. S1 The effects of ligand amounts on R_s, N and retention time of the analytes

Analyte type	Column NO.	almeIm (g)	Analytes	Retention time (min)	R_s	N (plates/m)
Sulfonamide antibiotics	Column 1	0	SM1	3.91	-	8453
			SDM	5.48	1.83	8972
			SD	7.46	1.46	2326
			SMZ	15.02	3.36	2352
	Column 2	0.01	SM1	3.89	-	-
			SDM	4.17	0.57	-
			SD	4.92	1.00	1389
			SMZ	6.06	1.14	2778
	Column 3	0.03	SM1	3.52	-	21122
			SDM	4.08	1.60	20744
			SD	4.91	1.87	20743
			SMZ	6.23	2.30	11377
	Column 4	0.05	SM1	3.59	-	-
			SDM	3.92	0.87	-
			SD	4.38	1.15	-
			SMZ	4.81	1.02	-
Acidic antibiotics	Column 1	0	CPL	3.00	-	7328
			DXC	5.02	2.50	-
			CTC	6.11	0.94	-
			CEL	7.92	1.63	7909
	Column 2	0.01	CPL	2.39	-	-
			DXC	2.65	0.88	-
			CTC	2.93	1.14	-
			CEL	3.24	1.21	-
	Column 3	0.03	CPL	3.11	-	44176
			DXC	3.32	1.5	25734
			CTC	3.73	1.95	10264
			CEL	4.48	3.49	57213
	Column 4	0.05	CPL	2.37	-	8036
			DXC	3.03	1.97	-
			CTC	3.45	1.00	-
			CEL	3.99	1.11	15936
	Column 1	0	VB1	1.61	-	15097
			VB6	3.09	5.48	5622
			NAM	3.53	1.37	-
	Column 2	0.01	VB2	3.70	0.63	-
			VB1	0.79	-	6942
			VB6	2.65	8.26	6952
			NAM	3.04	1.39	-

			VB2	3.21	0.57	-
	Column 3	0.03	VB1	1.67	-	46917
			VB6	3.03	9.71	25761
			NAM	4.15	5.46	36220
			VB2	5.31	3.27	14759
	Column 4	0.05	VB1	1.12	-	7849
			VB6	2.57	5.57	3840
			NAM	3.04	0.89	-
			VB2	3.23	0.80	-
Three alkaline amino acids and THU	Column 1	0	Lys	0.95	-	6680
			Arg	1.34	2.05	2714
			His	2.15	4.05	15508
			THU	2.60	3.07	68029
	Column 2	0.01	Lys	0.81	-	6940
			Arg	1.42	3.30	3651
			His	2.23	4.15	22184
			THU	2.87	4.00	76777
	Column 3	0.03	Lys	0.73	-	9387
			Arg	1.94	6.05	4127
			His	4.29	7.00	23809
			THU	6.30	7.58	96993
	Column 4	0.05	Lys	0.82	-	6106
			Arg	1.46	2.98	2281
			His	2.47	4.04	16555
			THU	3.12	3.71	78215

-represted that complete separation is not achieved, so *N* cannot be calculated.

Tab. S2 Pore structure parameters of TpBD, ZIF-93 and the ZIF-93/TpBD hybrid stationary phase

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
TpBD	522.19	0.81	3.54
ZIF-93	792.32	0.53	31.84
ZIF-93/TpBD	224.96	0.21	3.81, 31.27

Tab. S3 Effect of buffer salt system on the separation performance of ZIF-93/TpBD-coated OT column

Analyte type	Buffer salt system	Analytes	pH	Retention time (min)	*N* (plates/m)
Sulfonamide antibiotics	TBS	SM1	6	10.1	33276
		SDM			22053
		SD			4526
		SMZ			10568
	PBS	SM1		11.8	36443
		SDM			27256
		SD			7612
		SMZ			15767
	AB	SM1		10.0	3285
		SDM			-
		SD			-
		SMZ			10654
Acidic antibiotics	TBS	CPL	7	3.3	-
		DXC			-
		CTC			-
		CEL			-
	PBS	CPL		4.7	44176
		DXC			25734
		CTC			10264
		CEL			57213
	AB	CPL		5.2	-
		DXC			-
		CTC			-
		CEL			7796
Vitamin B compounds	TBS	VB1	5	4.7	34451
		VB6			14302
		NAM			-
		VB2			-
	PBS	VB1		5.8	46917
		VB6			25761

	NAM		36220
	VB2		14759
	VB1		13307
AB	VB6	6.4	8043
	NAM		-
	VB2		-

-represted that complete separation is not achieved, so *N* cannot be calculated.

