Supporting Information for

Non-porous silica support covalent organic frameworks as stationary phases for liquid chromatography

Meichao Xie,[‡,a,b] Kaijun Quan,[‡b] Hui Li,[b] Bei Liu,[b] Jia Chen,[b] Yong-Liang Yu,[*a] Jian-Hua Wang,[a] Hongdeng Qiu,[*,b,c]

[a] Research Center for Analytical Sciences, Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, China

[b] CAS Key Laboratory of Chemistry of Northwestern Plant Resources and Key Laboratory for Natural Medicine of Gansu Province, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.

[c] College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

[‡] These two authors contributed equally to this work.

[*] E-mail addresses: yuyl@mail.neu.edu.cn (Y. Yu), hdqiu@licp.cas.cn (H. Qiu).

Experimental section

Materials. All of the substances utilized in this research were of analytical grade or better and can be used without further treatment. 1,3,5-tris(4-aminophenyl)benzene (TPB) and 2,5-dimethoxyterephthalaldehyde (DMTP) were bought from Jilin Yanshen Technology, Ltd. (Jilin, China). Hexadecyltrimethylammonium bromide (CTAB, for molecular biology, ≥ 99%) and n-Octadecyltrichlorosilane (95%) were purchased from Alfa Aesar. Toluene, ethanol, tetrahydrofuran (THF), methanol and acetonitrile were obtained from Sinopharm Chemical Reagents Co., Ltd (Shanghai, China). 3-Aminopropyltrimethoxysilane (APTMS), aniline, 1-naphthylamine, 2-chloroaniline, diphenylamine, anisole, chlorobenzene, benzene, naphthalene, acenaphthene, anthracene, pyrene, 1,2-benzanthracene, toluene, ethylbenzene, propylbenzene, n-butylbenzene, dimethyl phthalate, dipropyl phthalate, dicyclohexyl phthalate, dioctyl phthalate, chromatographic grade acetonitrile and all positional isomeric analytes were acquired from Aladdin (Shanghai, China). The water is prepared by Direct-Q3 UV ultra-pure water purification equipment.

Instruments. Field emission scanning electron microscope (SEM) images were obtained with a JSM--6701F SEM instrument. Transmission electron microscopy (TEM) images were recorded using a TF20 TEM instrument. Fourier transform infrared (FT-IR) spectra were obtained with a V70 spectrometer. Powder X-ray diffractograms were obtained using a Smartlab-SE X-ray diffractometer with a scan rate of 2° min^{-1} and a scan range of 2-40°. BET surface area and pore size data were measured with the rapid specific surface area and pore size analyser ASAP 2010. The water contact angle was measured with a DSA100 measuring instrument. The liquid chromatography experiments were performed using an Agilent 1290 Infinity II two-dimensional liquid chromatograph.

Preparation of Non-Porous Silica Microspheres. Based on the improved Stöber method,[1] with appropriate adjustments, as follows. First, two solutions A and B are prepared. Solution A consisted of 225 mL ethanol and 37.5 mL ethyl orthosilicate. Solution B contained 175 mg KCl, 80 mL water, and 670 mL ethanol. When the temperature is 30 °C, solution A is added to solution B at a speed of 0.5 mL min^{-1} by a flow syringe pump. After all solution A was added to B, the reaction was continued for 0.5 h. The silica microspheres were collected by centrifugation and washed three times in turn with water and ethanol, dried overnight at 60 °C, and then calcined at 700 °C for 10 h.

Preparation of TPB-DMTP-COF. Took a centrifuge tube and added 0.06 mmol TPB, 0.09 mmol DMTP, 5 mL acetonitrile, and 0.6 mL acetic acid to this tube. The centrifuge tubes were sonicated

for 1 min. After one day at room temperature, the TPB-DMTP-COF were obtained by centrifugation and the products were washed sequentially with tetrahydrofuran and ethanol and dried overnight at 60 °C.[2]

Preparation of NPS@TPB-DMTP. 5 g NPS were refluxed with 10% hydrochloric acid for 10 h to activate the spheres. Then the activated spheres were washed sequentially with water and ethanol and dried overnight at 60 °C. The activated silica spheres were dispersed into 50 mL of toluene to which 3 mL of APTMS was added and then refluxed at 110 °C for 24 h. When the reaction was complete, the product NPS-NH_2 was collected by centrifugation.

The resulting NPS-NH_2 was washed sequentially with toluene and ethanol and then dried overnight at 60°C. 3 g of NPS-NH_2 was dispersed into 45 mL of acetonitrile, to which DMTP (0.45 mmol), HAc (12 M, 3.6 mL) was then added. The mixture was stirred for one day and the product (NPS-DMTP) was collected by centrifugation, then washed with ethanol and dried overnight at 60°C. The dried NPS-DMTP was dispersed into 45 mL of acetonitrile, to which TPB (0.3 mmol), DMTP (0.45 mmol), and HAc (12 M, 3.6 mL) were added. After stirring the mixture for three days, the product (NPS@TPB-DMTP) was collected by centrifugation, then the product was washed sequentially with THF, ethanol and dried overnight at 60 °C.

