

**Layer-by-layer preparation of 3D covalent organic framework/
silica composites for chromatographic separation of position
isomers**

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Experimental Section

Reagents. All chemicals and reagents used were at least of analytical grade. Tetra(4-anilyl)methane (TAM) was obtained from Bide Pharmatech Ltd. (Shanghai, China). Terephthalaldehyde (TPDA), dioxane, mesitylene and all the analytes used in the HPLC experiment were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). 5 μm Aminosilica ($\text{SiO}_2\text{-NH}_2$) and 5 μm C18 silica sphere were provided by Borui Jianhe Chromatographic Technology Co. (Tianjin, China). Analytical grade solvent of tetrahydrofuran (THF), N,N-dimethylformamide (DMF), Acetone and acetic acid were obtained from Sinopharm Chemical Reagent Co.,Ltd (Shanghai, China). Ultrapure water was obtained from Wahaha Foods Co. Ltd. (Shanghai, China).

Instrumentation. PXRD patterns were recorded on a D2 PHASER diffractometer (Bruker, German) using Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with a scanning speed of 8° min^{-1} and a step size of 0.02° in 2θ . Solid-state NMR experiments were performed on Infinityplus 300 (VARIAN, USA). SEM images were recorded on an S-3500N (Hitachi, Japan) scanning electron microscope. FTIR spectra were measured on a Nicolet IR IS10 spectrometer (Nicolet, USA) with pure KBr pellets. N_2 adsorption experiments were performed on Autosorb-iQ (Quantachrome, USA) using N_2 adsorption at 77 K. The pore size distribution of prepared COFs was calculated using the density functional theory model. An e 2695 alliance HPLC with 2998 PDA detector (Waters, USA) was used for HPLC experiments. The packed column was prepared with HY-HPLC-LC-M (Hydrosys, China).

Preparation of COF-300 via amorphous-to-crystalline transformation

The COF-300 was prepared according to the previous works with little modifications.^{1,2} TPDA (24 mg, 0.178 mmol) and TAM (40 mg, 0.104 mmol) were separately dissolved in 10 mL ethanol with 10 min sonication, mixed in a 100 mL flask, and refluxed for 4 hours to obtain the amorphous polymer. After rinsing with ethanol, the polymer was collected via centrifugation and evacuated in vacuum at room temperature overnight. Subsequently, the polymer was dispersed with 1.5 mL dioxane, 1.5 mL mesitylene and 0.3 mL 6 M aqueous acetic acid in a 35 mL Schlenk tube (OD 26 × L 125 mm). After degassed through three freeze–pump–thaw cycles, the tuber was heated at 120 °C for 3 d. The formed yellow product was collected via centrifugation and rinsed with DMF and THF. The isolated powder was then extracted with acetone and dried at 100 °C under vacuum for 24 h to obtain COF-300.

Preparation of COF-300@SiO₂ via LBL

To facilitate consistent COF-300@SiO₂ preparation, the repeated reaction cycles was performed. 0.1 g SiO₂-NH₂, 20 mL ethanol solution of TPDA (1.5 mmol L⁻¹) and 2 mL 6 M aqueous acetic acid were mixed in a 100 mL flask, and refluxed for 4 hours to obtain the SiO₂-PDA. After rinsed to remove the unreacted monomer, the SiO₂-PDA was refluxed with 20 mL TAM (0.75 mmol L⁻¹) and 2 mL 6 M aqueous acetic acid to obtain SiO₂-TAM for one cycle. The ploymer@SiO₂ formed for N cycles. After rinsing with ethanol, the polymer@SiO₂ was collected via centrifugation and evacuated in vacuum at room temperature overnight. Subsequently, the polymer@SiO₂ was dispersed with 1 mL dioxane, 1 mL mesitylene and 0.2 mL 6 M

aqueous acetic acid in a 35 mL Schlenk tube (OD 26 × L 125 mm). After degassed through three freeze–pump–thaw cycles, the tuber was heated at 120 °C for 3 d. The formed product was collected via centrifugation and rinsed with THF. The isolated powder was then extracted with acetone and dried at 100 °C under vacuum for 24 h to obtain COF-300@SiO₂.

