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# Electronic supplementary information

## Building-block exchange synthesis of amino-based three-dimensional covalent organic framework for gas chromatographic separation of isomers

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## Methods

### Chemicals and Materials

All chemicals and reagents were at least of analytical grade. 4-[tris(4-formylphenyl)methyl]benzaldehyde (TFPM) and was obtained from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. (Jilin, China). *p*-phenylenediamine (Pa), N,N-dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO) and 3-aminopropyltriethoxysilane (APTES) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). 3,3'-Diaminobenzidine (BD-$NH_2$) was bought from J&K scientific Co. Ltd. (Beijing, China). N,N-Dimethylformamide (DMF), tetrahydrofuran (THF), dichloromethane (DCM) and acetic acid were gotten from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water was purchased from Wahaha Foods Co., Ltd. (Shanghai, China). Fused silica capillary (10 m long × 0.53 mm i.d.) was obtained from Yongnian Optic Fiber Plant (Hebei, China).

### Instrumentation and Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a D2 PHASER X-ray diffractometer (Bruker, German) using Cu $K_\alpha$ radiation ($\lambda$ = 1.5418 Å) with a scanning speed of 8° $min^{-1}$ and a step size of 0.05° in $2\vartheta$. $^{13}C$ Solid-state nuclear magnetic resonance (SNMR) experiments were performed on Infinityplus 400 (VARIAN, USA). Scanning electron microscopy (SEM) images were recorded on an S-3500N (Hitachi, Japan) scanning electron microscope. Fourier transform infrared (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. Thermogravimetric analysis (TGA) experiments were performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) under air from room temperature to 700 °C at a ramp rate of 5 °C $min^{-1}$. Gas chromatographic measurements were performed on a GC-2030 system (Shimadzu, Japan) with flame ionization detector (FID) and Nitrogen (99.999%) as the carrier gas.

**Preparation of TFPM-PA**

A 35 mL Schlenk tube (OD 26 × L 125 mm) was filled with the pre-polymerization solution containing TFPM (21.6 mg, 0.05 mmol), PA (16.3 mg, 0.10 mmol), aqueous acetic acid (0.2 mL, 6 M), and DMAC/THF 1/2 (v/v, 2.0 mL). The tube was sonicated for 15 min and then frozen by liquid nitrogen. After degassing with three freeze–pump–thaw cycles, the tube was sealed and left undisturbed at 90 °C for 1 day. The obtained precipitate was centrifuged, rinsed with DMF and THF, extracted with DCM, dried under vacuum at 60 °C for 8 h to obtain TFPM-PA in ca.70.3% isolated yield.

**Preparation of JNU-5**

As to the preparation of JNU-5 via BBE, the beginning process was the same as the preparation of TFPM-PA, but the obtained precipitate was not collected after the reaction at 90 °C for 1 d. The BD-$NH_2$ (214.3 mg, 1.0 mmol, 10 eqv.), aqueous acetic acid (0.2 mL, 6 M), and dimethyl sulfoxide (DMSO) (2.0 mL) were further added and stired with glass rod. The tube was continuously degassed with three freeze–pump–thaw cycles, sealed and left undisturbed with at 90 °C for 3 days. The finally obtained dark red precipitate was centrifuged to remove the solvent. After rinsing with DMF and THF, the crude product was extracted with DCM followed by drying under

vacuum at 60 °C for 8 h to obtain JNU-5 in ca.86.3% isolated yield.

**Preparation of TFPM-PA covalently bonded capillary column**

A fused silica capillary (10 m × 0.53 mm) was treated sequentially with 1 M NaOH for 2 h, 0.1 M HCl for 2 h, water until the outflow reached pH 7.0, and methanol for 30 min. Then, the capillary was filled with a methanolic solution of APTES (50%, v/v), incubated at 40 °C overnight, rinsed with methanol, dried with a stream of nitrogen at 120 °C for 2 h, further filled with an ethanolic solution of TFPM (21.6 mg in 3 mL ethanol) and incubated at 60 °C for 2 h. Finally, the capillary column was rinsed with methanol to flush out the residuals and dried with a stream of nitrogen at 120 °C for 2 h to obtain an TFPM-modified capillary. The above-mentioned pre-polymerization solution of TFPM-PA was quickly injected into the TFPM-modified capillary. After incubation at 90 °C for 1 day, the capillary column was rinsed with DMF and ethanol, and conditioned with a temperature program: 80 °C for 30 °C min, ramp from 80 °C to 200 °C at a rate of 2 °C $min^{-1}$, and 200 °C for 5 h to obtain TFPM-PA bonded capillary column.

**Preparation of JNU-5 covalently bonded capillary column**

As for JNU-5 bonded capillary column, the beginning process was the same as the preparation of TFPM-PA, but the capillary was continuously filled with dimethyl sulfoxide (DMSO) solution of BD-$NH_2$ after the reaction of pre-polymerization solution of TFPM-PA at 90 °C for 1 day, and further reacted at 90 °C for another 3 days. The capillary column was rinsed with DMF and ethanol, and conditioned with a temperature program: 80 °C for 30 °C min, ramp from 80 °C to 200 °C at a rate of 2

°C $min^{-1}$, and 200 °C for 5 h to obtain JNU-5 bonded capillary column.

