Supplementary Information (SI) for Chemical Science.

Supplementary Information

Modulation of Nanoscale Sinuosity in Asymmetric Nano-Channel for High-Resolution Separation of Trace Xylene Isomer Impurities

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Section S1: Chemicals and Instrumentation

Chemicals. All chemicals employed were of analytical grade and used as supplied without further purification. The Aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$), formic acid (HCOOH), xylene isomers, ethyltoluene isomers, chlorotoluene isomers, dichlorobenzene isomers, ethylbenzene, styrene, benzene, n-hexane, 1-hexene, cyclohexane, n-heptane, 1-heptene, cycloheptane, n-octane, 1-octene, cyclooctane, 2,4-dimethylhexane, and 3-methylheptane were purchased from Aladdin Industrial Inc (Shanghai, China). The 3-aminopropyl triethoxysilane (APTES), methanol (MeOH), and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (H_4TCPB) and 1,2,4,5-tetrakis(4-carboxyphenyl)-3,6-dimethyl-benzene (H_4TCPB-Me_2) were purchased from Chemsoon Co., Ltd (Shanghai, China). Ultrapure water (18 MΩ·cm) from an ELGA purification system (Veolia Water Solutions & Technologies, UK) was used in this work.

Instrumentations. Powder X-ray diffraction (PXRD) patterns were obtained from a Rigaku SmartLab 9 Kw (Tokyo, Japan) diffractometer with a CuKα radiation (1.54056 Å). The scanning electron microscope (SEM) images were collected on a JSM-7600 scanning electron microscope (JEOL Ltd.). The ^{1}H nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a AVANCE III HD 400 spectrometer (Bruker). The ^{13}C solid-state NMR spectra were recorded on a AVANCE NEO 400MHZ spectrometer (Bruker). The Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris Diamond 1 TGA analyzer. N_2 adsorption-desorption experiments of Al-TCPB and Al-TCPB-Me_2 were conducted on ASAP 2020 Plus 2.00. Each sample was activated under a high vacuum at 120 °C for 6 h before measurement. All of the separations were performed on Agilent 7890B and PANNA A91 plus gas chromatographic systems with a flame ionization detector (FID). Data acquisition and processing were controlled by ChemStation software. Nitrogen (99.999%, Air Liquide, France) was employed as the carrier gas. The inlet temperature of the GC was set to 250 °C, while the temperature of the FID was set to 300 °C. A 2.5 μL analyte was introduced to a 20 mL gastight sealed glass vial and homogenized at 100 °C before the injection for gas chromatographic separation.

Section S2. Calculation of Sinuosity Ratio

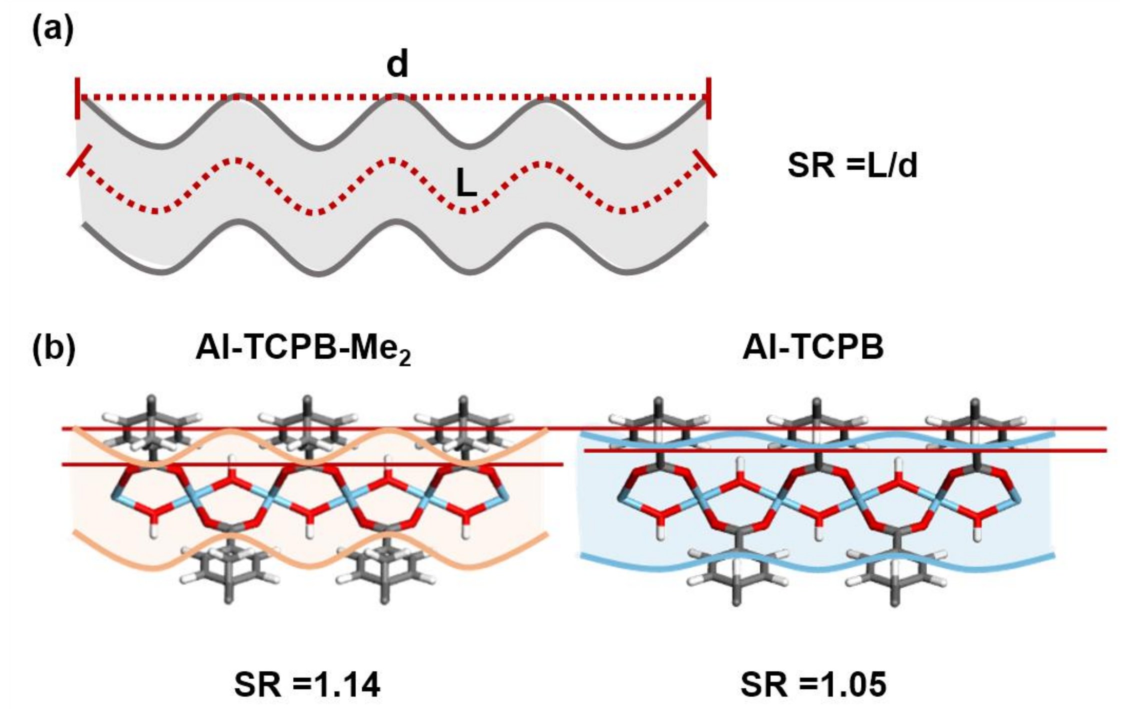


Fig. S1. Schematic illustration of the calculation method to obtain the sinuosity ratio (SR) value.[1]

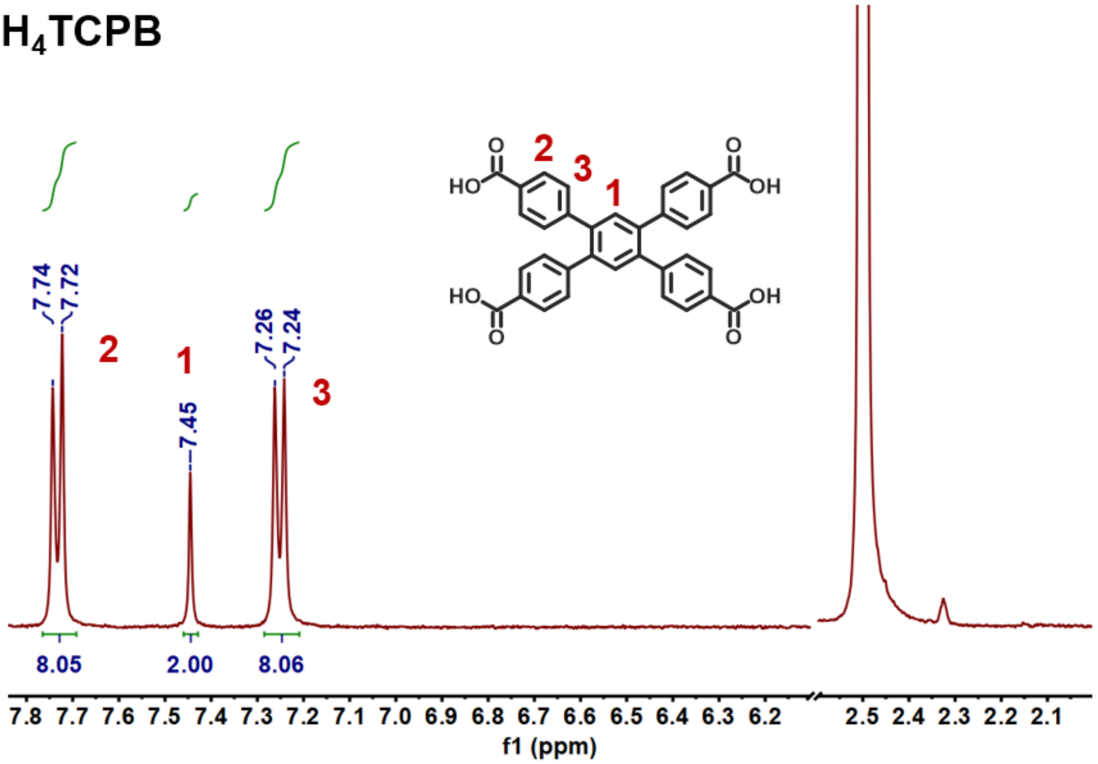
Section S3. Synthesis of MOFs.

Synthesis of Al-TCPB. The samples of Al-TCPB were synthesized according to the reported literature with a small modification.[2] In a 20 mL glass vial it was added $Al(NO_3)_3 \cdot 9H_2O$ (15.0 mg, 0.0400 mmol) and H_4TCPB (8.4 mg, 0.0150 mmol), and the mixture was suspended in 2 mL of DMF while sonicating to obtain a homogeneous solution. Then 300 μL of HCOOH was added. After sonication for 10 minutes, the mixtures were transferred to 5 mL Teflon-lined autoclaves and slowly heated to 150 °C from room temperature in 5 hours, and then kept at 150 °C for 1 day. After being slowly cooled to 30 °C in 10 hours, the product was washed three times with DMF and MeOH, respectively. To remove the residual solvent molecules in the pore channel, they were activated at 60 °C overnight under a vacuum. Finally, the white powder was obtained.