Preparation of superficially porous silica particles. Superficially porous silica (SPS) particles was prepared according to the method reported in the literature.[3] Briefly, 0.5 g of NPS, 0.5 g of CTAB and 0.3 g of urea were dissolved in 15 mL of H2O. Afterwards, 15 mL of cyclohexane, 0.46 mL (6.0 mmol) of isopropanol and 0.5 mL of ethyl orthosilicate were added and stirred at room temperature. The reaction was then heated to 70 °C and 0.5 mL TEOS was added while stirring. The resulting product was calcined at 550 °C.

Preparation of C18 modified superficially porous silica (SPS@C18). The C18 stationary phase was synthesised according to the steps in the literature.[4] Briefly, 0.5 g superficially porous silica and 0.5 mL of n-octadecyltrichlorosilane were added to 20 mL of anhydrous toluene. The mixture was refluxed for 12 h.

Column packing. First, 0.5 g of NPS@TPB-DMTP was dispersed in methanol: isopropanol (9:1, v/v, 20 mL). The packing was then loaded into a column (2.1 ×100 mm) under 40 MPa pressure using methanol as the propellant solvent. The packed columns were treated with methanol at a flow rate of 0.4 mL min-1 for 24 h before being used for the chromatography experiments. The NPS-DMTP

column was loaded in the same way as the NPS@TPB-DMTP column. The SPS@C18 packing is loaded into the column (2.1 ×50mm) in the same way as the NPS@TPB-DMTP column.

Calculation of the Chromatographic Parameters. The retention factor (k), selectivity factor (α), and resolution (R) were calculated from equations (1), (2), (3) and (4) respectively.[5,6]

$$k_1 = \frac{t_1 - t_0}{t_0} \qquad (1)$$

$$k_2 = \frac{t_2 - t_0}{t_0} \qquad (2)$$

$$R = \frac{t_2 - t_1}{w_{1/2(1)} + w_{1/2(2)}} \qquad (3)$$

where t_1 is the retention time for the faster moving analytes and t_2 for the slower, t_0 is the column void time, meanwhile $W_{1/2(1)}$ and$W_{1/2(2)}$ is the corresponding peak width at half height.

Calculation of thermodynamic parameters. The Gibbs free energy change (ΔG, kJ·mol^{-1}), entropy change (ΔS, J·mol^{-1}·K^{-1}) and enthalpy change (ΔH, kJ·mol^{-1}) for the transfer of a solute from the mobile phase to the stationary phase are calculated using the following equations (4) and (5).[5,6] The k, R, T and Φ in the equation are the retention factor, gas constant, absolute temperature and phase ratio respectively.

$$\ln k = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + \ln \Phi \qquad (5)$$

$$\Delta G = \Delta H - T\,\Delta S \qquad (6)$$

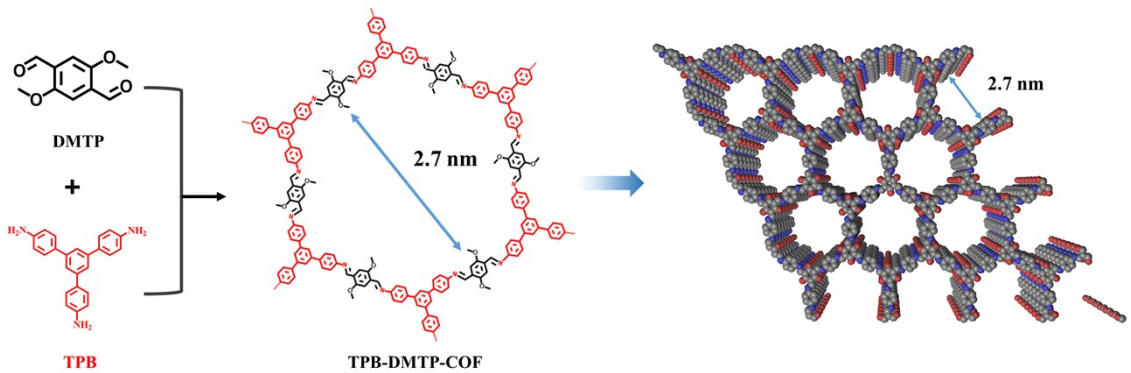

Fig. S1. Synthesis and structure of TPB-DMTP-COF.

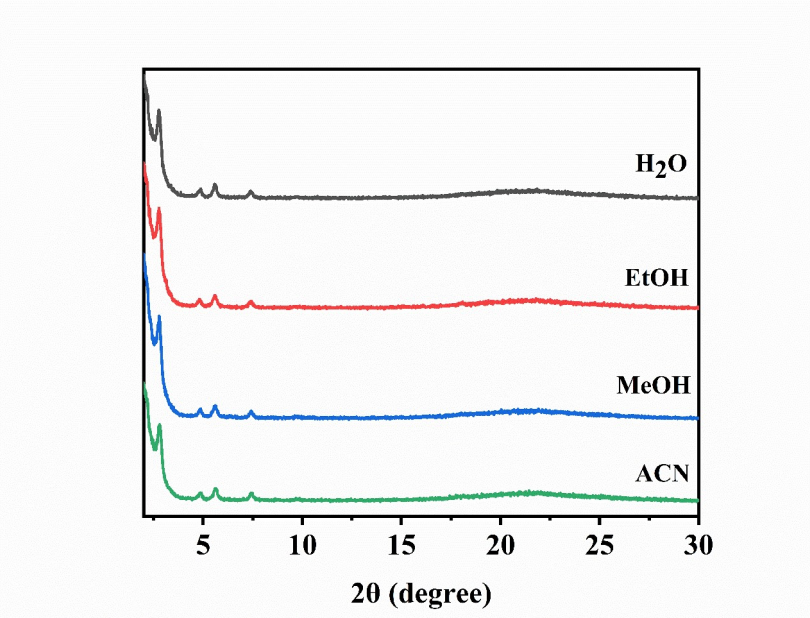

Fig. S2. PXRD patterns of the NPS@TPB-DMTP microspheres after soaking at different solvents for 3 days.