Preparation of packed column for HPLC

3.0 g of COF-300@SiO₂ was dispersed in a vessel with 40 mL ethanol under ultrasonication for 5 min. The suspension was then downward packed into a stainless steel column (15 cm length; 4.6 mm i.d.) under 6000 psi. The C₁₈, control SiO₂-NH₂ and SiO₂-NH₂ columns were prepared in the same way as the COF-300@SiO₂ columns. The all the prepared packed column was conditioned with ethanol at a flow of 1 mL min for 2 h before chromatographic experiments.

Calculation of thermodynamic parameters

The enthalpy change (ΔH) and entropy change (ΔS) for the transfer of the analyte between the mobile phase and the prepared COF-300@SiO₂ stationary phase were calculated according to the van't Hoff equation.³

$$\ln k' = -\Delta H/(RT) + \Delta S/R + \ln \Phi \quad (1)$$

k' is retention factor, R is gas constant, T is absolute temperature, and Φ is the phase ratio, which is defined as the volume ratio of the stationary phase (V_s) to the mobile phase (V_m).

$$k' = (t - t_0)/t_0 \quad (2)$$

where t is the retention time, t_0 the column void time which was determined by

injecting a small plug of acetone and recording the perturbation signal.

$$V_s = V_{\text{Col}} - V_0 \quad (3)$$

$$V_0 = t_0 \times F \quad (4)$$

where V_{Col} is the geometrical volume of the column, and F the flow rate of the mobile phase.

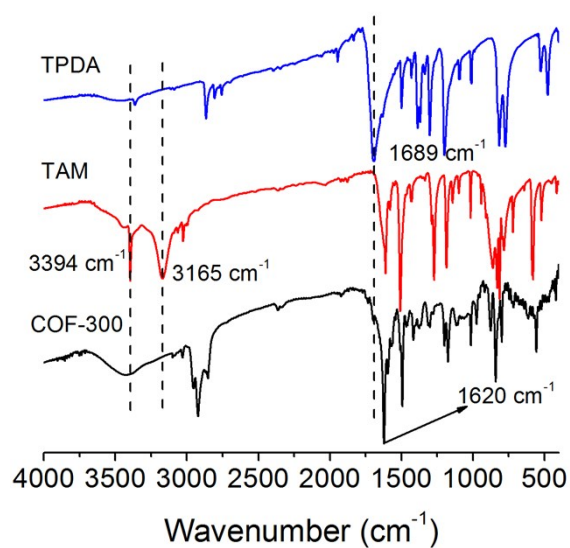


Fig. S1 FTIR spectra of COF-300, TAM and TPDA.

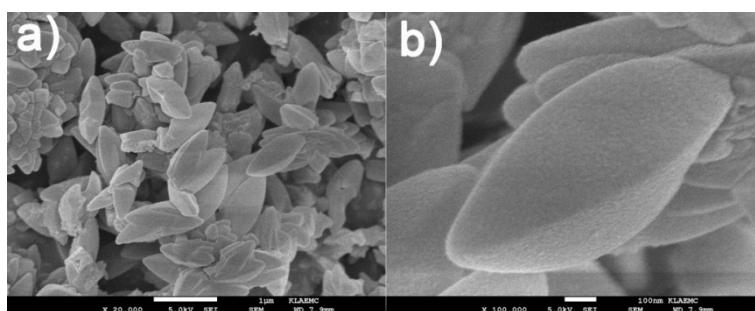


Fig. S2 SEM images of the COF-300 prepared via amorphous-to-crystalline transformation.

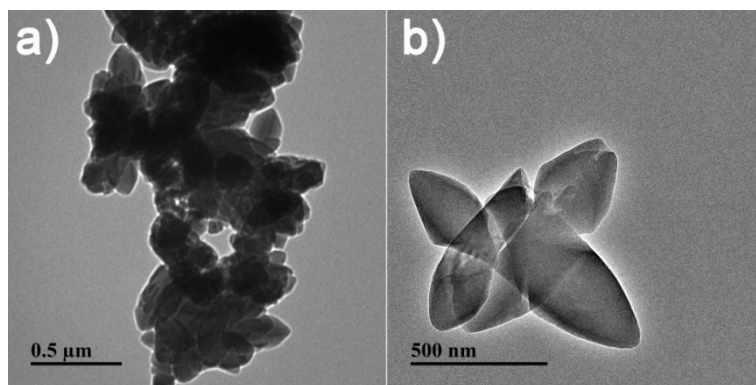


Fig. S3 TEM images of the COF-300 prepared via amorphous-to-crystalline transformation.

