Electronic Supplementary Information

Facile room-temperature solution-phase synthesis of spherical covalent organic framework for high-resolution chromatographic separation

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Materials. All chemicals and reagents used were at least of analytical grade. Ultrapure water was obtained from Wahaha Foods Co. Ltd. (Tianjin, China). 1,3,5-Triformylphloroglucinol, and benzidine, alkanes, cyclohexane, benzene, α-pinene, and β-pinene, were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Methanol, ethanol, propanol, butanol, hexane, acetonitrile, acetone, and *N*,*N*-dimethylformamide were obtained from Concord Chemical Research Institute (Tianjin, China). HCl and NaOH were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China).

Room-temperature solution-phase synthesis of TpBD. In a typical synthesis, 1,3,5-triformylphloroglucinol (Tp, 0.30 mmol) and benzidine (BD, 0.45 mmol) were separately dissolved with 20 mL ethanol, and then mixed in a 100-mL flask under stirring at room temperature. After stirring for 30 min, the light brown suspension was collected by centrifugation at 10000 rpm for 5 min and then thoroughly washed with ethanol. The obtained TpBD was refluxed with DMF for 4 h to remove unreated residual Tp and BD, then with ethanol for 2 h to exchange the DMF, evacuated in vacuum at room temperature overnight to remove the ethanol. The yield of the final TpBD after purification was 50%. The elemental analysis gave 74.0% C, 4.1% H, 9.0% N for the final TpBD.

Characterization of TpBD. The purified TpBD was used for all subsequent chracterization. XRD, TGA, SEM, TEM, N_2 adsorption experiments, and FT-IR were employed to characterize the as-prepared TpBD. The XRD patterns were recorded with a D/max-2500 diffractometer (Rigaku, Japan) using CuKa radiation (λ=1.5418 Å) with a scan speed of 8° min^{-1} and a step size of 0.02° in 2θ. The TGA experiments were performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) under air from room temperature to 700 ^oC at a ramp rate of 5 ^oC min^{-1}. The SEM images were recorded on a Shimadzu SS-550 scanning electron microscope at 15.0 kV. TEM were performed on a JEOL-100CXII microscope (JEOL, Japan). The FT-IR spectra were measured on a Nicolet IR AVATAR-360 spectrometer (Nicolet, USA) with pure KBr as background. N_2 adsorption experiments were performed on an ASAP 2010 micropore physisorption analyzer (Micromeritics, Nor-cross, GA, USA) using nitrogen adsorption at 77 K. The pore size distribution of as-prepared TpBD was calculated using the density functional theory (DFT) method. Elemental analysis was carried out on a vario EL CUBE analyzer (Elementar, Germany).

Fabrication of TpBD coated capillary column. Fused silica capillary (20-m long × 0.25 mm i.d., Yongnian Optic Fiber Plant, Hebei, China) was pretreated according to the following recipe before dynamic coating: the capillary was washed with 1 M NaOH for 2 h, ultrapure water for 30 min, 0.1 M HCl for 2 h, and ultrapure water until the outflow reached pH 7.0.

The capillary was then dried with N_2 at 100 °C overnight. TpBD were coated onto the pretreated capillary column via a dynamic coating method. 0.3-mL Methanol suspension of TpBD (1 mg mL^{-1}) was first filled into the capillary column under gas pressure, and then pushed through the column at a constant N_2 pressure of 20 KPa to leave a wet coating layer on the inner wall of the capillary column. After coating, the capillary column was settled for 2 h for conditioning under nitrogen. Further conditioning of the capillary column was carried out using a temperature program: 30 °C for 10 min, ramp from 30 °C to 150 °C at a rate of 3 °C min^{-1}, and 150 °C for 2 h.

Instrumentation. Gas chromatographic measurements were performed on a GC-14B (Shimadzu, Japan) system with flame ionization detector. Nitrogen (99.999%) was used as the carrier gas.