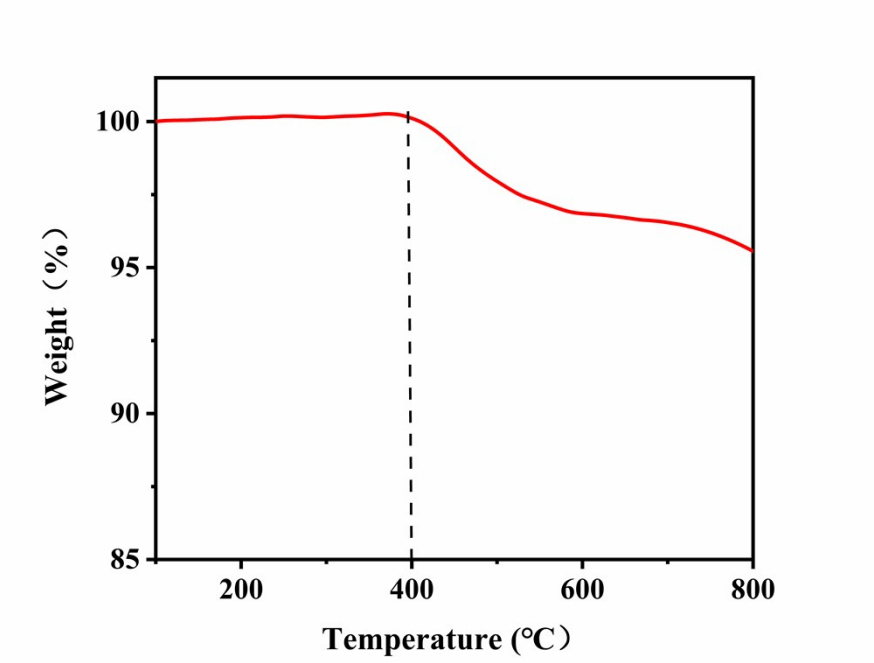

Fig. S3. TGA curves of NPS@TPB-DMTP.

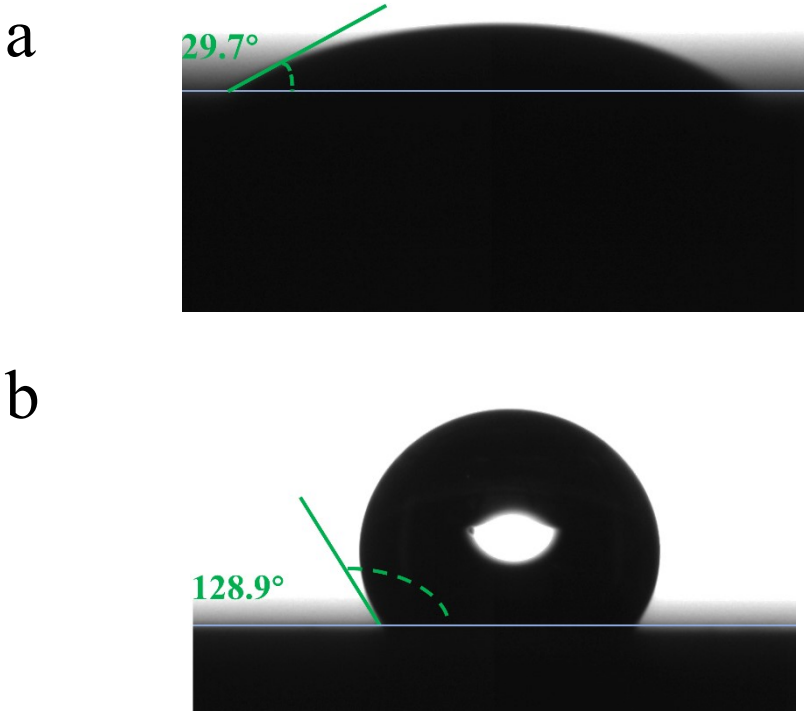

Fig. S4. Water contact angle of NPS-NH_2 (a) and NPS@TPB-DMTP microspheres (b).