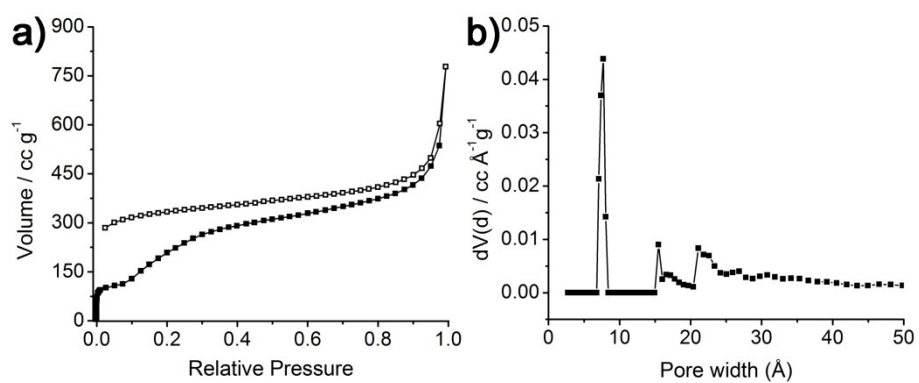


Fig. S4 (a) N₂ adsorption-desorption isotherms and (b) pore size distribution curves of the COF-300 prepared via amorphous-to-crystalline transformation.

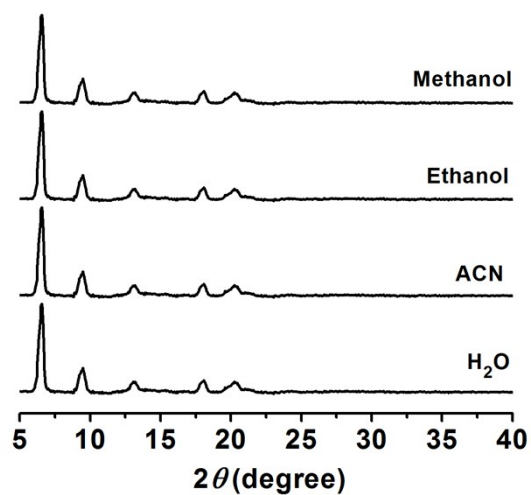


Fig. S5 The stability of COF-300 in various solvents.

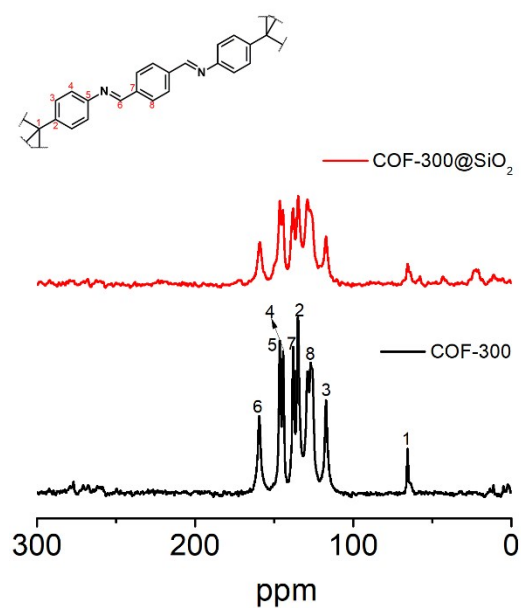


Fig. S6 Solid-state ¹³C CP-MAS spectra of COF-300 and COF-300@SiO₂.