Calculation of thermodynamic parameters. The enthalpy change (ΔH) and entropy change (ΔS) for the transfer of solutes from the mobile phase to the stationary phase TpBD were calculated from the van't Hoff equation:

$$\ln k' = -\Delta H / \mathrm{RT} + \Delta S / R + \ln \Phi$$

where k' is retention factor, R gas constant, T absolute temperature, and Φ the phase ratio (the ratio of the volume of the stationary phase in the column (V_s) to the void volume of the column (V_0)). To obtain Φ, V_s was calculated from the density and the mass of the stationary phase in the coated capillary column, which was obtained by differentiating the masses of the capillary column after and before coating the stationary phase, while V_0 was calculated from the density of ultrapure water and the difference between the masses of the coated capillary column after and before filling with ultrapure water. Thus, the $\ln \Phi$ was estimated to be -4.87.

The k' was calculated according to the following equation:

$$k' = (t - t_0) / t_0$$

where t is retention time for the analyte, and t_0 is the column void time.

The Gibbs free energy change (ΔG) of the transfer of the analyte from mobile phase to stationary phase was calculated according to the following equation:

$$\Delta G = \Delta H - T\Delta S$$

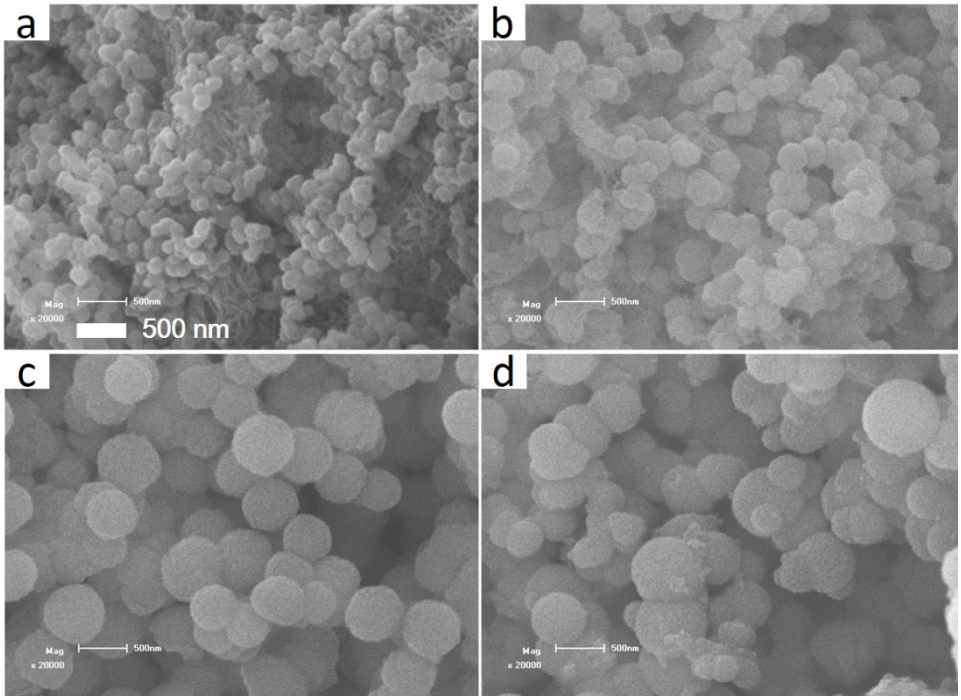

Fig. S1 SEM images of the as-prepared TpBD obtained from 30 min room-temperature stirring with different concentrations of BD and Tp, respectively: (a) 0.1125 and 0.075 mM; (b) 0.22 and 0.15 mM; (c) 0.45 and 0.30 mM; and (d) 0.90 and 0.60 mM. The yield of TpBD (%): (a) 15; (b) 29; (c) 50; (d) 35.