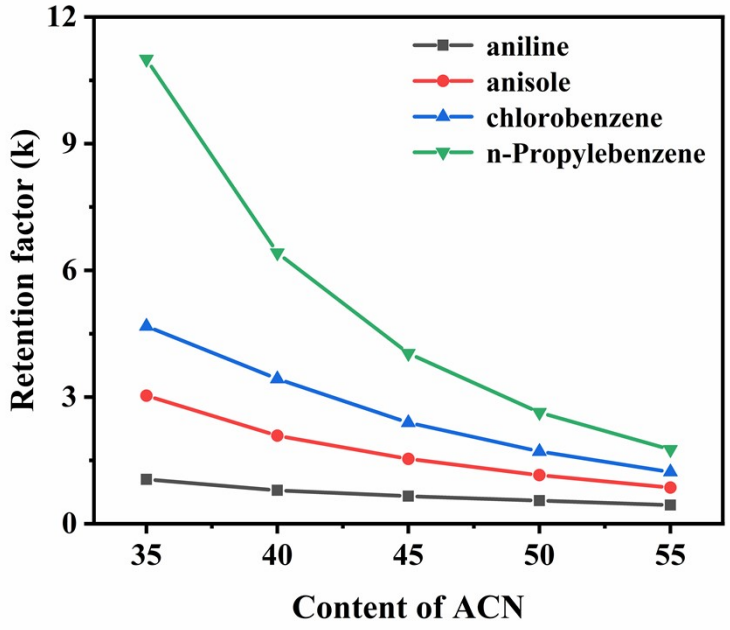

Fig. S5. Relationship between retention factor and acetonitrile concentration on the NPS@TPB-DMTP column.

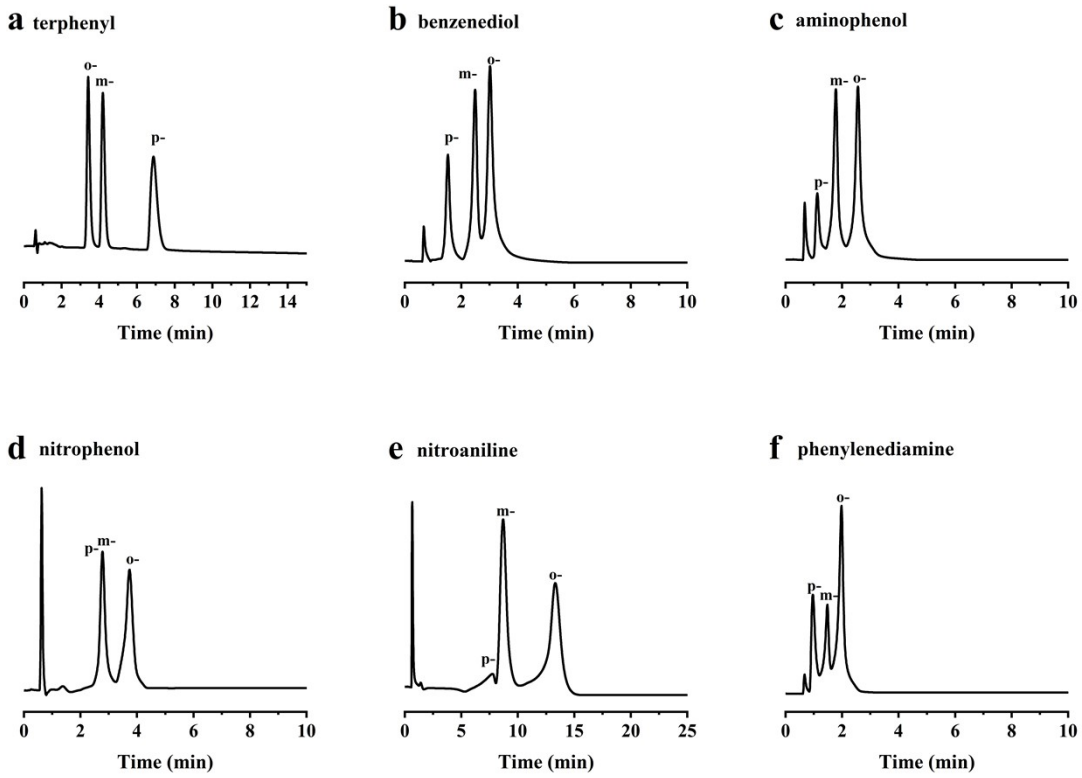

Fig. S6. Separation of positional isomers of triphenyl (a), benzenediol (b), aminophenol (c), nitrophenol (d), nitroaniline (e) and phenylenediamine (f). Mobile phase: ACN/H2O (60/40, v/v) (a); ACN/H2O (10/90, v/v) (b,c,d,e,f). Flow rate: 0.4 mL/min. Detection wavelength: 214 nm.

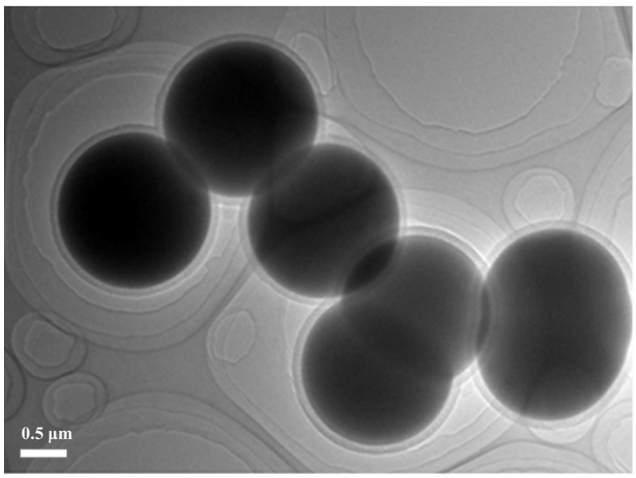

Fig. S7. TEM images of the SPS@C18.