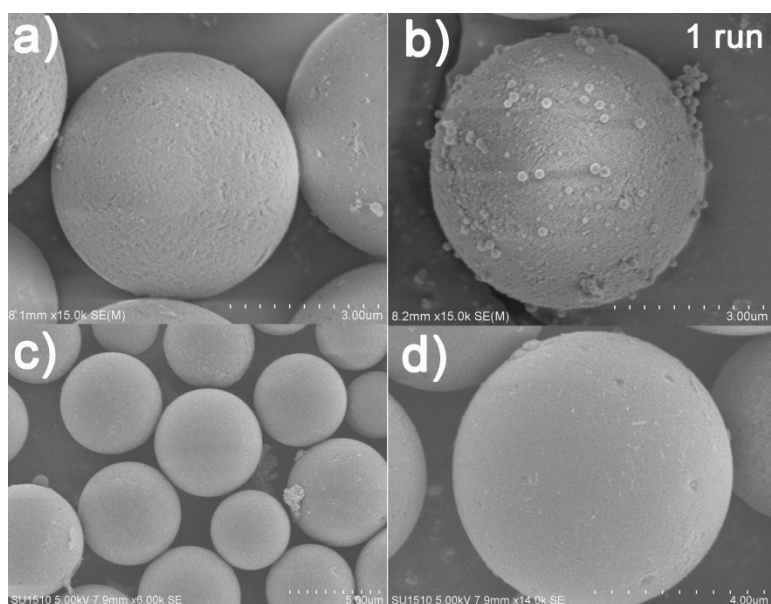


Fig. S7 SEM images: (a) SiO₂-NH₂; (b) COF-300@SiO₂ after 1 run reaction; (c, d) SiO₂-NH₂ treated under the same reaction conditions but no precursors for COF-300.

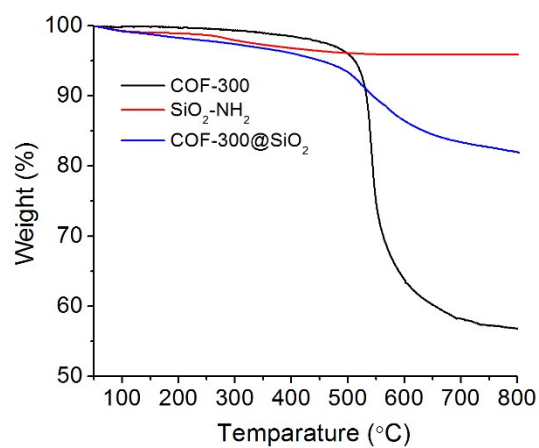


Fig. S8 TGA curves of COF-300, SiO₂-NH₂ and COF-300@SiO₂.

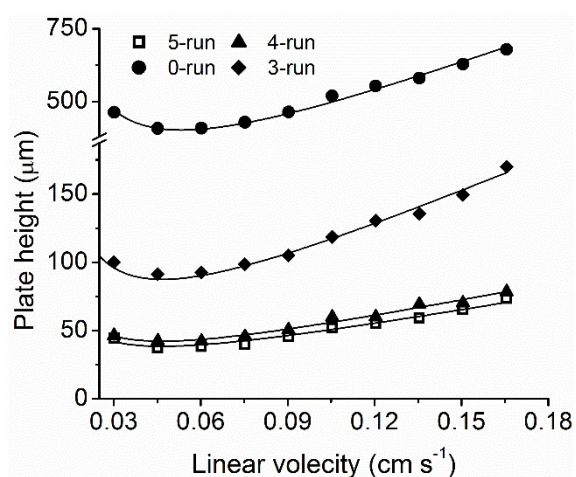


Fig. S9 Van Deemter plots of the H (plate height) as a function of u (velocity) for COF-300@SiO₂ with different runs. Conditions: column, 150 mm × 4.6 mm i.d.. Mobile phase: ACN/H₂O (45/55, v/v), 1.0 mL min⁻¹; UV detection at 210 nm. Analyte: toluene.