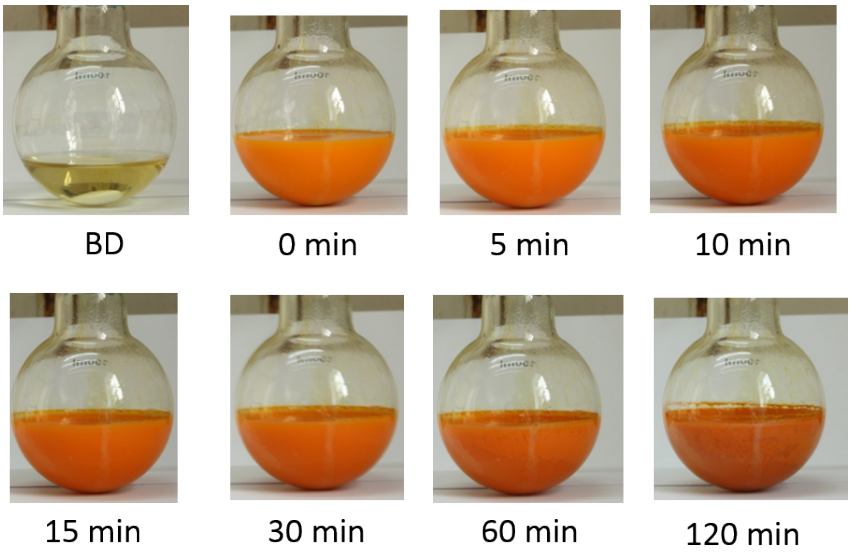

Fig. S2 Photos for the room-temperature solution-phase synthesis of TpBD for different stirring periods. The concentration of BD and Tp is 0.45 and 0.30 mM, respectively.

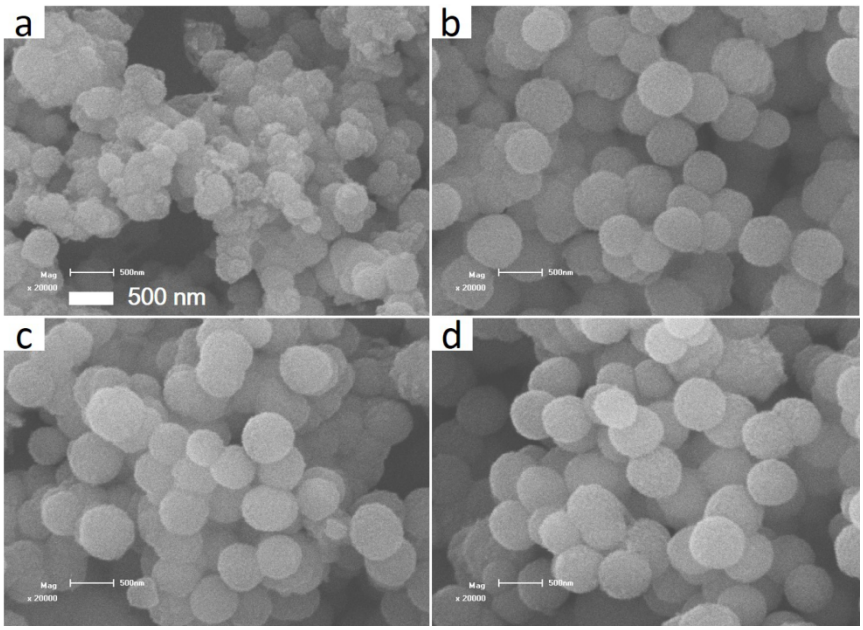

Fig. S3 SEM images of the as-prepared TpBD obtained from room-temperature solution-phase synthesis for different stirring periods (min): (a) 15; (b) 30; (c) 60; (d) 120. The concentration of BD and Tp is 0.45 and 0.30 mM, respectively. The yields of TpBD (%): (a) 0; (b) 50; (c) 52; (d) 53.