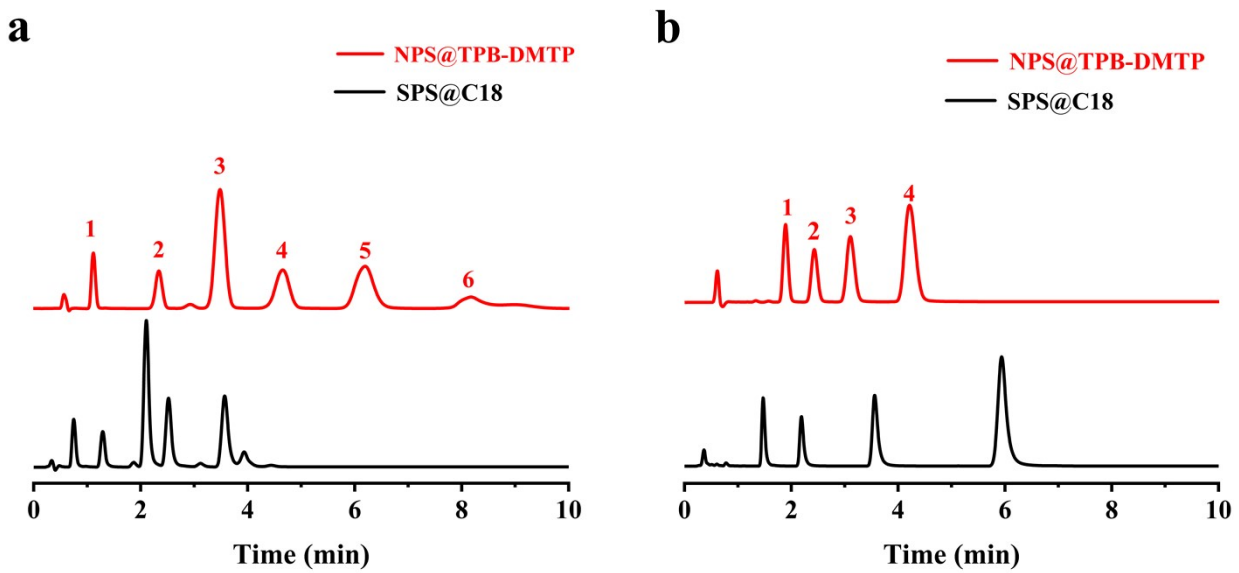

Fig. S8. Separation of PAHs (a) and alkylbenzenes (b). (a) Analytes: (1) benzene, (2) naphthalene, (3) fluorene, (4) phenanthrene, (5) fluoranthene and (6) pyrene. (b) Analytes: (1) toluene, (2) ethylbenzene, (3) propylbenzene and (4) n-butylbenzene. Mobile phase: (a) ACN/H2O (53/47, v/v); (b) ACN/H2O (45/55, v/v). Flow rate: 0.4 mL/min. Detection wavelength: 214 nm

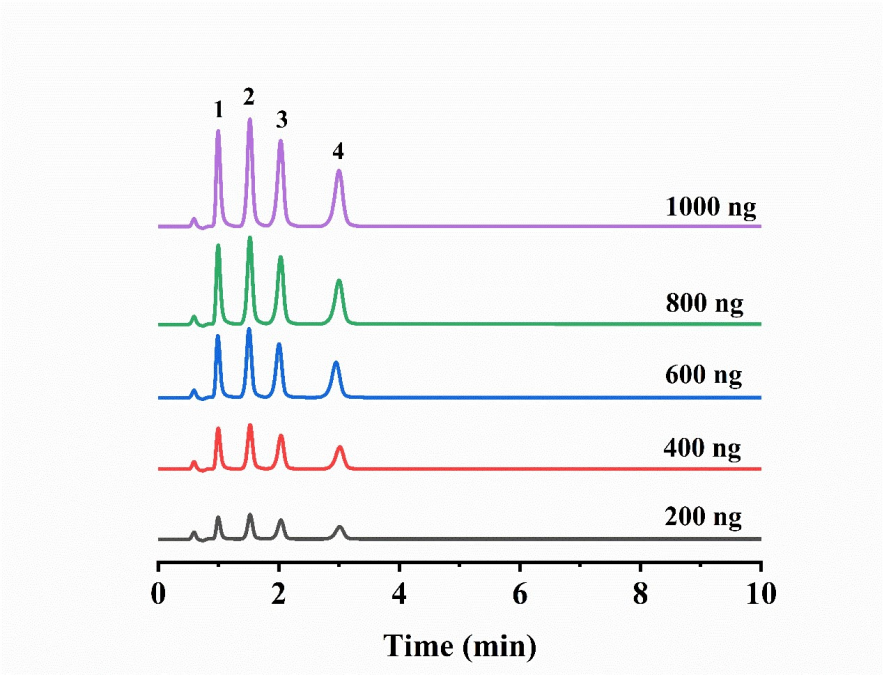

Fig. S9. Effect of analyte mass on the NPS@TPB-DMTP column for the separation of monosubstituted benzene. Mobile phase: ACN/H_2O (45/55, v/v). Flow rate: 0.4 mL/min. Detection wavelength: 214 nm.