**Calculation of thermodynamic parameters**

The enthalpy change ($\Delta H$) and entropy change ($\Delta S$) for the transfer of the analyte between the mobile phase and the stationary phase were calculated according to the van't Hoff equation:

$$\ln k' = -(\Delta H / R)\, 1/T + (\Delta S / R + \ln \Phi) \qquad (1)$$

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

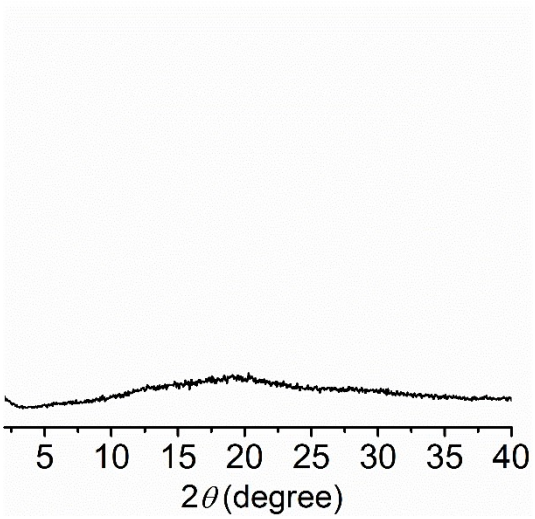


**Fig. S1** PXRD pattern of the product via direct condensation of TFPM and BD-$NH_2$.

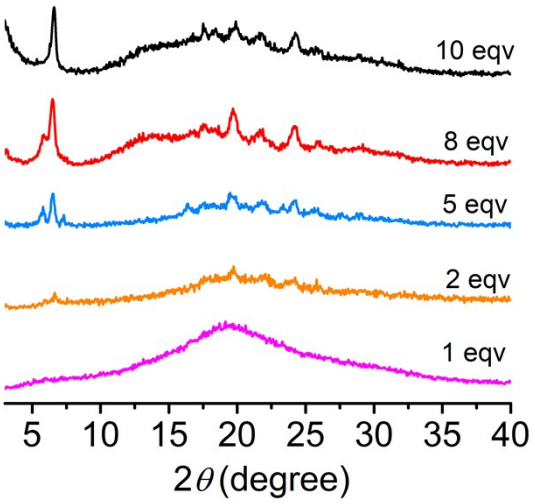


**Fig. S2** Effect of the content of BD-$NH_2$ on the PXRD pattern of BBE product.

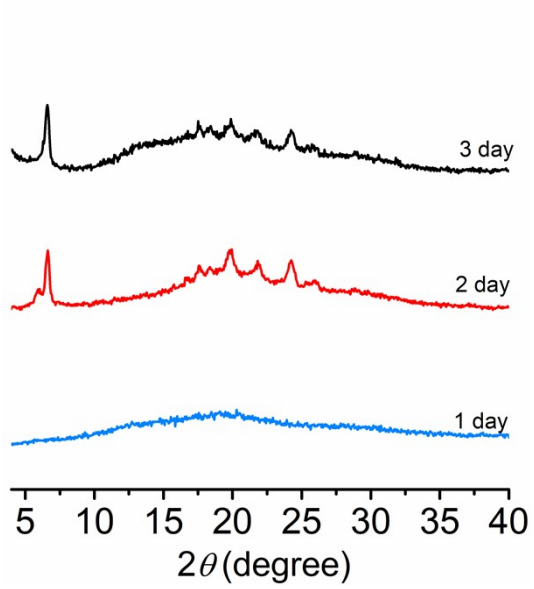


**Fig. S3** Effect of reaction time on the PXRD pattern of BBE product.

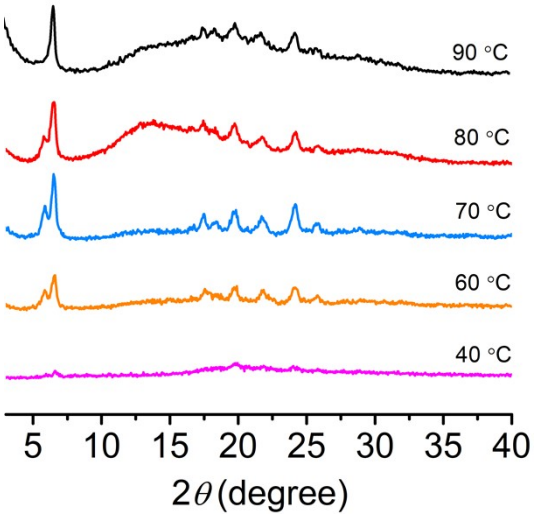