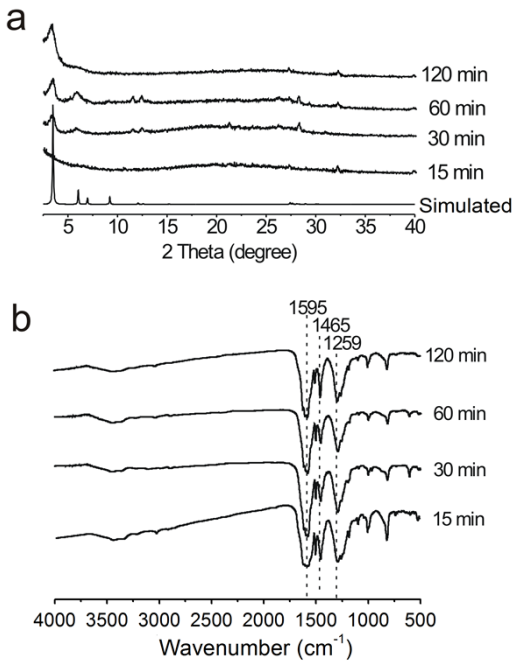

Fig. S4 (a) XRD patterns, and (b) FT-IR spectra of the as-prepared TpBD obtained after different time stirring. The characteristic XRD signal of the TpBD appears when the stirring time is no less than 30 min. The concentration of BD and Tp is 0.45 and 0.30 mM, respectively.

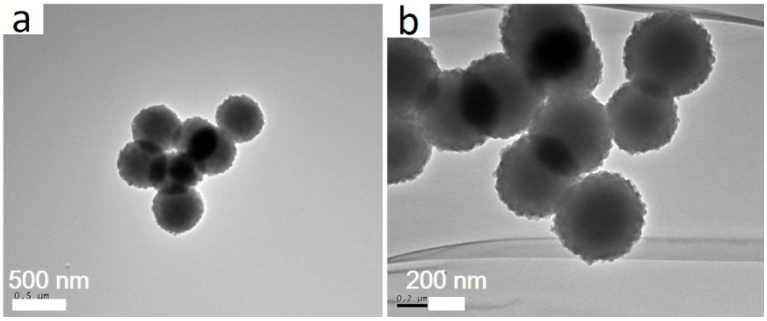

Fig. S5 TEM images of the as-prepared TpBD obtained from 30-min room-temperature stirring. The concentration of BD and Tp is 0.45 and 0.30 mM, respectively.

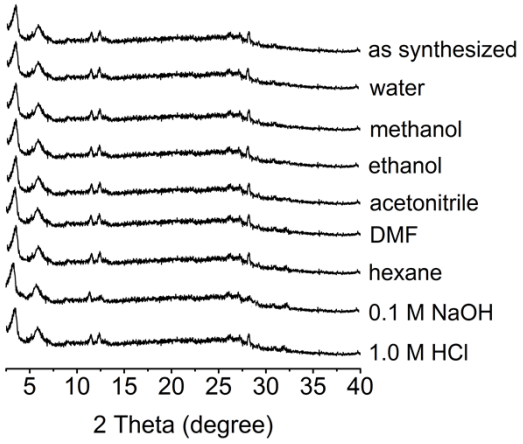

Fig. S6 XRD patterns of the TpBD after staying in different solvents for 3 days.

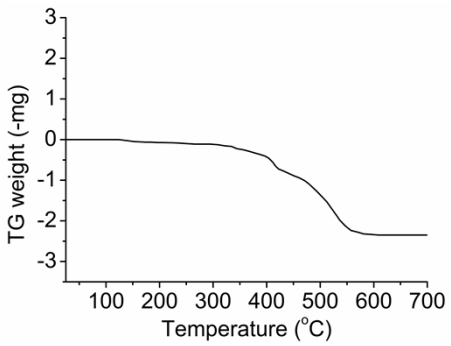

Fig. S7 TGA curve of the as-prepared TpBD obtained from 30-min room-temperature stirring. The TGA experiments were performed under air from room temperature to 700 ^{o}C at a ramp rate of 5 ^{o}C min^{-1}.