Synthesis of Al-TCPB-Me_2. Al-TCPB-Me_2 was synthesized by the same method as Al-TCPB, except 8.8 mg of H_4TCPB-Me_2 was added instead of 8.4 mg of H_4TCPB.

Section S4. Characterization of MOFs

(a) H_4TCPB



(b) $H_4TCPB\text{-}Me_2$

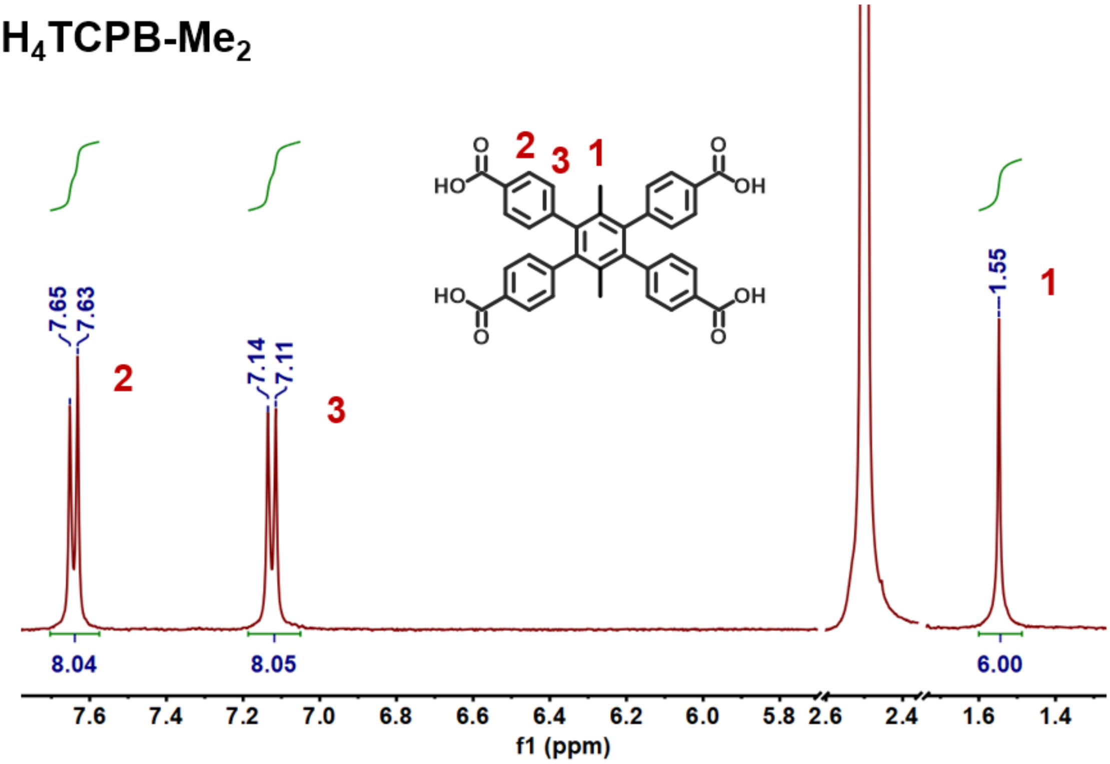
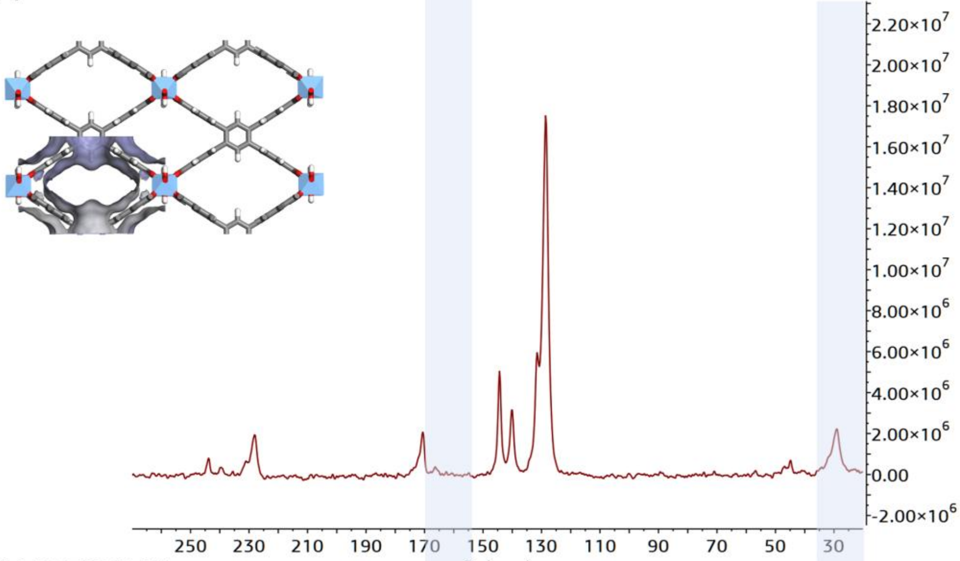


Fig. S2. The ^{1}HNMR of (a) ligand H_4TCPB and (b) ligand $H_4TCPB\text{-}Me_2$.

(a) Al-TCPB



(b) Al-TCPB-Me$_2$

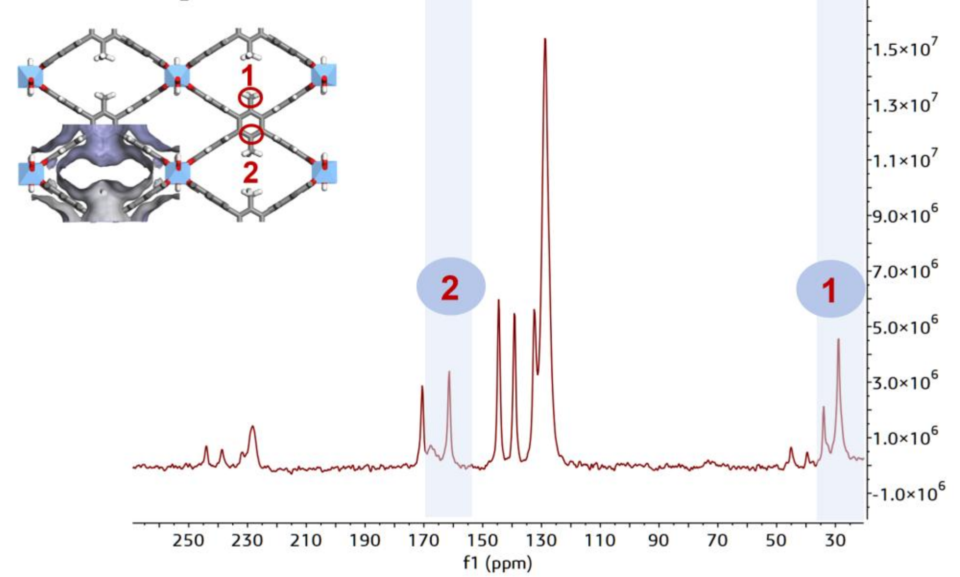


Fig. S3. The solid-state ^{13}C NMR spectra of (a) Al-TCPB and (b) Al-TCPB-Me$_2$.

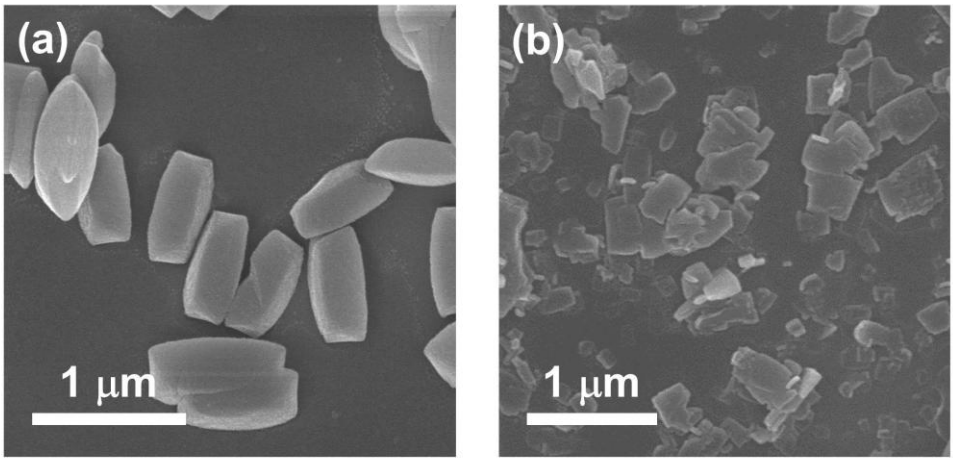


Fig. S4. SEM images of (a) Al-TCPB, (b) Al-TCPB-Me_2.