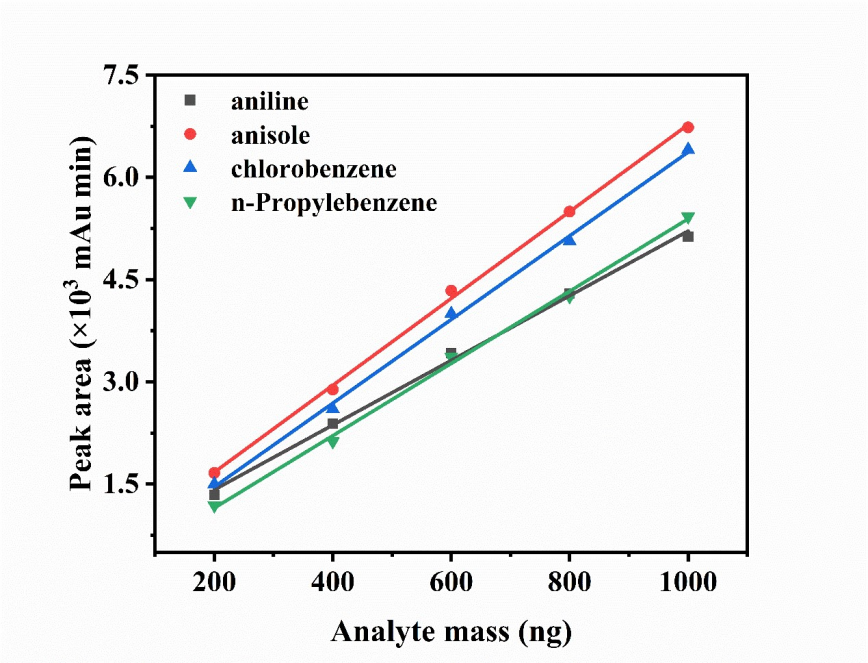

Fig. S10. Effect of analyte mass on the NPS@TPB-DMTP column for the separation of monosubstituted benzene.

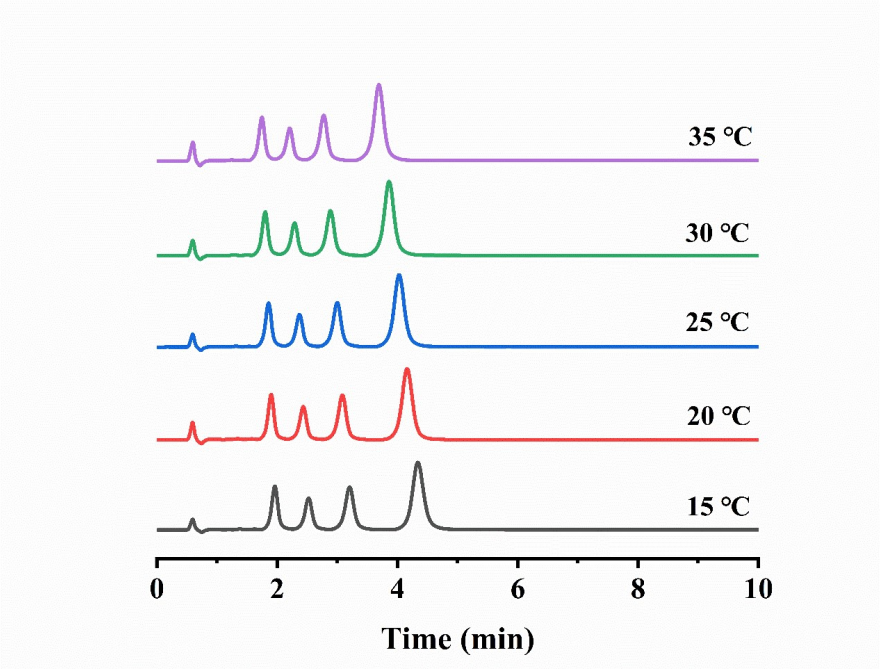

Fig. S11. Effect of temperature on the NPS@TPB-DMTP column for the separation of alkylbenzenes.

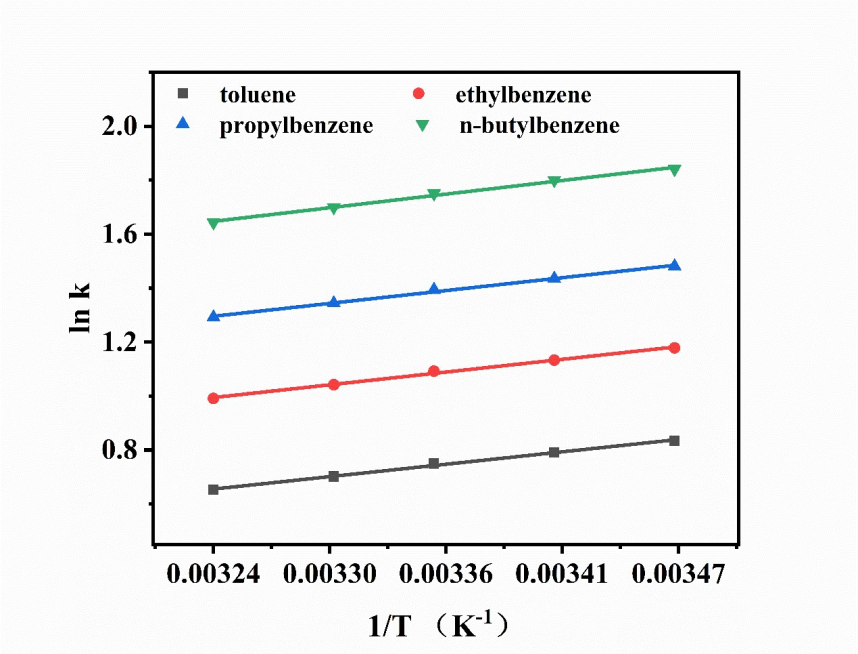

Fig. S12. Van't Hoff plots of alkylbenzenes on NPS@TPB-DMTP column.