**Fig. S4** Effect of reaction temperature on the PXRD pattern of BBE product.

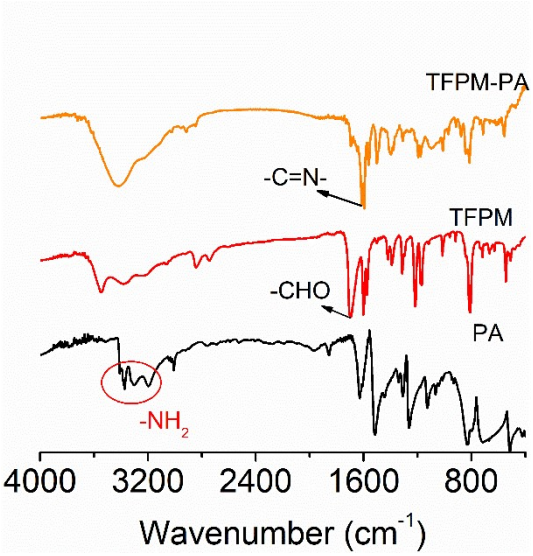


**Fig. S5** FTIR spectra of TFPM, PA and TFPM-PA.

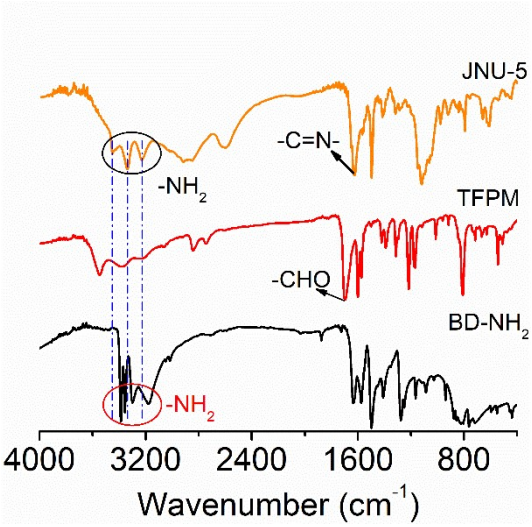


**Fig. S6** FTIR spectra of TFPM, BD-$NH_2$ and JNU-5.

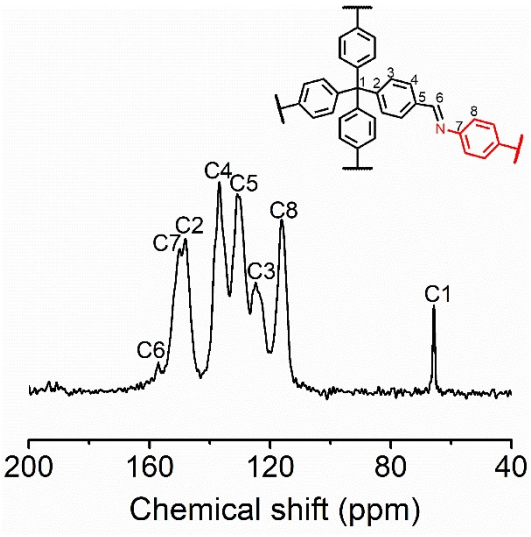


**Fig. S7** $^{13}C$ SNMR spectra of TFPM-PA.

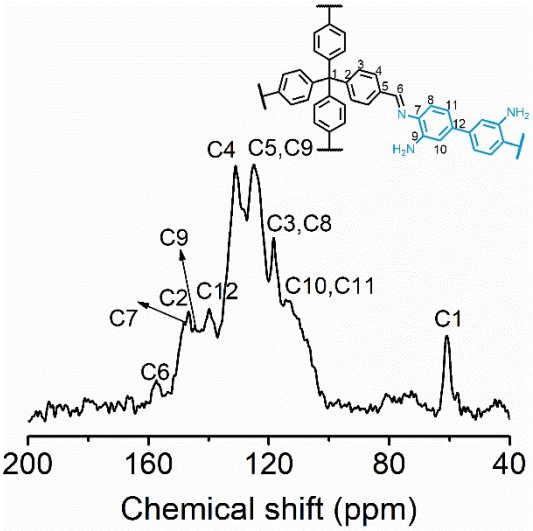


**Fig. S8** $^{13}C$ SNMR spectra of JNU-5.

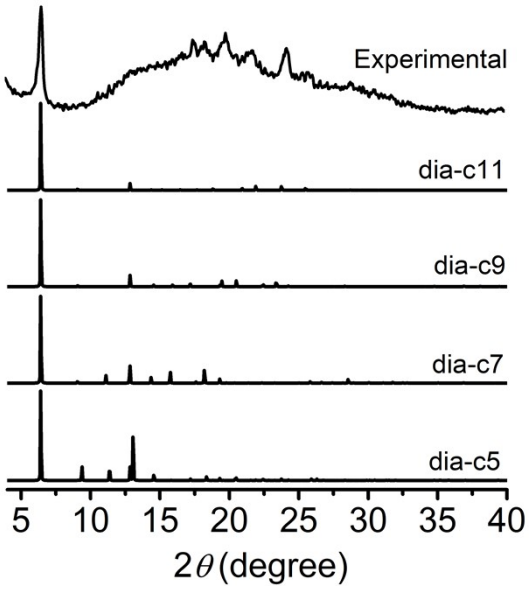


**Fig. S9** Experimental and simulated PXRD patterns (different degrees of interpenetration) of JNU-5.

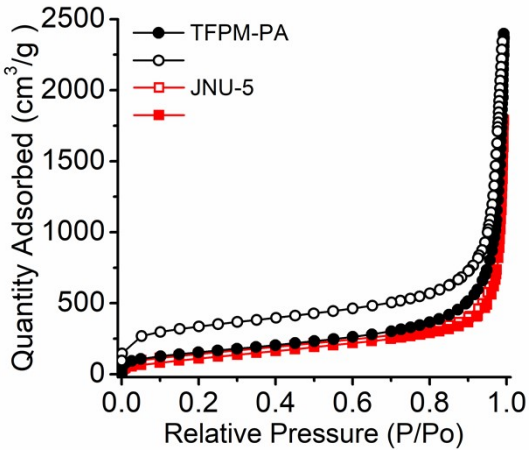


**Fig. S10** $N_2$ adsorption–desorption isotherms of TFPM-PA and JNU-5.

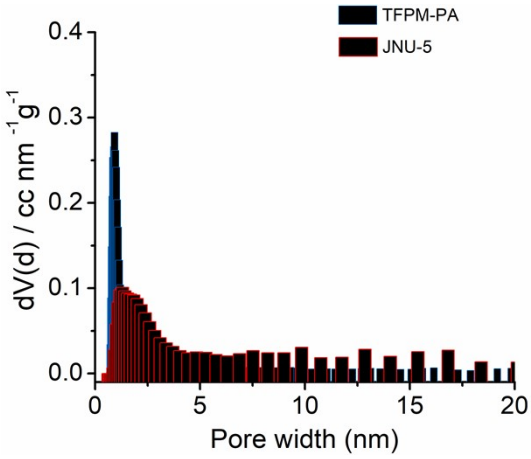