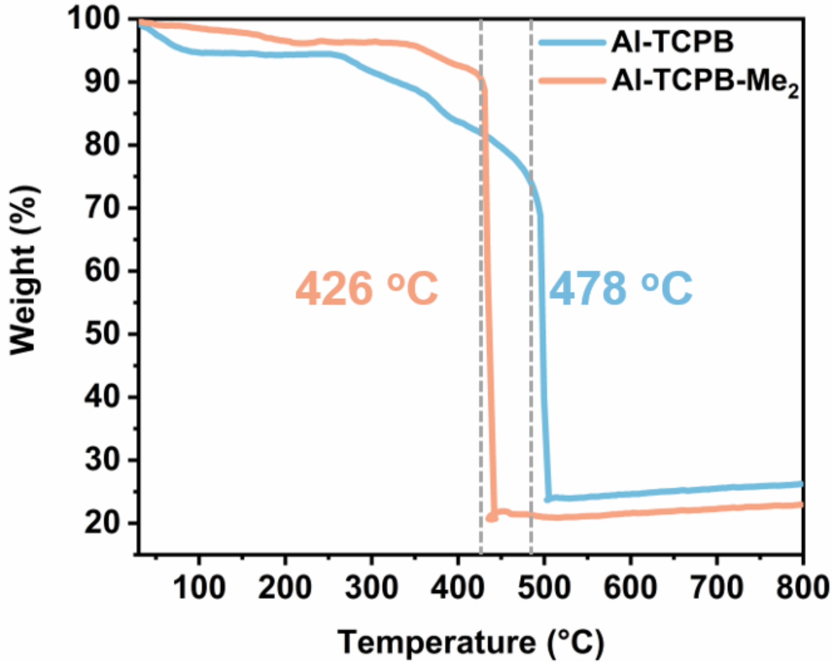


Fig. S5. TGA plots of Al-TCPB and Al-TCPB-Me$_2$. Experiment condition: temperature ramp from room temperature to 800 °C at 10 °C/min under an oxygen atmosphere.

Table S1. Porosity parameters of the MOFs from N_2 adsorption-desorption isotherms.

MOF	BET surface area (m^2/g)	Main pore size (Å)
Al-TCPB	1331	7.3, 9.3, 11.8
Al-TCPB-Me_2	1141	6.8, 9.3, 11.8

Section S5. Preparation of Al-TCPB and Al-TCPB-Me_2 Coated Capillary Columns.

Capillary Pretreatment. A fused silica capillary (15 m long × 0.25 mm i.d., 30 m long × 0.25 mm i.d., Yongnian Optic Fiber Plant, Hebei, China) was pretreated according to the following process before dynamic coating: the capillary was washed sequentially with 1 $mol \cdot L^{-1}$ NaOH, ultrapure water, 0.1 $mol \cdot L^{-1}$ HCl, ultrapure water again until the outflow reached pH=7.0, and finally MeOH. The pretreated capillary was filled with a 1:1 (v/v) mixture of MeOH and APTES and then incubated in a 40 °C water bath overnight with both ends of the capillary sealed. The APTES-modified capillary was rinsed with MeOH to flush out the residuals and dried with a stream of nitrogen at 120 °C for 180 min.

Capillary Coating Method. MOFs were coated on the pretreated capillary columns by the dynamic coating method as follows: 1 mL methanol suspension of each material (0.5 $mg \cdot mL^{-1}$) was first filled into the insulin syringe. The insulin syringe was connected to the capillary column. Then the MOF suspension was pushed through the column by a syringe pump at a velocity of 4.5 mL min^{-1} to leave a wet coating layer on the inner wall of the capillary column. After coating, the capillary column was settled for conditioning under nitrogen to remove the solvent. Further conditioning of the capillary column was carried out using a temperature program: maintain 30 °C for 30 min, then ramp to 250 °C at a rate of 5 °C min^{-1} and keep at 250 °C for 240 min.

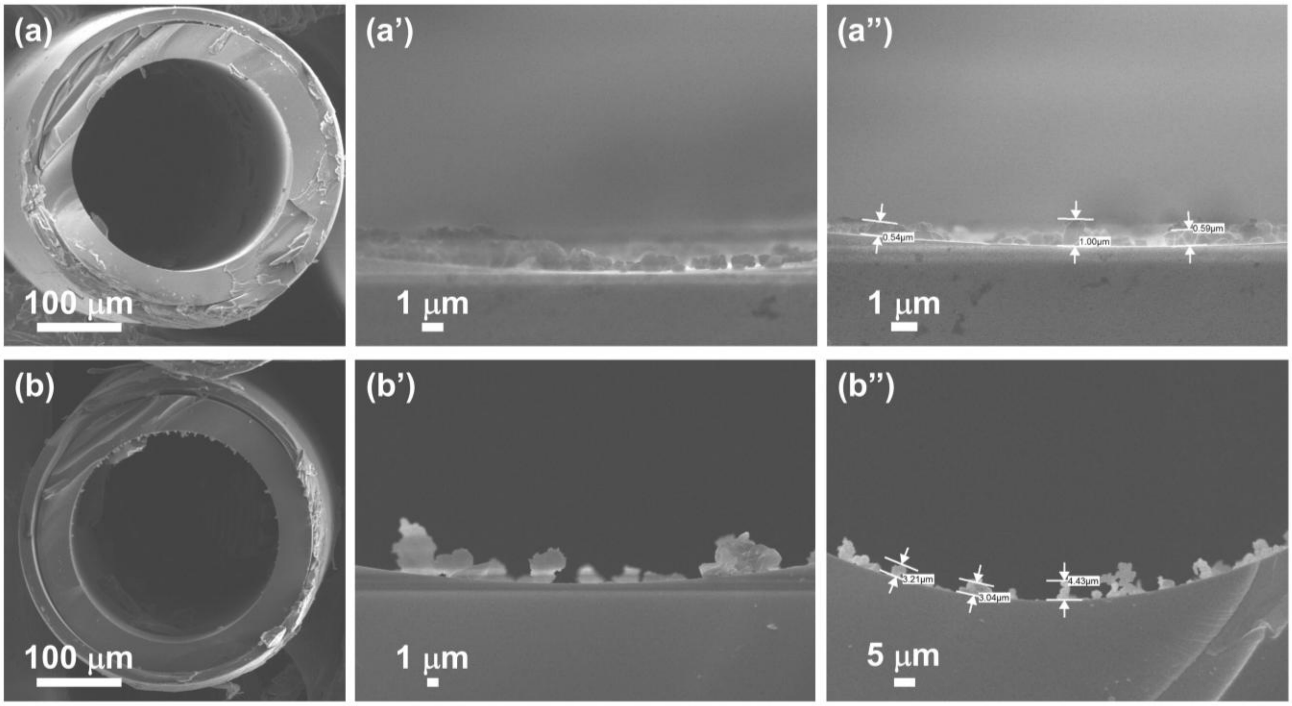


Fig. S6. The SEM images with the cross-section view of (a) Al-TCPB, (b) Al-TCPB-Me$_2$ coated column.

Section S6. Calculation of Kinetic Parameters.

The kinetic diffusion constant (D_s) was calculated from the Golay equation:

$$H = \frac{2D_g}{u} + \frac{1+6k+11k^2}{24(1+k)^2} \times \frac{r^2}{D_g} \times u + \frac{2}{3} \times \frac{k}{(1+k)^2} \times \frac{d_f^2}{D_s} \times u \qquad (2)$$

Here, D_g is the diffusion constant of the analyte in the gas phase, D_s is the diffusion constant of the analyte in the stationary phase, r is the radius of the capillary column (r=125 μm), d_f is the thickness of the stationary phase, u is the linear velocity of the carrier gas, H is the height equivalent of the theoretical plate.

The resistance to mass transfer coefficient (C_s) is calculated according to equation (3):

$$C_s = \frac{2}{3} \times \frac{k}{(1+k)^2} \times \frac{d_f^2}{D_s} \qquad (3)$$

H is calculated according to equation (4):

$$H = \frac{L}{16(\frac{t}{w})^2} \qquad (4)$$

L was the length of the capillary column (L=15 m). w represents the full width of the analyte.

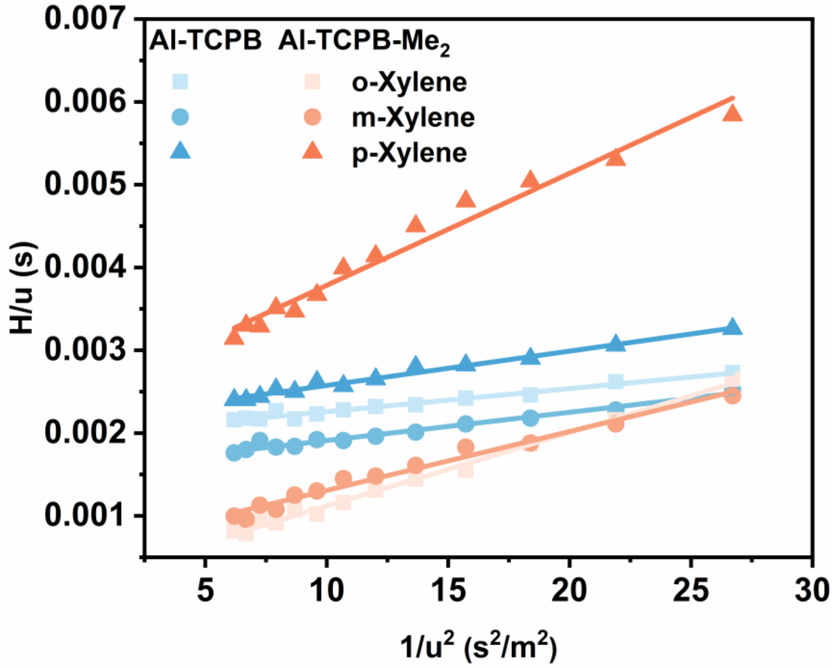


Fig. S7. The Golay plots of Al-TCPB and Al-TCPB-Me$_2$ coated column determined by using o-xylene, m-xylene, and p-xylene as the targets at 503.15 K.