Tab. S4 The basic information of six groups of structural analogs separated by ZIF-93/TpBD-coated OT column

Analytes	Molecular weight	pKa_1 / pKa_2 / pKa_3 [a]	log *P* [b]	Molecular volume (Å^3) [c]	Retention time (min)	Optimal separation pH	R_s	*N* (plates/m)
SM1	264.30	2.06/6.90/-	0.34	14.0×7.3×5.8	3.52	6.0	-	21122
SDM	310.33	1.30/6.21/-	1.48	13.5×9.4×7.0	4.08		1.60	20744
SD	250.28	2.00/6.48/-	2.59	11.7×8.9×5.7	4.91		1.87	20743
SMZ	253.28	1.70/5.60/-	0.89	11.0×9.1×6.3	6.23		2.30	11377
CPL	323.13	-2.80/7.50/-	1.62	15.0×7.5×6.6	3.11	7.0	-	44176
DXC	480.90	3.50/7.70/9.50	1.15	19.3×10.1×8.4	3.32		1.50	25734
CTC	515.34	3.30/7.60/9.30	1.94	13.3×12.9×10.0	3.73		1.95	10264
CEL	347.39	2.56/6.88/-	0.65	14.8×8.3×7.1	4.48		3.49	57213
VB1	337.27	4.80/9.20/-	-3.93	17.7×10.7×7.6	1.67	5.0	-	46917
VB6	205.64	5.00/8.80/-	-1.10	11.5×9.5×4.2	3.03		9.71	25761
NAM	122.12	3.60/13.30/-	-0.24	9.1×6.5×3.2	4.15		5.46	36220
VB2	376.36	1.90/10.20/-	-2.01	15.2×9.9×6.6	5.31		3.27	14759
G	151.13	3.40/9.71/12.72	-2.03	9.6×7.8×3.2	8.46	8.0	-	40372
ACV	225.21	2.34/9.23/-	-3.31	13.7×8.3×4.0	9.08		1.60	44918
ATL	266.34	9.60	0.10	14.8×8.8×5.7	2.63		-	16567
LH	364.87	9.30	2.31	16.1×11.4×7.1	3.59	7.0	2.63	6120
CVD	406.47	7.80	4.11	17.4×12.5×9.0	5.97		7.10	249403

[a] See Ref. [37], [38], [39], [40], [41], [52], [53], [54], [55] and [56]. [b] log *P* from https://www.chemsrc.com/

[c] Molecular volume (Å^3) from Chemdraw 3D 20.0. -represted that complete separation is not achieved.

Tab. S5 Comparison of separation performance of three types of coated OT columns

OT column	Analytes	Retention time (min)	R_s	N (plates/m)
TpBD-coated OT column	SM1	3.91	-	8453
	SDM	5.48	1.83	8972
	SD	7.46	1.46	2326
	SMZ	15.02	3.36	2352
ZIF-93-coated OT column	SM1	4.22	-	127382
	SDM	6.57	5.87	41234
	SD	9.30	4.20	20517
	SMZ	24.07	8.68	7393
ZIF-93/TpBD-coated OT column	SM1	3.52	-	21122
	SDM	4.08	1.60	20744
	SD	4.91	1.87	20743
	SMZ	6.23	2.30	11377
TpBD-coated OT column	CPL	3.00	-	7328
	DXC	5.02	2.50	-
	CTC	6.11	0.94	-
	CEL	7.92	1.63	7909
ZIF-93-coated OT column	CPL	3.10	-	16017
	DXC	4.80	3.27	-
	CTC	6.30	1.28	-
	CEL	8.90	2.08	9136
ZIF-93/TpBD-coated OT column	CPL	3.11	-	44176
	DXC	3.32	1.5	25734
	CTC	3.73	1.95	10264
	CEL	4.48	3.49	57213
TpBD-coated OT column	VB1	1.61	-	15097
	VB6	3.09	5.48	5622

	NAM	3.53	1.37	-
	VB2	3.70	0.63	-
	VB1	1.78	-	25663
	VB6	3.64	8.27	11447
ZIF-93-coated OT column	NAM	4.04	1.53	-
	VB2	4.27	0.67	-
	VB1	1.67	-	46917
ZIF-93/TpBD-coated OT	VB6	3.03	9.71	25761
column	NAM	4.15	5.46	36220
	VB2	5.31	3.27	14759
	Lys	0.95	-	6680
	Arg	1.34	2.05	2714
TpBD-coated OT column	His	2.15	4.05	15508
	THU	2.60	3.07	68029
	Lys	0.60	-	855
	Arg	1.45	2.88	1247
ZIF-93-coated OT column	His	2.63	4.00	12439
	THU	3.62	4.50	49112
	Lys	0.73	-	9387
ZIF-93/TpBD-coated OT	Arg	1.94	6.05	4127
column	His	4.29	7.00	23809
	THU	6.30	7.58	96993

-represted that complete separation is not achieved, so *N* cannot be calculated.

Tab. S6 The linear equation and correlation coefficient (R^2) of vitamin B

Analytes	Linearity (μg/mL)	Linear equation	R^2

VB1	10~500	y=0.62x+134.75	0.99706
VB6	10~500	y=0.98x+374.28	0.99195
NAM	10~500	y=2.12x+709.86	0.99049
VB2	10~500	y=6.84x+1447.69	0.99520

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