**Fig. S11** Pore size distribution of TFPM-PA and JNU-5.

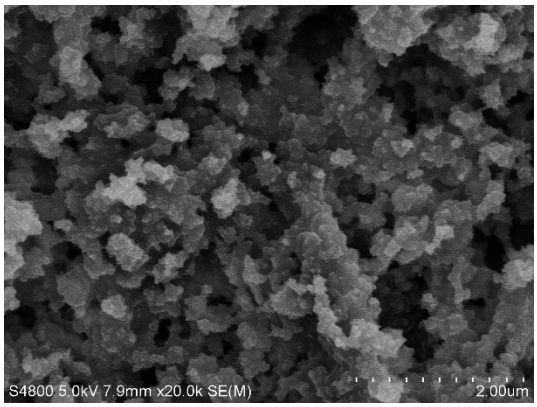


**Fig. S12** SEM image of TFPM-PA.

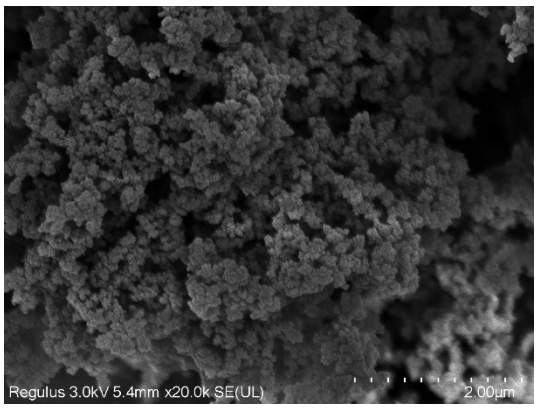


**Fig. S13** SEM image of JNU-5.

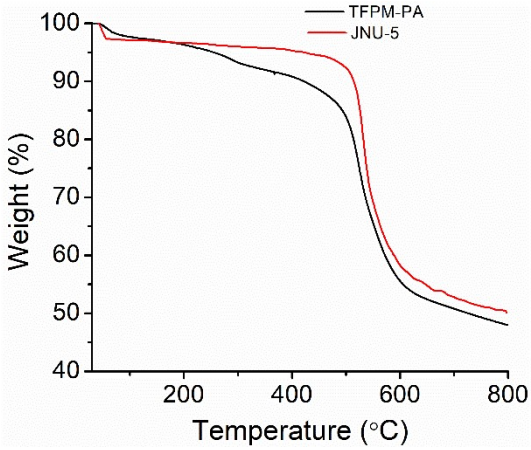


**Fig. S14** Thermogravimetric curve of TFPM-PA and JNU-5.

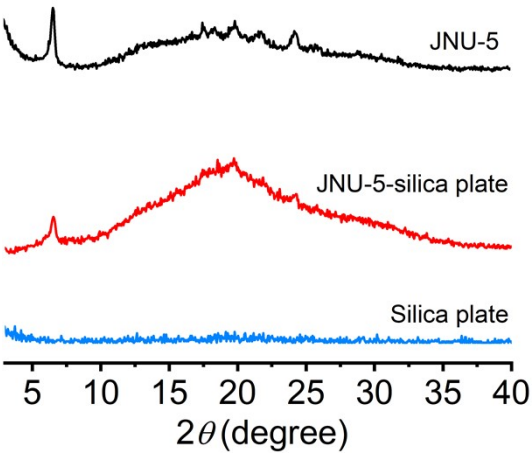


**Fig. S15** PXRD patterns of silica plate, JNU-5, and JNU-5 bonded silica plate.

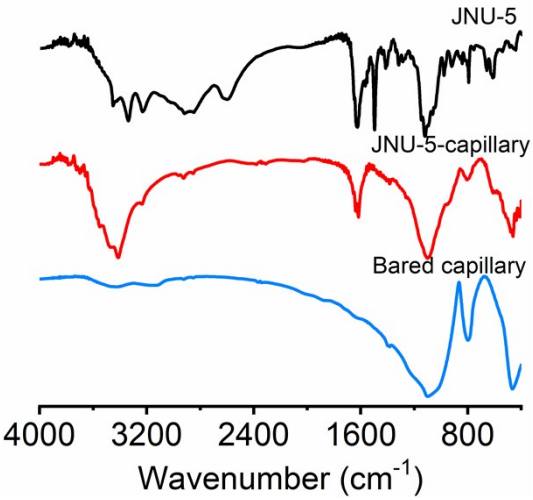


**Fig. S16** FTIR spectra of bare capillary, JNU-5 and JNU-5-capillary.

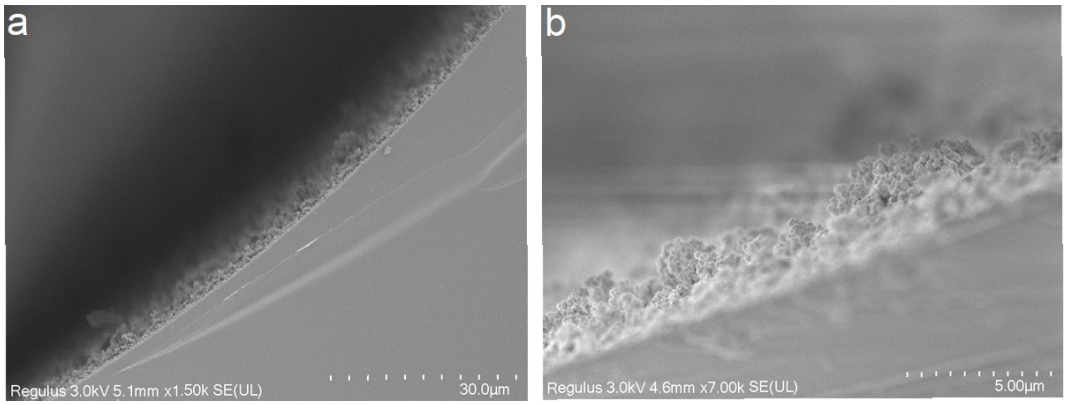


**Fig. S17** (a) SEM image of the edge of JNU-5-capillary. (b) SEM image of the inner wall of JNU-5-capillary.

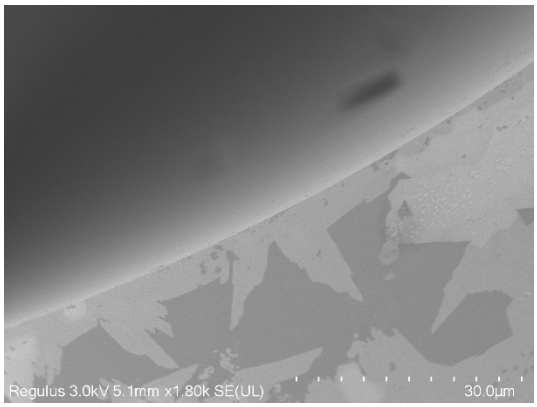