Table S2. The diffusion constants (D_s) and mass transfer coefficients (C-term) of different isomers on Al-TCPB and Al-TCPB-Me$_2$ coated capillary columns.

Column	Analyte	D_s ($m^2 \cdot s^{-1}$)	C-term (s)
Al-TCPB	o-xylene	$9.4 \pm 0.2 \times 10^{-11}$	$1.8 \pm 0.1 \times 10^{-3}$
	m-xylene	$12.1 \pm 0.3 \times 10^{-11}$	$1.4 \pm 0.1 \times 10^{-3}$
	p-xylene	$8.2 \pm 0.1 \times 10^{-11}$	$2.0 \pm 0.1 \times 10^{-3}$
Al-TCPB-Me$_2$	o-xylene	$41.1 \pm 6.3 \times 10^{-11}$	$2.1 \pm 0.3 \times 10^{-4}$
	m-xylene	$15.6 \pm 0.9 \times 10^{-11}$	$6.0 \pm 0.3 \times 10^{-4}$
	p-xylene	$6.5 \pm 0.2 \times 10^{-11}$	$2.6 \pm 0.1 \times 10^{-3}$

Section S7. Single-Component Vapor Adsorption.

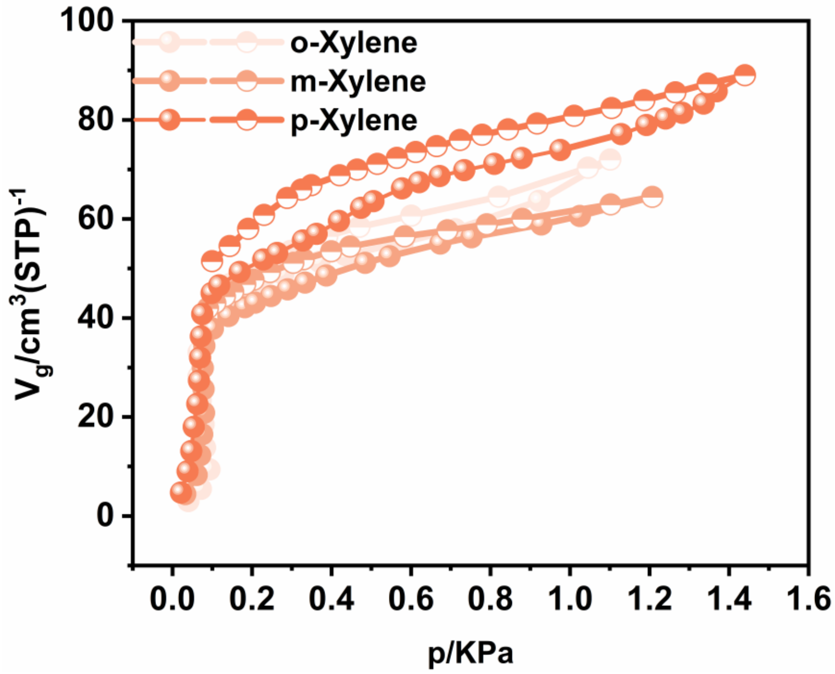


Fig. S8. Adsorption isotherms of o-xylene, m-xylene, and p-xylene on Al-TCPB-Me_2 at 303.15 K.

Section S8. Calculation of Thermodynamic Parameters.

The adsorption enthalpy (ΔH) was calculated from the van't Hoff equation (5):

$$lnk' = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + ln\emptyset \qquad (5)$$

Here, k' is the retention factor, R is the gas constant ($R = 8.314\ J\cdot mol^{-1}\cdot K^{-1}$), T is the absolute temperature, and $\emptyset$ is the phase ratio (the ratio of the volume of the stationary phase (V_s) to that of the mobile phase (V_m)). To obtain $\emptyset$, V_s was calculated from the thickness of MOFs coated on the capillary column, while V_m was calculated from the column internal volume, subtracting V_s.

k' is calculated from equation (6):

$$k' = \frac{t - t_0}{t_0} \qquad (6)$$

t is the retention time of the analyte, and t_0 is the retention time of an unretained compound on the column.

$\emptyset$ is calculated from equation (7):

$$\emptyset = \frac{V_s}{V_m} = \frac{r^2 - (r - d_f)^2}{(r - d_f)^2} \qquad (7)$$

r is the radius of the capillary column, and d_f is the thickness of the stationary phase.

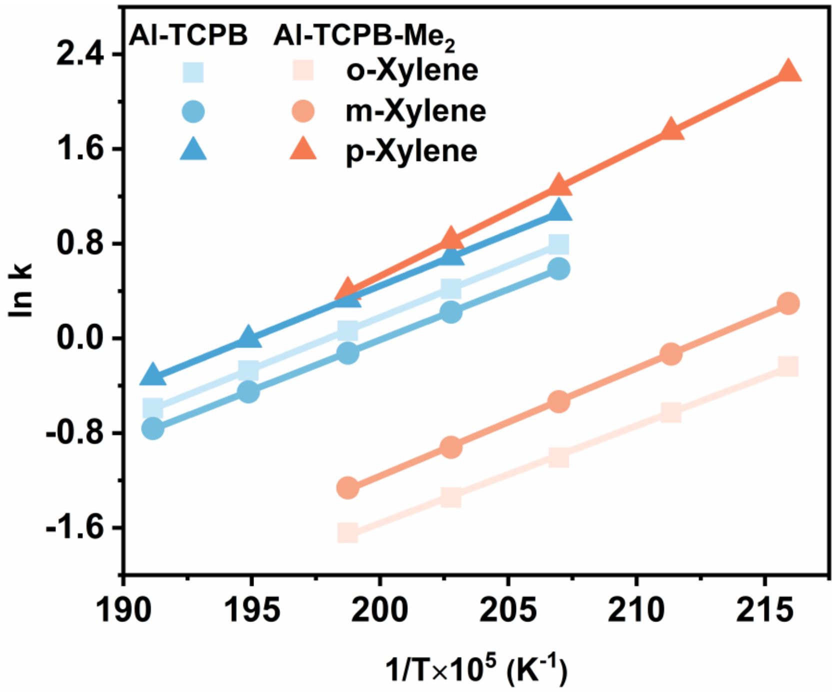


Fig. S9. The van’t Hoff plots of o-xylene, m-xylene, and p-xylene on Al-TCPB and Al-TCPB-Me$_2$ coated capillary columns.

Table S3. Thermodynamic parameters of different analytes on Al-TCPB and Al-TCPB-Me$_2$ coated capillary columns.

Column	Analyte	Δ*H* (kJ·mol^{-1})	Δ*S* (J·mol^{-1}·K^{-1})	Δ*G* (kJ·mol^{-1})
Al-TCPB	o-xylene	-72.7 ± 0.3	-109.6 ± 0.7	-17.5 ± 0.7
	m-xylene	-70.9 ± 0.4	-107.7 ± 0.8	-16.8 ± 0.8
	p-xylene	-73.2 ± 0.4	-108.4 ± 0.8	-18.6 ± 0.8
Al-TCPB-Me$_2$	o-xylene	-68.5 ± 1.2	-115.7 ± 2.5	-12.6 ± 2.4
	m-xylene	-75.7 ± 0.7	-126.8 ± 1.6	-14.4 ± 1.5
	p-xylene	-89.4 ± 0.1	-140.1 ± 0.2	-21.7 ± 0.2

Section S9. Computational Details.

DFT Calculations. All spin-polarized first-principles computations were performed using the Vienna ab initio simulation package.[3] Projector-augmented wave (PAW) method was utilized to describe the ion-electron interaction.[4] The electron exchange-correlation function was treated using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).[5] The cutoff energy was 400 eV, and the convergence criteria for force and energy were set to be 1×10^{-5} eV and 0.1 eV $Å^{-1}$, respectively. The gamma-centered k-point mesh was adopted for structure relaxation. The DFT+D3 dispersion correction scheme with the Becke-Johnson damping function included the van der Waals interaction.[6] The initial model of $[Al_2(OH)_2(TCPB\text{-}Me_2)]$ was built by replacing the four hydrogen atoms of $[Al_2(OH)_2(TCPB)]$ with four methyl groups.[7] Through ab initio molecular dynamics (AIMD) simulation and structural optimization, an optimized model of $[Al_2(OH)_2(TCPB\text{-}Me_2)]$ was obtained and further used in adsorption energy (E_{ads}) calculations. Different binding modes between MOFs and organic molecules were explored for each system, and the most stable configuration with lower energy was reported. The adsorption energy E_{ads} was calculated using the following equation:

$$E_{\mathrm{ads}} = E_{\mathrm{mol+MOFs}} - E_{\mathrm{MOFs}} - E_{\mathrm{mol}} \qquad (1)$$

where E_{mol}, E_{MOFs}, and $E_{\mathrm{mol+MOFs}}$ represent the energy of the organic molecule, MOFs, and MOFs combined with the organic molecule, respectively.