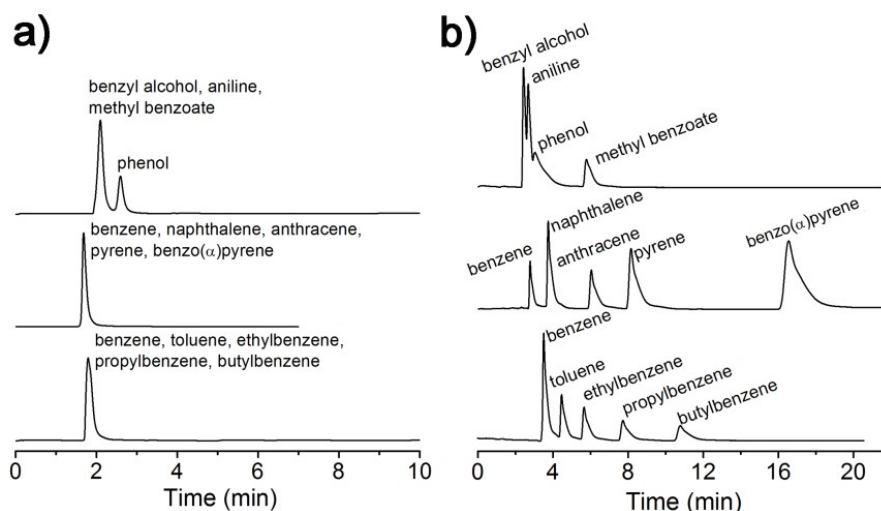


Fig. S10 HPLC chromatograms: (a) SiO₂-NH₂ column; (b) C₁₈ column. Experimental conditions: column, 15 cm × 4.6 mm i.d.; mobile phase, ACN/H₂O (20/80, v/v) and 1.0 mL min⁻¹ for benzene homologue and substituted aromatics in (a), ACN/H₂O (50/50, v/v) and 1.0 mL min⁻¹ for PAHs in (a), ACN/H₂O (70/30, v/v) and 1.0 mL min⁻¹ for benzene homologue in (b), ACN/H₂O (80/20, v/v) and 1.0 mL min⁻¹ for PAHs in (b), ACN/H₂O (30/70, v/v) and 1.0 mL min⁻¹ for substituted aromatics in (b); UV detection at 210 nm.

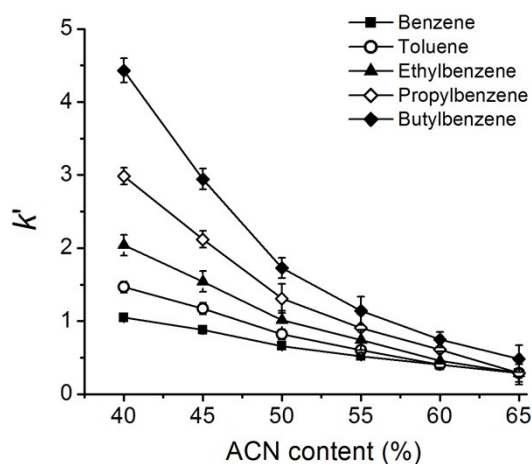


Fig. S11 Effect of ACN content in mobile phases on the retention factors of benzene homologue on COF-300@SiO₂ packed column (15 cm × 4.6 mm i.d.) with ACN/H₂O as the mobile phase at a 1.0 mL min⁻¹ and UV detection at 210 nm.

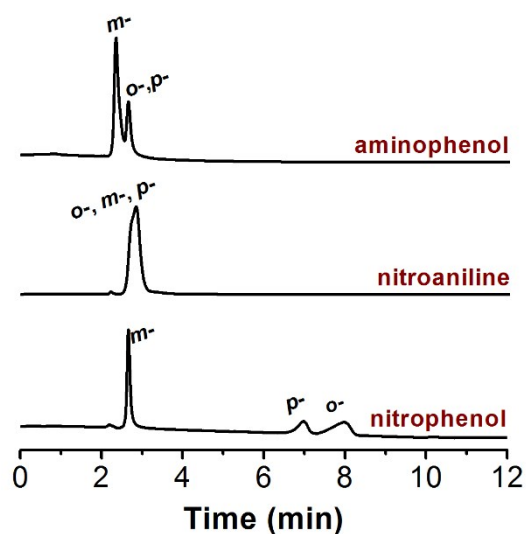


Fig. S12 HPLC chromatograms of isomers on the modified $\text{SiO}_2\text{-NH}_2$ packed column ($15\text{ cm} \times 4.6\text{ mm i.d.}$) prepared in 1 mL dioxane, 1 mL mesitylene and 0.2 mL 6 M aqueous acetic acid without precursors of COF-300 at $120\text{ }^\circ\text{C}$ for 3 d. Experimental conditions: ACN/ H_2O (25/75, v/v), 1.5 mL min^{-1} and UV detection 230 nm for nitrophenol, ACN/ H_2O (20/80, v/v), 1.5 mL min^{-1} and UV detection 254 nm for nitroaniline, ACN/ H_2O (30/70, v/v), 1.0 mL min^{-1} and UV detection 210 nm for aminophenol.