**Fig. S18** SEM image of bared capillary column.

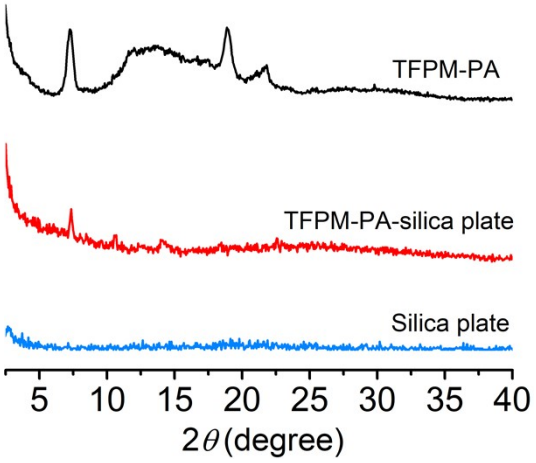


**Fig. S19** PXRD patterns of silica plate, TFPM-PA bonded silica plate, and TFPM-PA.

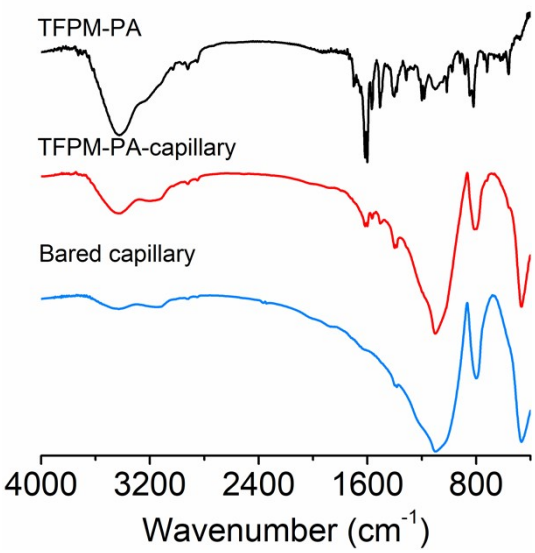


**Fig. S20** FTIR spectra of bared silica column, TFPM-PA bonded capillary column, and TFPM-PA.

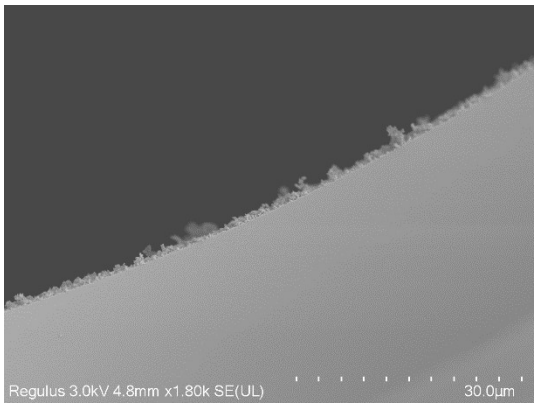


**Fig. S21** SEM image of TFPM-PA bonded capillary column.

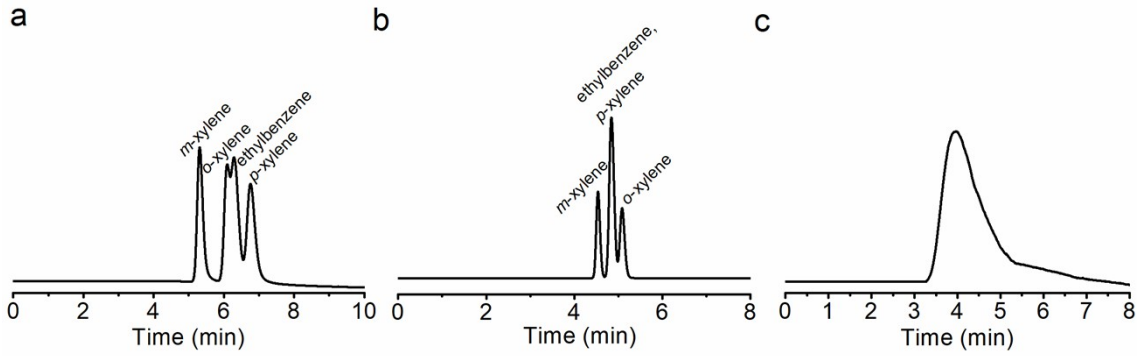


**Fig. S22** GC chromatograms of xylene isomers on different capillaries (10 m long × 0.53 mm i.d.): (a) TFPM-PA-capillary (220 °C, 20 cm $s^{-1}$ of $N_2$), (b) TFPM-BD-capillary (240 °C, 20 cm $s^{-1}$ of $N_2$). (c) ATPES-capillary (60 °C, 20 cm $s^{-1}$ of $N_2$). Separation conditions were optimized to give the best separation of isomers.