Section S10. Gas Chromatographic Separation.

All of the separations were performed on Agilent 7890B and PANNA A91 plus gas chromatographic system with a flame ionization detector (FID). Data acquisition and processing were controlled by ChemStation software. Nitrogen (99.999%, Air Liquide, France) was employed as the carrier gas. The inlet temperature of the GC was set to 250 °C, while the temperature of the FID was set to 300 °C. A 2 μL analyte was introduced to a 20 mL gastight-sealed glass vial and homogenized at 100 °C before the injection for gas chromatographic separation.

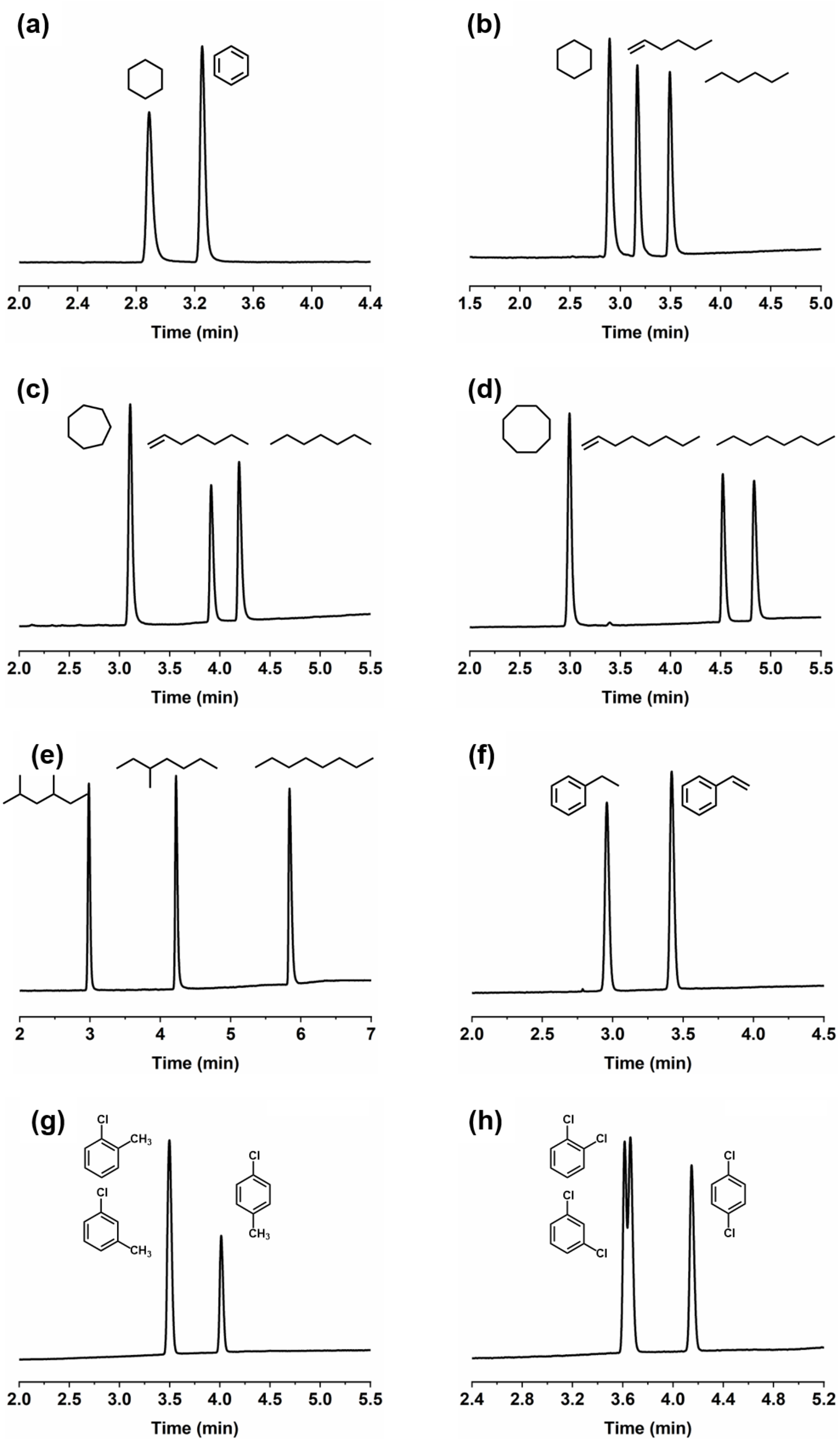


Fig. S10. Gas chromatograms on the Al-TCPB coated capillary column (15 m long × 0.25 mm i.d.) at a N_2 flow rate of 0.5 $mL\cdot min^{-1}$ for the separation of (a) benzene/cyclohexane, (b) n-hexane/1-hexene/cyclohexane, (c) n-heptane/1-heptene/cycloheptane, (d) n-octane/1-octene/cyclooctane, (e) n-octane/3-methylheptane/2,4-dimethylhexane, (f) ethylbenzene/styrene, (g) chlorotoluene isomers, and (h) dichlorobenzene isomers. The concentration of coating material was controlled as 1 mg/mL (1mL).

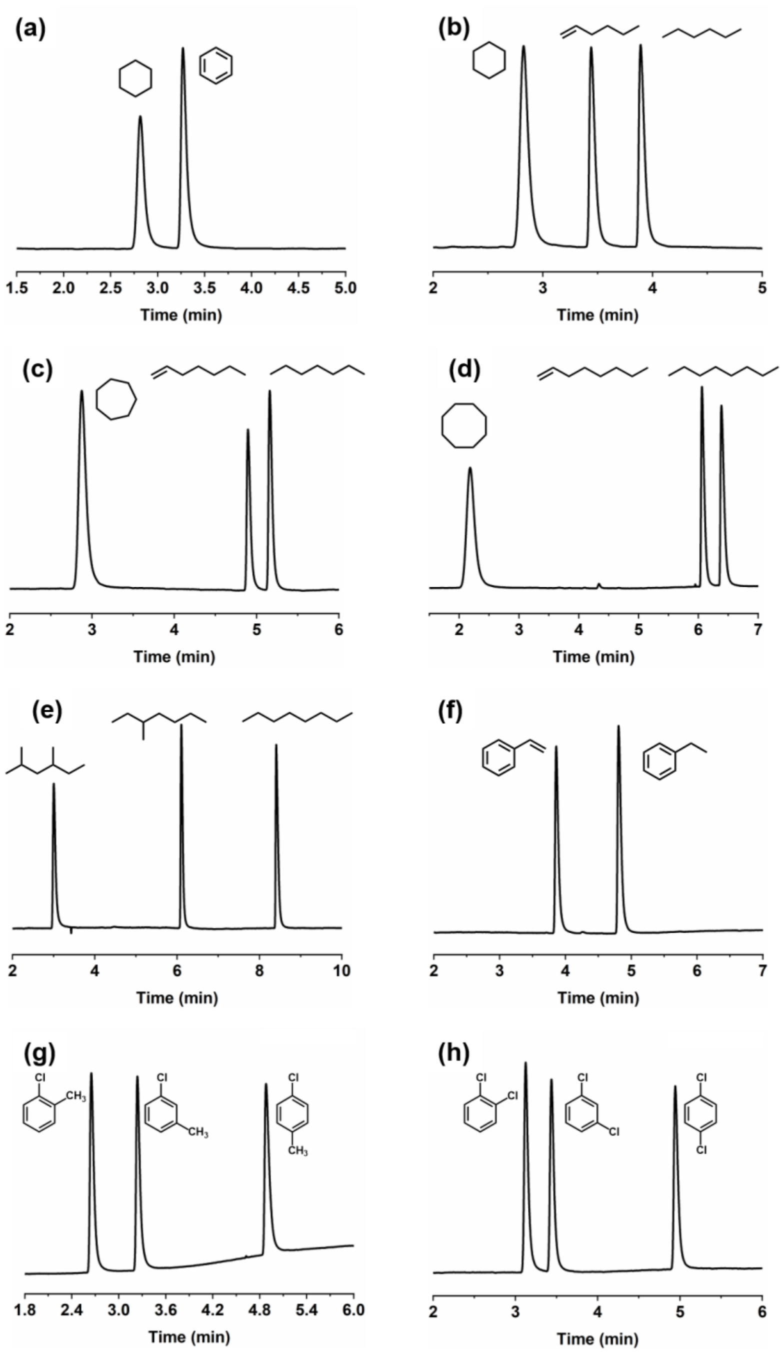


Fig. S11. Gas chromatograms on the Al-TCPB-Me$_2$ coated capillary column (15 m long × 0.25 mm i.d.) at a N_2 flow rate of 0.5 mL·min^{-1} for the separation of (a) benzene/cyclohexane, (b) n-hexane/1-hexene/cyclohexane, (c) n-heptane/1-heptene/cycloheptane, (d) n-octane/1-octene/cyclooctane, (e) n-octane/3-methylheptane/2,4-dimethylhexane, (f) ethylbenzene/styrene, (g) chlorotoluene isomers, and (h) dichlorobenzene isomers. The concentration of coating material was controlled as 1 mg/mL (1mL).