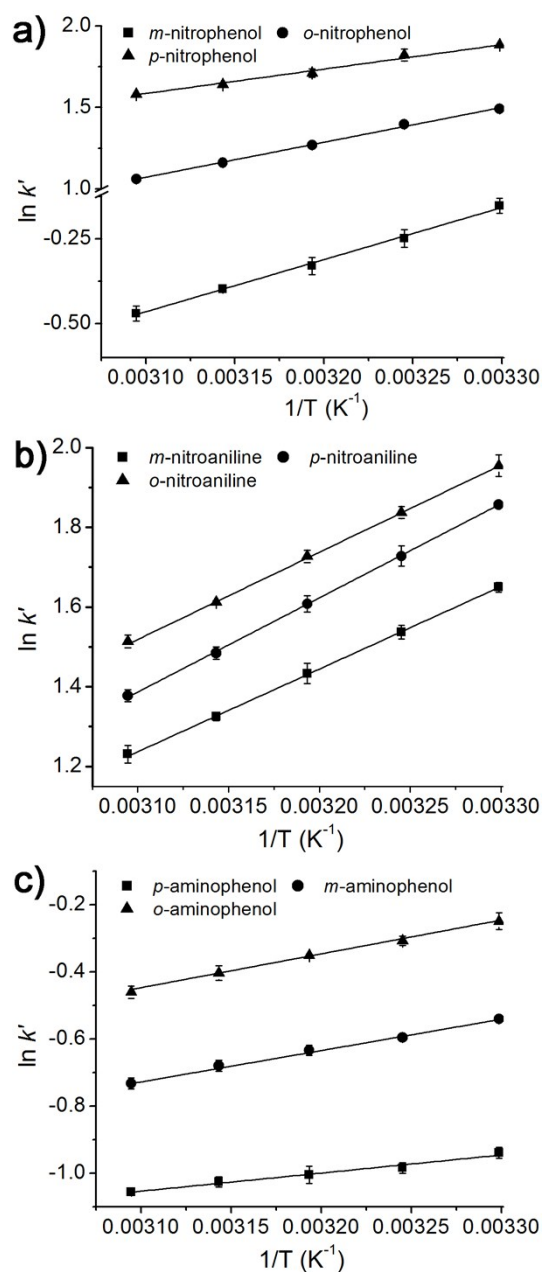



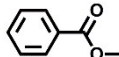

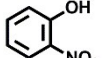
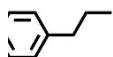
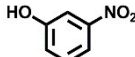
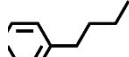


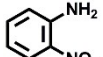
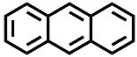
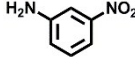
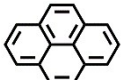
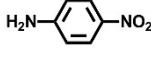
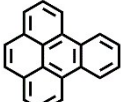
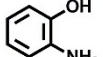
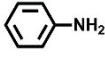
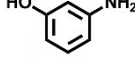
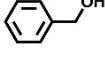



Fig. S13 Van't Hoff plots on the COF-300@SiO₂ packed column: (a) *o*-, *m*-, *p*-nitrophenol; (b) *o*-, *m*-, *p*-nitroaniline; (c) *o*-, *m*-, *p*-aminophenol. Experimental conditions are as shown in Fig. 4.

Table S1 Van Deemter coefficients obtained from the fitting curve of Fig. S10

Column	Van Deemter coefficients		
	A (μm)	B ($\mu\text{m}^2 \text{s}^{-1}$)	C (ms)
0-run	1.29	107151	375.5
3-run	2.09	19903	91.5
4-run	2.57	9232	42.5
5-run	3.23	9465	40.1

Table S2 Structure and Log K_{ow} of analytes

Analytes	Structure	Log K_{ow} ^a	Analytes	Structure	Log K_{ow} ^a
Benzene		2.13	phenol		1.46
Toluene		2.73	methyl benzoate		2.12
ethylbenzene		3.15	<i>o</i> -nitrophenol		1.79
propylbenzene		3.69	<i>m</i> -nitrophenol		2.00
butylbenzene		4.38	<i>p</i> -nitrophenol		1.91
naphthalene		3.30	<i>o</i> -nitroaniline		1.85
anthracene		4.45	<i>m</i> -nitroaniline		1.37
Pyrene		4.88	<i>p</i> -nitroaniline		1.39
benzo(α)pyrene		6.13	<i>o</i> -aminophenol		0.62
Aniline		0.90	<i>m</i> -aminophenol		0.62
benzyl alcohol		1.01	<i>p</i> -aminophenol		0.62

^a The octanol-water partitioning coefficients were from EPI Suite (V. 4.11).