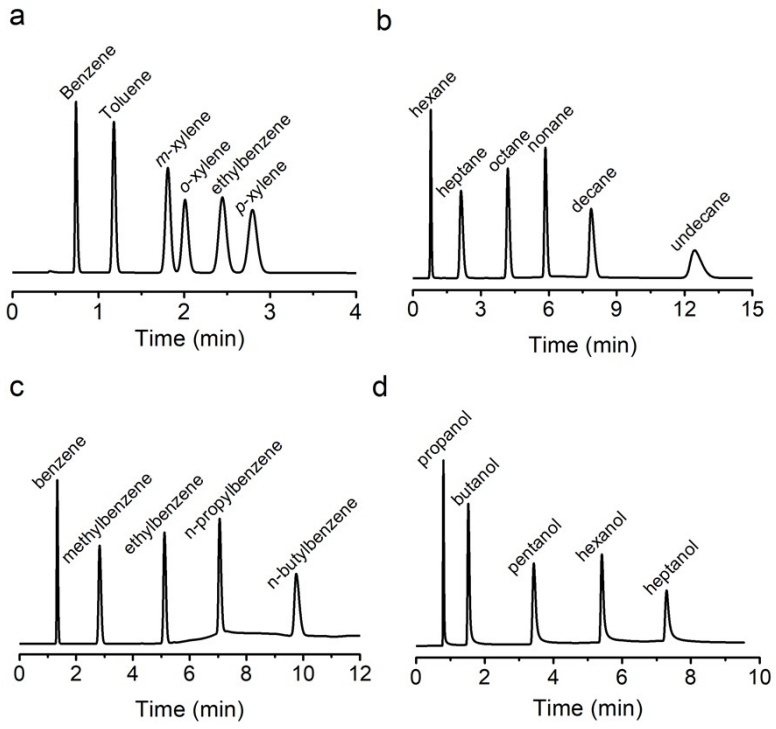


**Fig. S23** GC chromatograms of (a) BTEX at 70 cm $s^{-1}$ of $N_2$ (240 °C), (b) n-alkanes at 140 cm $s^{-1}$ of $N_2$ (200 °C for 2 min, then 20 °C $min^{-1}$ to 260 °C, keeping 260 °C to the end of the separation), (c) benzene homologue at 60 cm $s^{-1}$ of $N_2$ (200 °C for 2.5 min, then 20 °C $min^{-1}$ to 260 °C, keeping 260 °C to the end of the separation), and (d) n-alcohols at 60 cm $s^{-1}$ of $N_2$ (160 °C for 2 min, then 20 °C $min^{-1}$ to 260 °C, keeping 280

°C to the end of the separation).

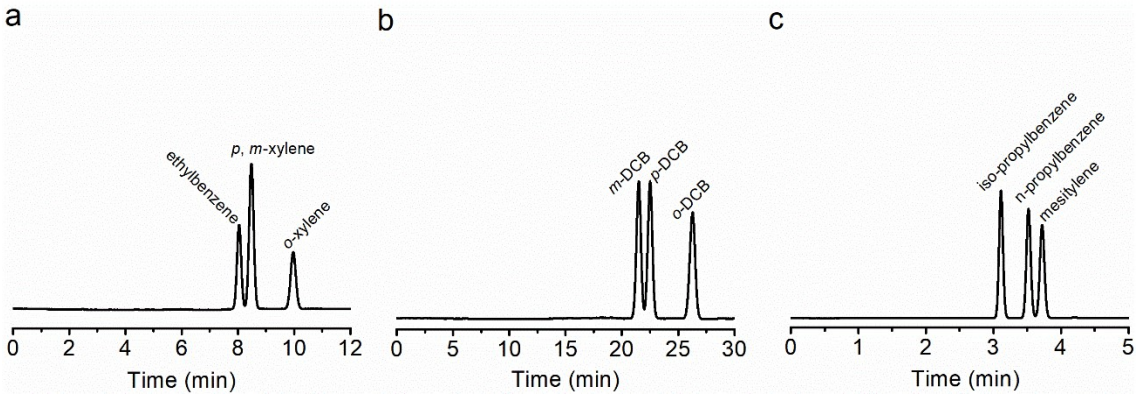


**Fig. S24** GC chromatograms of (a) xylene isomers (70 °C), (b) dichlorobenzene isomers (70 °C), (c) propylbenzene isomers (120 °C) at 20 cm $s^{-1}$ of $N_2$ on commercial DB-5 capillary column (Agilent J&W GC columns, 10 m long × 0.53 mm i.d.). Separation conditions were optimized to give the best separation of isomer.