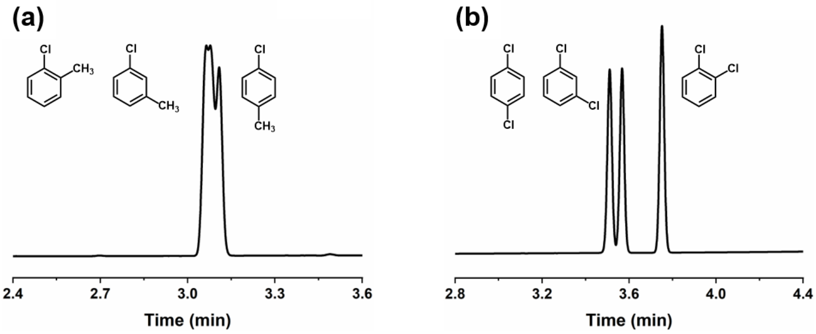


Fig. S12. Gas chromatograms on the Agilent HP-5 gas chromatographic columns (30 m long × 0.25 mm i.d.) at a N_2 flow rate of 0.5 mL·min^{-1} for the separation of (a) chlorotoluene isomers, and (b) dichlorobenzene isomers.

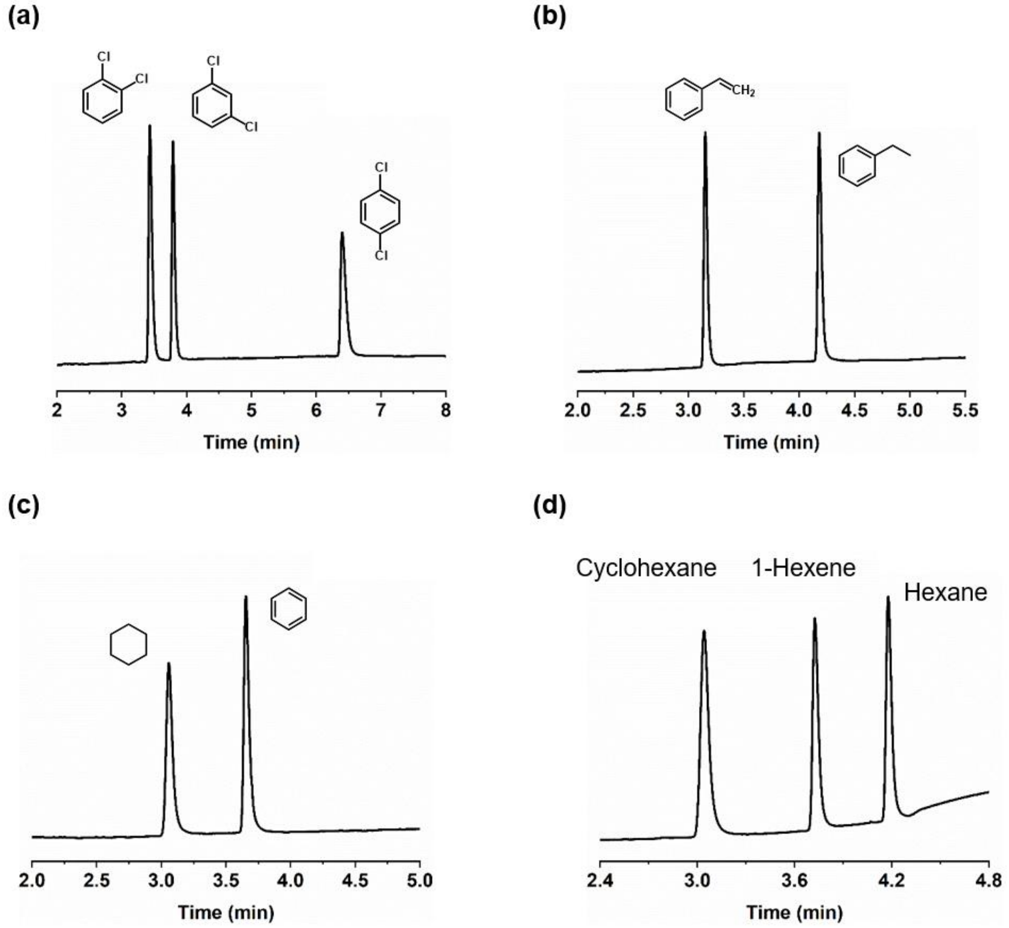


Fig. S13. Gas chromatograms on the Al-TCPB-Me$_2$ coated capillary column (15 m long × 0.25 mm i.d.) at a N$_2$ flow rate of 0.5 mL·min^{-1} for the separation of (a) dichlorobenzene isomers, (b) ethylbenzene/styrene, (c) benzene/cyclohexane, and (d) n-hexane/1-hexene/cyclohexane. The concentration of coating material was controlled as 2 mg/mL (1mL).

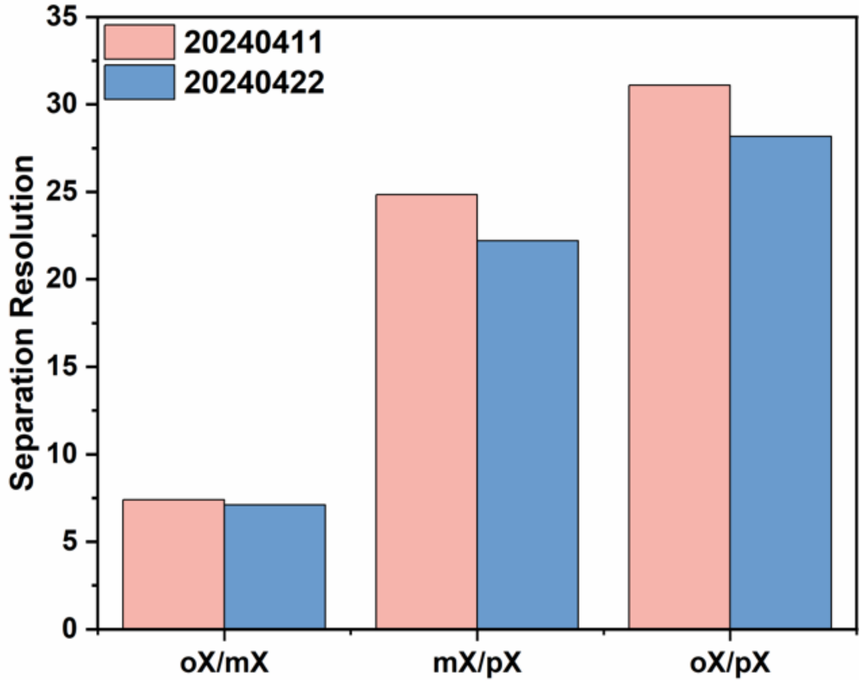


Fig. S14. Separation resolution of xylene isomers on the Al-TCPB-Me$_2$ coated capillary column (15 m long × 0.25 mm i.d.) at a N_2 flow rate of 0.5 mL·min^{-1}. The two columns were conducted on April 11th, 2024 and April 22nd, 2024, respectively. The results confirmed that the coating afforded reliable reproducibility and stable separation performance across batches.