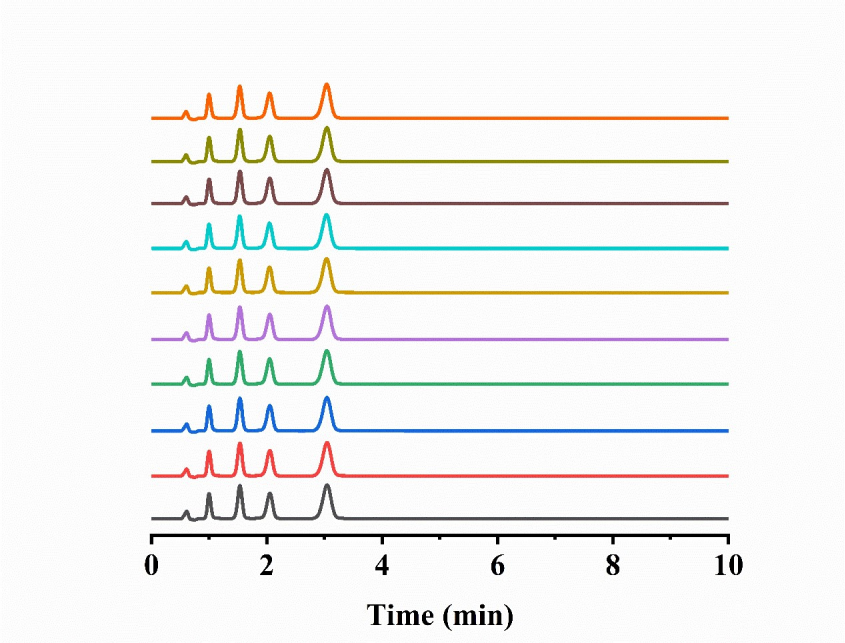

Fig. S13. The chromatograms for continuous 10 times separation of monosubstituted benzene.

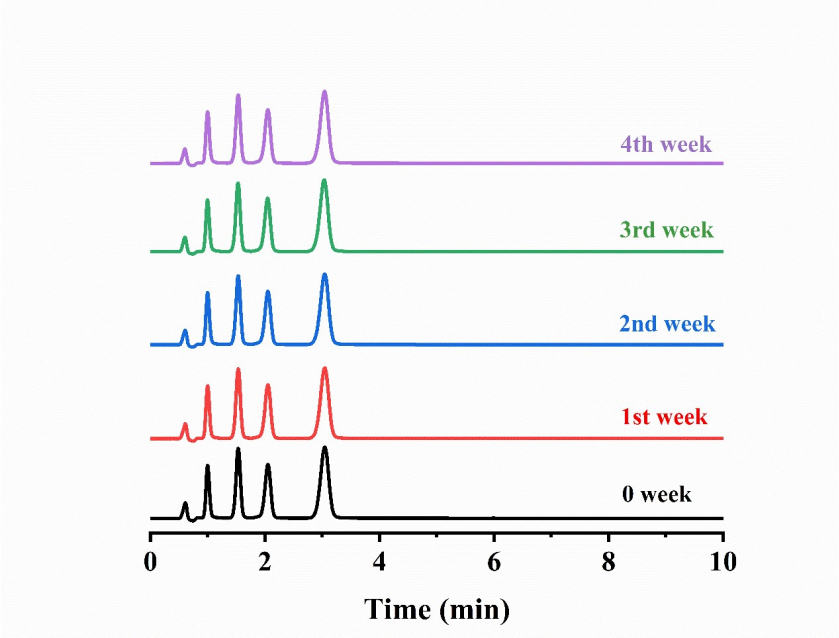

Fig. S14. The chromatograms for separation of monosubstituted benzene on the NPS@TPB-DMTP column at different times.

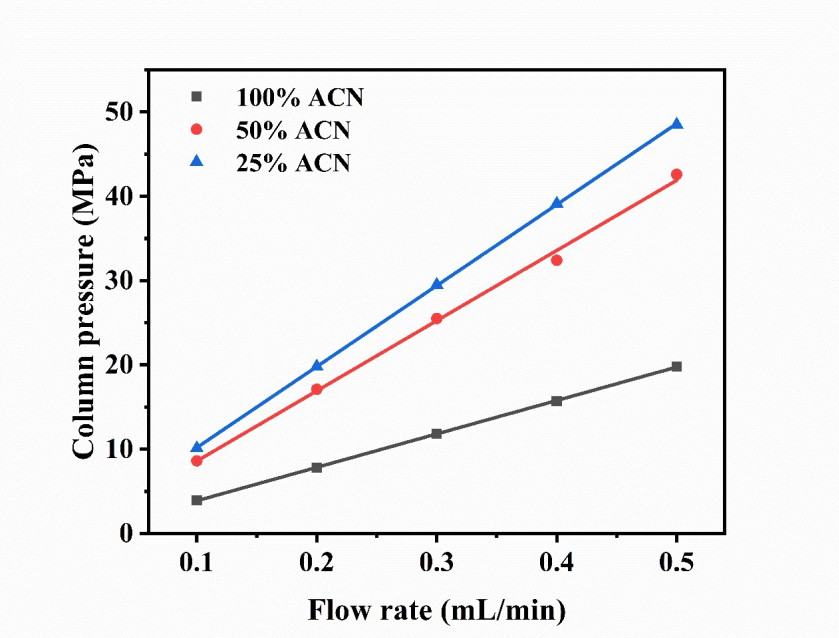

Fig. S15. Back pressure against flow rate for NPS@TPB-DMTP column; flow rate, 0.1-0.5 mL/min.