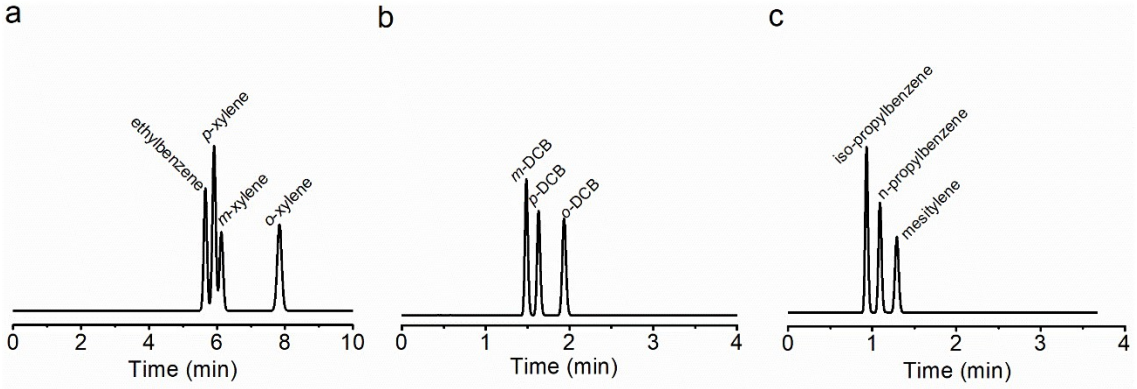


**Fig. S25** GC chromatograms of (a) xylene isomers (60 °C, 20 cm $s^{-1}$ of $N_2$), (b) dichlorobenzene isomers (120 °C, 50 cm $s^{-1}$ of $N_2$), (c) propylbenzene isomers (80 °C, 80 cm $s^{-1}$ of $N_2$) on commercial HP-FFAP capillary column (Agilent J&W GC columns, 10 m long × 0.53 mm i.d.). Separation conditions were optimized to give the best separation of isomer.

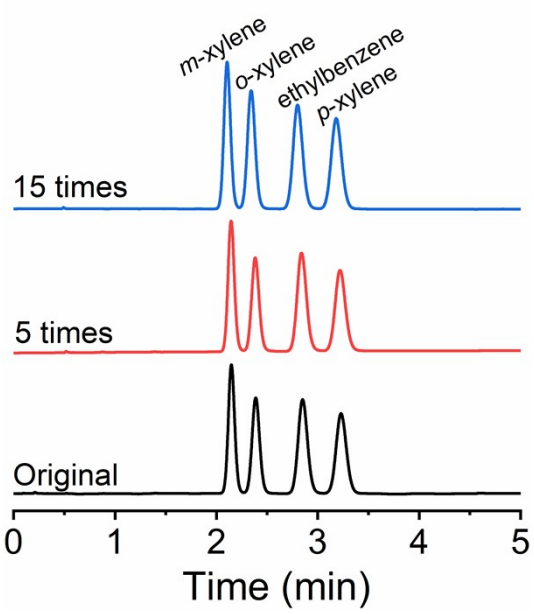


**Fig. S26** GC chromatograms of xylene isomers on JNU-5-capillary with different runs of programed temperature.

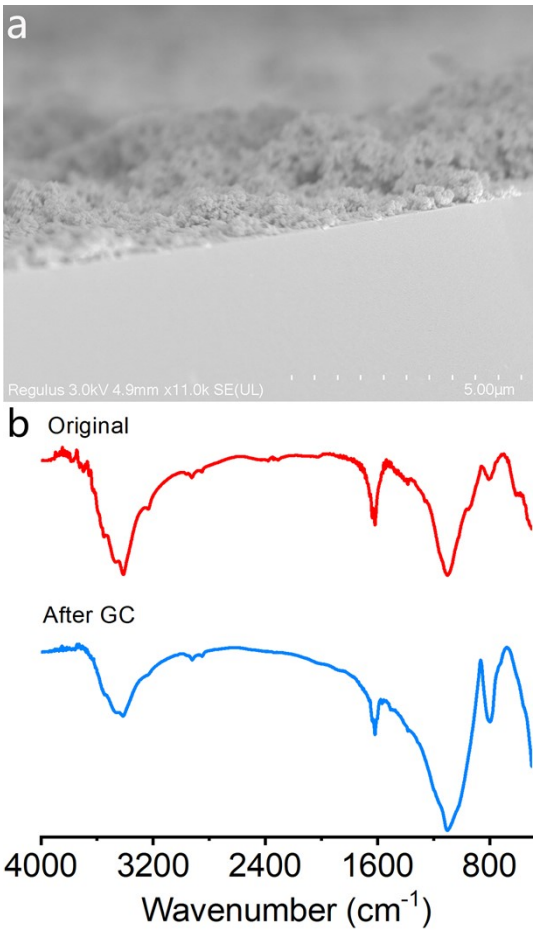


**Fig. S27** (a) SEM and (b) FTIR spectra of JNU-5-capillary after GC separation.

**Table S1** Fractional main atomic coordinates for the unit cell of JNU-3 after Pawley refinement

| Space group: I41/A<br>a = b = 26.8148 Å, c = 8.1893, $\alpha = \beta = \gamma = 90°$ | | | |
|---|---|---|---|
| Atom | x | y | z |
| C1 | 0.00514 | -0.76559 | -1.43817 |
| C2 | -0.02294 | -0.78305 | -1.51718 |
| C3 | -0.02132 | -0.81294 | -1.65428 |
| C4 | 0.00881 | -0.82723 | -1.72094 |
| C5 | 0.03692 | -0.81001 | -1.64304 |
| C6 | 0.03513 | -0.78008 | -1.50571 |
| N7 | 0.01327 | -0.85709 | -1.85803 |
| C8 | -0.01104 | -0.87467 | -1.93772 |
| C9 | -0.00728 | -0.90578 | -2.08051 |
| C10 | -0.03491 | -0.92352 | -2.16082 |
| C11 | -0.03212 | -0.95339 | -2.29791 |
| C12 | -0.00163 | -0.96697 | -2.36133 |
| C13 | 0.02596 | -0.94886 | -2.2793 |
| C14 | 0.02335 | -0.91902 | -2.14238 |
| H15 | -0.06425 | -0.77765 | -1.49082 |
| N16 | -0.05908 | -0.83366 | -1.74785 |
| H17 | 0.07815 | -0.8156 | -1.67022 |
| H18 | 0.07113 | -0.76685 | -1.44643 |
| H19 | -0.05297 | -0.87108 | -1.91967 |
| H20 | -0.07637 | -0.9185 | -2.13623 |
| H21 | -0.06768 | -0.96702 | -2.35905 |
| H22 | 0.06752 | -0.95361 | -2.30266 |
| H23 | 0.05899 | -0.90547 | -2.08157 |
| H24 | -0.04985 | -0.8605 | -1.84579 |
| H25 | -0.09846 | -0.82335 | -1.72462 |
| C26 | 0.00000 | -1.00000 | -2.50000 |