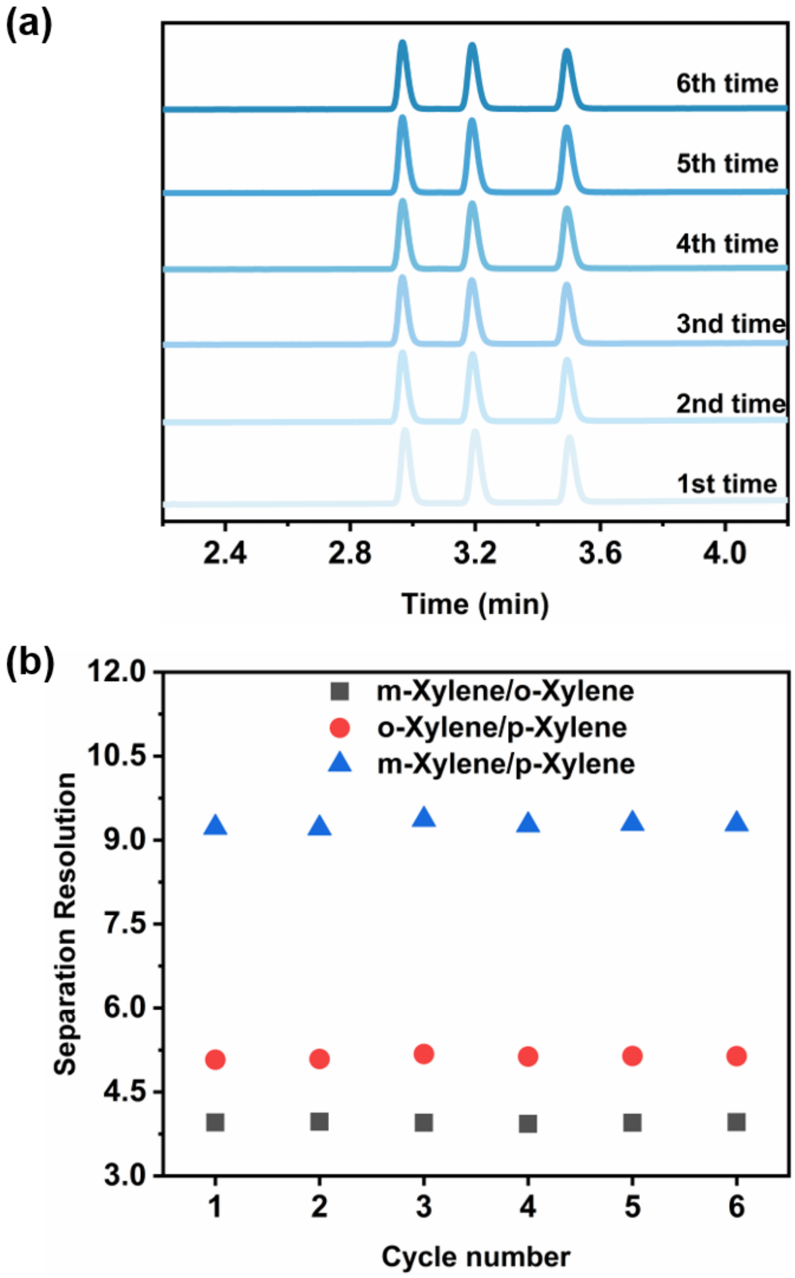


Fig. S15. (a) The repeatability and (b) separation resolution of Al-TCPB coated capillary column for the separation of xylene isomers six times continuously.

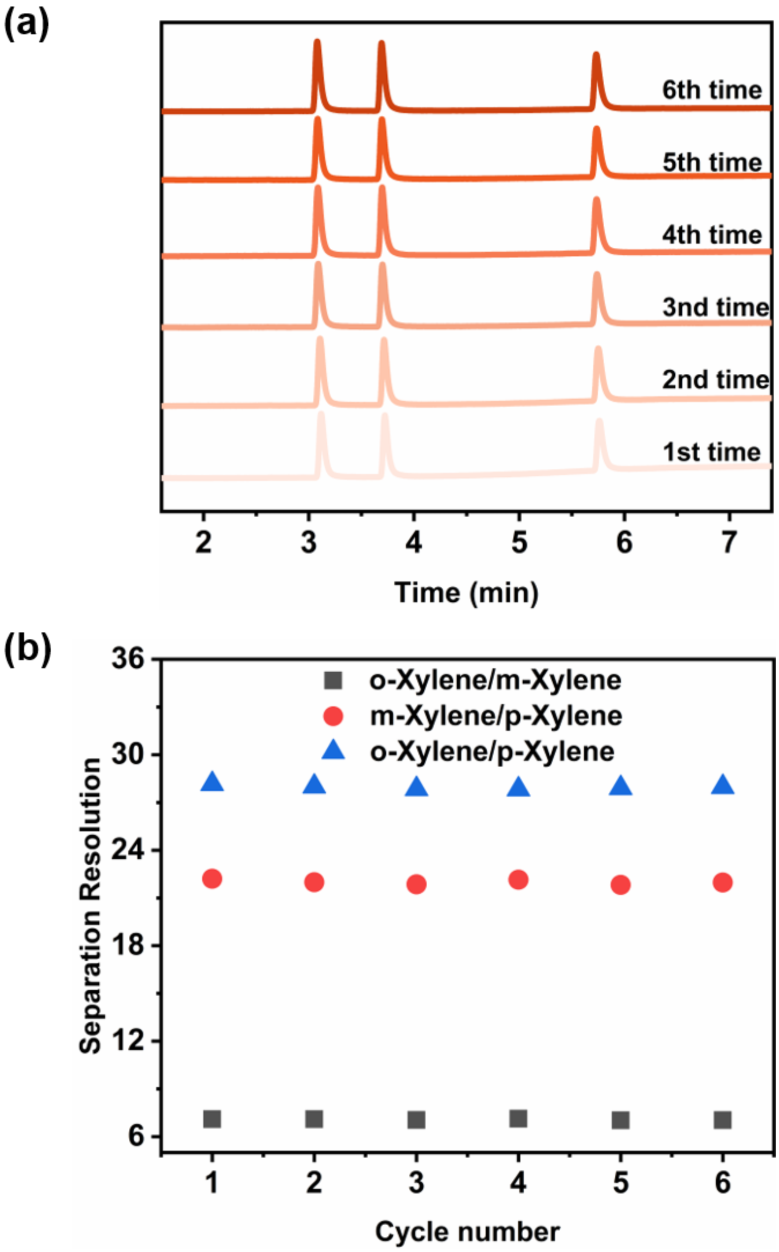


Fig. S16. (a) The repeatability and (b) separation resolution of Al-TCPB-Me$_2$ coated capillary column for the separation of xylene isomers six times continuously.

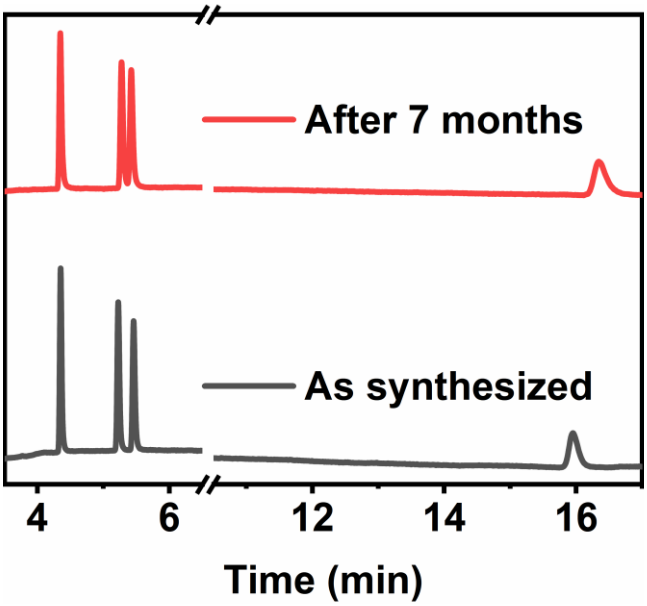


Fig. S17. Gas chromatograms on the Al-TCPB-Me_2 coated capillary column (30 m long × 0.25 mm i.d.) at a N_2 flow rate of 0.5 mL·min^{-1} for the separation of xylene isomers before and after the 7-month storage.

Table S4. The separation resolution (R_s) for different analytes on Al-TCPB and Al-TCPB-Me_2 coated capillary columns.

Analytes	Al-TCPB	Al-TCPB-Me_2
o-xylene/m-xylene	3.83	7.4
m-xylene/p-xylene	9.06	24.85
o-xylene/p-xylene	5.30	31.09
o-ethyltoluene/m-ethyltoluene	3.48	11.91
m-ethyltoluene/p-ethyltoluene	12.63	23.18
o-ethyltoluene/p-ethyltoluene	15.95	32.52
o-chlorotoluene/m-chlorotoluene	0	6.71
m-chlorotoluene/p-chlorotoluene	7.22	17.24
o-chlorotoluene/p-chlorotoluene	7.22	23.05
o-dichlorobenzene/m-dichlorobenzene	0.76	3.67
m-dichlorobenzene/p-dichlorobenzene	7.61	17.12
o-dichlorobenzene/p-dichlorobenzene	9.17	20.80
ethylbenzene/styrene	8.33	10.54
benzene/cyclohexane	5.37	3.76
n-hexane/1-hexene	4.75	4.89
1-hexene/cyclohexane	3.79	5.31
n-hexane/cyclohexane	8.13	9.17
n-heptane/1-heptene	4.33	3.35
1-heptene/cycloheptane	13.21	16.72
n-heptane/cycloheptane	16.46	18.88
n-octane/1-octene	4.65	3.19
1-octene/cyclooctane	23.37	22.63
n-octane/cyclooctane	26.85	23.41
n-octane/3-methylheptane	24.15	24.60
n-octane/2,4-dimethylhexane	43.34	51.19
3-methylheptane/2,4-dimethylhexane	20.91	31.84

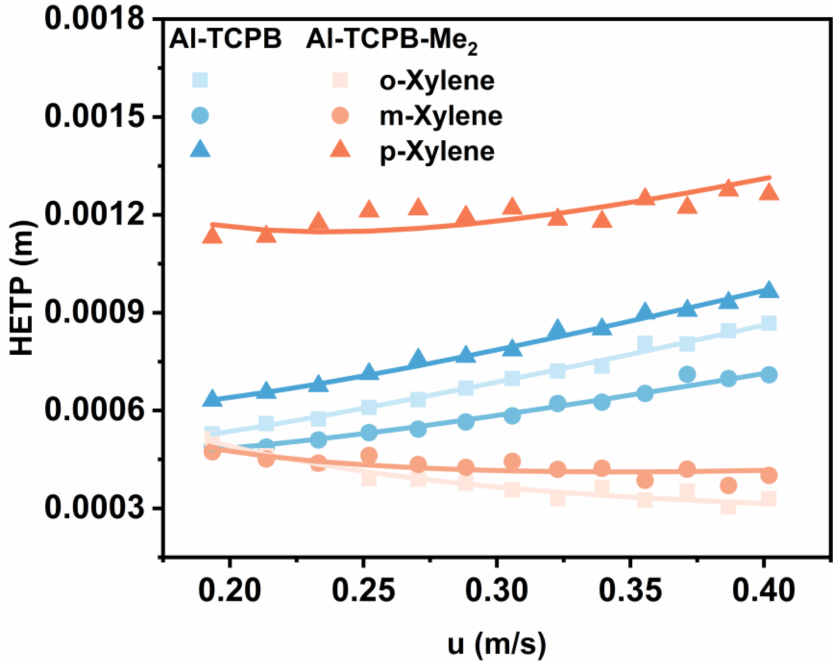


Fig. S18. The Golay plots of Al-TCPB and Al-TCPB-Me$_2$ coated column determined by using o-xylene, m-xylene, and p-xylene as the targets at 503.15 K.