Table S3 Retention factors k' for alkylbenzenes on COF-300@SiO₂ packed columns and C-18 column with ACN/H₂O (60/40, v/v) as the mobile phase at a 1.0 mL min⁻¹ and UV detection at 210 nm

k'	COF-300@SiO ₂	C-18
Benzene	0.40	1.00
Toluene	0.40	1.55
Ethylbenzene	0.41	2.24
Propylbenzene	0.62	3.42
Butylbenzene	0.75	5.17

Table S4 Precision for isomers on the COF-300@SiO₂ packed column

Analytes	RSD (%) (n=10)		
	T	Peak height	Peak area
<i>m</i> -nitrophenol	0.14	0.94	1.03
<i>o</i> -nitrophenol	0.10	0.80	1.05
<i>p</i> -nitrophenol	0.12	0.93	0.98
<i>m</i> -nitroaniline	0.17	1.18	0.93
<i>p</i> -nitroaniline	0.17	1.16	0.97
<i>o</i> -nitroaniline	0.16	1.09	0.92
<i>p</i> -aminophenol	0.13	0.68	0.83
<i>m</i> -aminophenol	0.12	0.82	0.94
<i>o</i> -aminophenol	0.12	0.73	0.85

Table S5 The column efficiency of COF-300@SiO₂ for the isomers under the separation conditions as shown in Fig. 4b-4d

Analytes	N (plates/m)
<i>m</i> -nitrophenol	28767
<i>o</i> -nitrophenol	34327
<i>p</i> -nitrophenol	39593
<i>m</i> -nitroaniline	33200
<i>p</i> -nitroaniline	35987
<i>o</i> -nitroaniline	36800
<i>p</i> -aminophenol	14407
<i>m</i> -aminophenol	17133
<i>o</i> -aminophenol	15280

Table S6 Selectivity of isomers on COF-300@SiO₂ packed column in the temperature range of 30–50 °C

T (°C)	Selectivity (α)					
	Nitrophenol		nitroaniline		aminophenol	
	<i>o-/m-</i>	<i>p-/o-</i>	<i>p-/m-</i>	<i>o-/p-</i>	<i>m-/p-</i>	<i>o-/m-</i>
30	5.18	1.48	1.23	1.12	1.49	1.34
35	5.19	1.53	1.21	1.13	1.48	1.33
40	4.95	1.56	1.20	1.14	1.45	1.33
45	4.76	1.61	1.18	1.15	1.41	1.32
50	4.62	1.68	1.17	1.17	1.38	1.31

Table S7 p*K*_a of the isomers

Analytes	p <i>K</i> _a ^a (25 °C)
<i>m</i> -nitrophenol	8.36
<i>o</i> -nitrophenol	7.23
<i>p</i> -nitrophenol	7.15
<i>m</i> -nitroaniline	2.46
<i>p</i> -nitroaniline	1.02
<i>o</i> -nitroaniline	-0.25
<i>p</i> -aminophenol	5.48
<i>m</i> -aminophenol	4.37
<i>o</i> -aminophenol	4.78

^a CRC Handbook of Chemistry and Physics 99th Edition

Table S8 Thermodynamic parameters and R^2 (correlation coefficient) for isomer analytes calculated from the van't Hoff plots in Fig S13

Analytes	ΔH (KJ mol ⁻¹)	ΔS (J mol ⁻¹ K ⁻¹)	ΔG^a (KJ mol ⁻¹)	R^2
<i>o</i> -nitrophenol	-17.87 ± 0.17	-36.34 ± 0.49	-7.04 ± 0.22	0.9972
<i>m</i> -nitrophenol	-12.77 ± 0.19	-33.32 ± 0.55	-2.84 ± 0.25	0.9986
<i>p</i> -nitrophenol	-12.87 ± 0.14	-16.60 ± 0.36	-7.92 ± 0.18	0.9970
<i>o</i> -nitroaniline	-18.03 ± 0.16	-33.03 ± 0.50	-8.18 ± 0.22	0.9997
<i>m</i> -nitroaniline	-17.12 ± 0.14	-32.61 ± 0.45	-7.40 ± 0.19	0.9997
<i>p</i> -nitroaniline	-19.60 ± 0.17	-39.09 ± 0.55	-7.95 ± 0.24	0.9987
<i>o</i> -aminophenol	-8.45 ± 0.22	-19.82 ± 0.56	-2.54 ± 0.28	0.9959
<i>m</i> -aminophenol	-7.61 ± 0.25	-19.47 ± 0.39	-1.81 ± 0.27	0.9986
<i>p</i> -aminophenol	-4.48 ± 0.17	-12.49 ± 0.36	-0.76 ± 0.20	0.9991

^a Calculated with T = 298.15

Reference

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