**Table S2** Comparison of the separation factor ($\alpha$) and resolution (R) of xylene isomers on the JNU-5, commercial DB-5 and HP-FFAP capillary column

| Column | $\alpha$ | | | R | | |
|---|---|---|---|---|---|---|
| JNU-5 | 1.14 | 1.23 | 1.15 | 1.85 | 2.89 | 1.97 |
| DB-5 | 1.07 | 1 | 1.21 | 1.46 | 0 | 4.48 |
| HP-FFAP | 1.06 | 1.05 | 1.35 | 1.38 | 1.09 | 7.46 |

$\alpha_{(2/1)} = t_2' / t_1'$, where t' is relative retention time.

$R_{(2/1)} = 2(t_2-t_1) / (W_1+W_2)$, where t is retention time, W is peak width.

The footnotes 1 and 2 refer to the first and second peaks of the two adjacent isomers, respectively.

**Table S3** Indicative interaction distance of xylene isomers on JNU-5-capillary

| Analyte | Indicative interaction distance (Å) | | | |
|---|---|---|---|---|
| | $\pi$-$\pi$ | C-H$\cdots\pi$ | hydrogen bonding | |
| *m*-xylene | 3.924 | 2.169 | 2.802 | / |
| *o*-xylene | 3.942 | 2.104 | 2.768 | 2.718 |
| ethylbenzene | 3.907 | 2.038 | 2.781 | 2.511 |
| *p*-xylene | 3.655 | 2.091 | 2.598 | 2.507 |

**Table S4** Thermodynamic parameters for GC resolution of xylene isomers on JNU-5-capillary column

| Analytes | $\Delta H$ (KJ mol$^{-1}$) | $\Delta S$ (J mol$^{-1}$ K$^{-1}$) | $\Delta G$ (KJ mol$^{-1}$) | $R^2$ |
|---|---|---|---|---|
| *m*-xylene | -58.1 $\pm$ 2.4 | -102.2 $\pm$ 7.2 | -57.3 $\pm$ 2.3 | 0.9967 |
| *o*-xylene | -57.0 $\pm$ 2.2 | -98.7 $\pm$ 6.8 | -56.2 $\pm$ 2.1 | 0.9970 |
| ethylbenzene | -60.3 $\pm$ 3.2 | -103.5 $\pm$ 8.9 | -59.4 $\pm$ 2.8 | 0.9943 |
| *p*-xylene | -71.3 $\pm$ 2.9 | -124.4 $\pm$ 8.2 | -70.3 $\pm$ 2.8 | 0.9967 |

**Table S5** Comparison of the separation factor ($\alpha$) and resolution (R) of dichlorobenzene isomers on the JNU-5, commercial DB-5 and HP-FFAP capillary column

| Column | $\alpha$ | | R | |
|---|---|---|---|---|
| JNU-5 | 1.22 | 1.32 | 2.07 | 2.80 |
| DB-5 | 1.05 | 1.18 | 1.42 | 4.68 |
| HP-FFAP | 1.15 | 1.27 | 2.06 | 3.82 |

$\alpha_{(2/1)} = t_2' / t_1'$, where t' is relative retention time.

$R_{(2/1)} = 2(t_2-t_1) / (W_1+W_2)$, where t is retention time, W is peak width.

The footnotes 1 and 2 refer to the first and second peaks of the two adjacent isomers, respectively.

**Table S6** Comparison of the separation factor ($\alpha$) and resolution (R) of propylbenzene isomers on the JNU-5, commercial DB-5 and HP-FFAP capillary column

| Column | $\alpha$ | | R | |
|---|---|---|---|---|
| JNU-5 | 1.87 | 1.36 | 3.18 | 1.64 |
| DB-5 | 1.24 | 1.49 | 3.47 | 1.59 |
| HP-FFAP | 1.26 | 1.26 | 2.38 | 2.58 |

$\alpha_{(2/1)} = t_2' / t_1'$, where t' is relative retention time.

$R_{(2/1)} = 2(t_2-t_1) / (W_1+W_2)$, where t is retention time, W is peak width.

The footnotes 1 and 2 refer to the first and second peaks of the two adjacent isomers, respectively.

**Table S7** Precision for the retention time of xylene isomers on the JNU-5-capillary

| Analytes | RSD for retention time (%) | |
|---|---|---|
| | run-to-run (*n* = 8) | day to day(*n* = 8) |
| *m*-xylene | 0.13 | 1.79 |
| *o*-xylene | 0.12 | 1.84 |
| ethylbenzene | 0.23 | 2.00 |
| *p*-xylene | 0.33 | 1.45 |

**Table S8** Comparison of k for xylene isomers on JNU-5-capillary with different run of programed temperature

| Analyte | *k* | | | RSD for *k* (%) |
|---|---|---|---|---|
| | 0 run | 5 runs | 15 runs | |
| *m*-xylene | 8.33 | 8.33 | 8.17 | 1.12 |
| *o*-xylene | 9.38 | 9.36 | 9.19 | 1.12 |
| ethylbenzene | 11.39 | 11.34 | 11.18 | 0.97 |
| *p*-xylene | 13.04 | 13.00 | 12.83 | 0.86 |

$k = t' / t_0$, where t' and $t_0$ are relative retention time and dead time, respectively.