Table S5. Column efficiency of Al-TCPB and Al-TCPB-Me_2 coated capillary columns.

Column	Analyte	Temperature (°C)	HETP (mm)	Column efficiency (plates/m)	Velocity (cm/s)
Al-TCPB	o-xylene	230	0.53	1895	19.35
	m-xylene	230	0.49	2051	21.37
	p-xylene	230	0.63	1586	19.35
Al-TCPB-Me_2	o-xylene	230	0.30	3289	38.68
	m-xylene	230	0.37	2703	38.68
	p-xylene	230	1.13	882	21.37

Section S11. Trace Impurity Analysis.

The analysis was performed on p-xylene (pX) with ≥99.8% labeled purity to determine impurity species and mass fractions using Al-TCPB-Me_2 coated capillary column (30 m long × 0.25 mm i.d.). n-Heptane was employed as the solvent due to the column's demonstrated baseline separation capability for heptane and all four xylene isomers without peak overlap. Chromatographic conditions included a 250:1 split ratio with 0.4 μL liquid sample injection following three syringe rinses. Initial characterization of pure pX identified o-xylene (oX), m-xylene (mX), and ethylbenzene (EB) as major impurities through retention time matching with authentic standards. The quantitative analysis involved: (1) preparation of standard solutions containing oX, mX, pX and EB (1:1:1:1 molar ratio) in n-heptane at multiple concentration levels, (2) triplicate minimum injections at each concentration, (3) establishment of peak area-concentration calibration curves ($R^2 \geq 0.99$), (4) the peak areas of all components in both pure p-xylene and its diluted samples were recorded and ensure they fall within the linear range of the calibration curve, and (5) quantitative determination of all component mass fractions was performed using the established calibration curve.

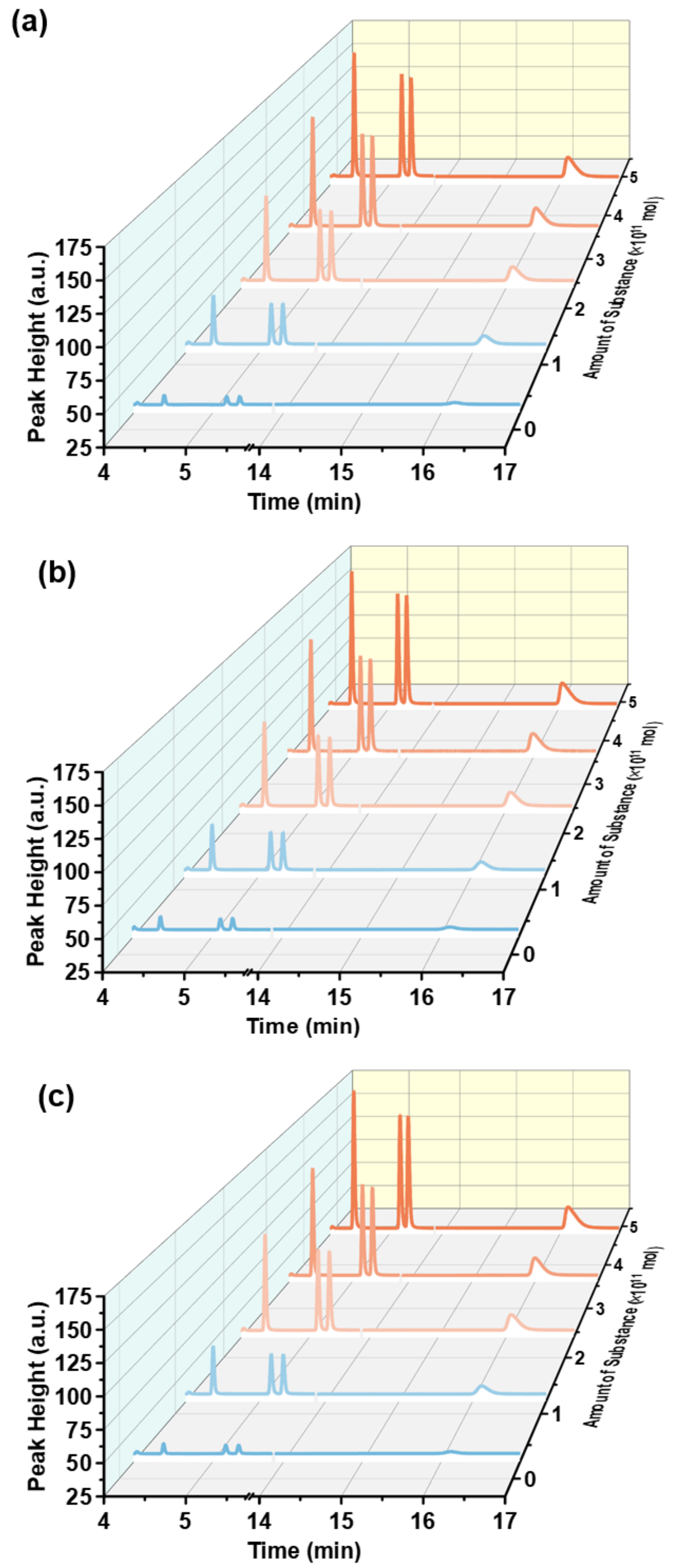


Fig. S19. The gas chromatograms obtained from triplicate injections of xylene isomer mixtures at varying concentrations on the Al-TCPB-Me$_2$ coated capillary column (30 m long × 0.25 mm i.d.).

Table S6. Relative Mass Correction Factors for oX, mX, pX, and EB on the FID.

Component (*i*)	m-xylene	o-xylene	ethylbenzene	p-xylene
f_i	1.045	1.128	1.103	1.000

Reference chemical: p-xylene.

Table S7. Limit of detection of oX, mX, pX, and EB on the 30-m Al-TCPB-Me_2 column.

Component	m-xylene	o-xylene	ethylbenzene	p-xylene
LOD	3.11 ± 0.22 pg	2.59 ± 0.22 pg	3.08 ± 0.13 pg	15.39 ± 1.99 pg

Table S8. The mass percentage distribution of the four xylene isomers in the pX sample, with a certified purity of ≥ 99.8%.

Component	m-xylene	o-xylene	ethylbenzene
mass percentage	0.08±0.001%	0.02±0.003%	0.02±0.002%

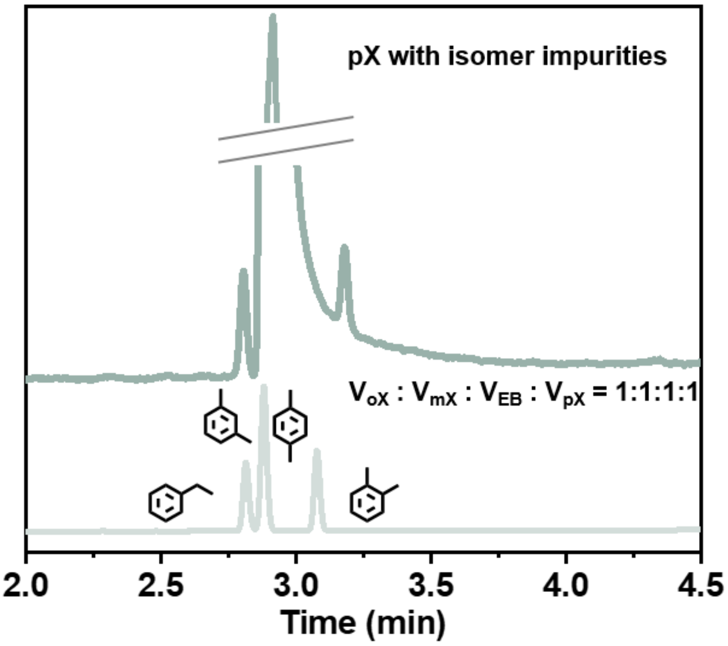


Fig. S20. Separation chromatograms of pX with isomer impurities, four xylene isomers in equal volume proportions on the HP-5 column.

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