Table S1. Elemental analysis result of NPS-NH_2, NPS-DMTP and NPS@TPB-DMTP.

	Elements		
	C	H	N
NPS-NH_2	1.07	0.32	0.13
NPS-DMTP	1.23	0.34	0.12
NPS@TPB-DMTP	6.58	0.60	0.44

Table S2. The log K_{ow} values of the studied analytes.

Analytes	Log K_{ow} [a]	Analytes	Log K_{ow} [a]
aniline	0.90	pyrene	4.88
1-naphthylamine	2.25	fluoranthene	5.16
2-chloroaniline	1.90	toluene	2.73
diphenylamine	3.5	ethylbenzene	3.15
anisole	2.11	propylbenzene	3.69
chlorobenzene	2.84	n-butylbenzene	4.38
benzene	2.13	dimethyl phthalate	1.60
naphthalene	3.30	dipropyl phthalate	3.27
fluorene	4.18	dicyclohexyl phthalate	6.20
phenanthrene	4.46	dioctyl phthalate	8.10
o-terphenyl	5.52	2-aminophenol	0.62
m-terphenyl	5.52	3-aminophenol	0.21
p-terphenyl	5.52	4-aminophenol	0.04
o-benzenediol	0.88	2-nitrophenol	1.79
resorcinol	0.80	3-nitrophenol	2.00
hydroquinone	0.59	4-nitrophenol	1.91
o-phenylenediamine	0.15	2-nitroaniline	1.85
m-phenylenediamine	-0.33	3-nitroaniline	1.37
p-phenylenediamine	-0.25	4-nitroaniline	1.39

[a]: Data from: https://pubchem.ncbi.nlm.nih.gov/ and http://www.chemspider.com/

Table S3. The separation results of positional isomers on the NPS@TPB-DMTP column.

Position isomers	Retention factors (k)			Separation factors (α)	
	o	m	p	α1	α2
triphenyl	4.59	5.88	10.27	1.28	1.75
benzenediol	3.02	2.48	1.52	2.12	1.30
aminophenol	2.56	1.78	1.13	2.77	1.70
nitrophenol	3.74	2.78	2.78	1.00	1.45
nitroaniline	19.37	12.31	10.76	1.15	1.57
phenylenediamine	1.96	1.22	0.45	2.71	1.61

Table S4. The retention time (t_R, min), peak widths at half height ($W_{1/2}$, min) and resolution (R) of PAHs.

Analytes	t_R		$W_{1/2}$		R	
	a	b	a	b	a	b
benzene	1.12	0.75	0.08	0.08		
naphthalene	2.34	1.29	0.14	0.09	2.96	1.19
fluorene	3.48	2.10	0.21	0.10	1.68	1.39
phenanthrene	4.15	2.52	0.29	0.11	2.77	2.25
fluoranthene	6.19	3.57	0.38	0.13	2.73	2.09
pyrene	8.17	3.93	0.42	0.14	2.92	1.55

a : NPS@TPB-DMTP column ; b : SPS@C18 column

Table S5. The retention time (t_R, min), peak widths at half height ($W_{1/2}$, min) and resolution (R) of alkylbenzenes.

Analyte	t_R		$W_{1/2}$		R	
	a	b	a	b	a	b
toluene	1.89	1.47	0.11	0.06		
ethylbenzene	2.43	2.19	0.12	0.08	2.69	5.84
propylbenzene	3.10	3.56	0.15	0.11	2.68	8.62
n-butylbenzene	4.21	5.94	0.19	0.16	3.31	10.11

a : NPS@TPB-DMTP column ; b : SPS@C18 column

Table S6. Thermodynamic parameters for separation of the studied analytes on the NPS@TPB-DMTP packed column. (T = 298.15 K)

Analytes	△H ($KJ \cdot mol^{-1}$)	△S ($J \cdot mol^{-1} \cdot K^{-1}$)	△G ($KJ \cdot mol^{-1}$)	R^2
toluene	-6.59	-15.90	-1.85	0.9965
ethylbenzene	-6.77	-13.67	-2.58	0.9958
propylbenzene	-6.83	-11.36	-3.39	0.9959
n-butylbenzene	-7.24	-14.38	-4.32	0.9947

Table S7. Precision for analytes on the NPS@TPB-DMTP column.

Analyte	RSD (%) (n=10)		
	T	Peak height	Peak area
aniline	0.070	1.245	0.450
anisole	0.084	0.871	0.404
chlorobenzene	0.095	0.342	0.467
n-propylbenzene	0.127	0.855	0.123

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