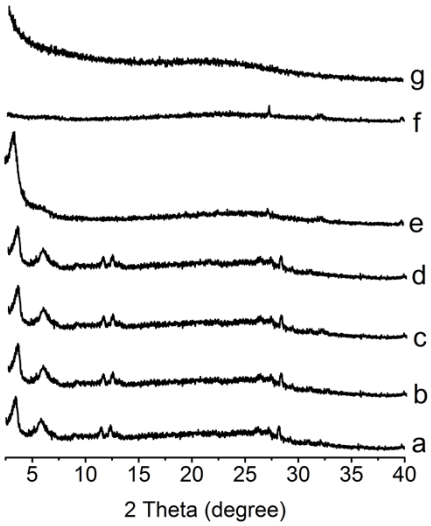

Fig. S8 XRD patterns of the as-prepared TpBD before (a) and after heating to (b) 150 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C, (f) 350 °C, and (g) 400 °C for 1 h.

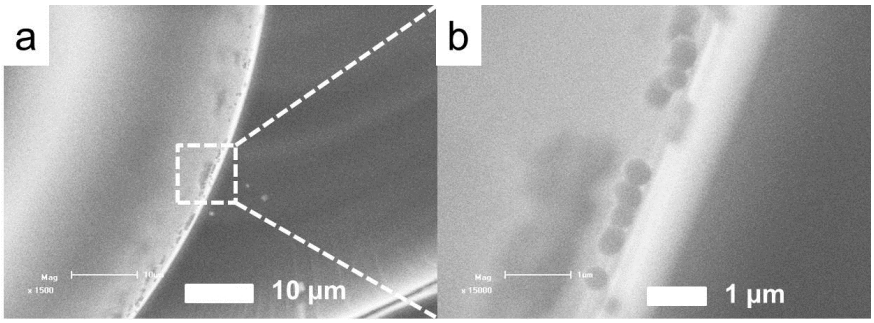

Fig. S9 SEM images of the TpBD coated capillary column with the scale bar of (a) 10 μm and (b) 1 μm.

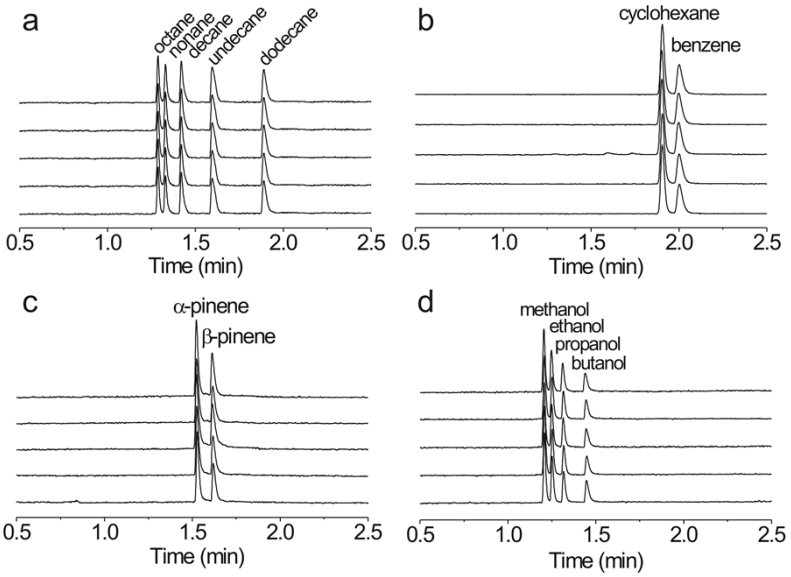

Fig. S10 Five replicate GC separations of (a) alkanes with a temperature program of 20 ^{o}C min^{-1} from 40 ^{o}C to 80 ^{o}C at a constant N_2 pressure of 80 KPa, (b) cyclohexane and benzene with a temperature program of 10 ^{o}C min^{-1} from 40 ^{o}C to 100 ^{o}C at a constant N_2 pressure of 40 KPa, (c) α-pinene and β-pinene with a temperature program of 65 ^{o}C for 0.5 min and then 10 ^{o}C min^{-1} to 100 ^{o}C at a constant N_2 pressure of 60 KPa, and (d) alcohols with a temperature program of 23 ^{o}C min^{-1} from 95 ^{o}C to 150 ^{o}C at a constant N_2 pressure of 80 KPa on a TpBD coated capillary column (20-m long × 0.25 mm i.d.).

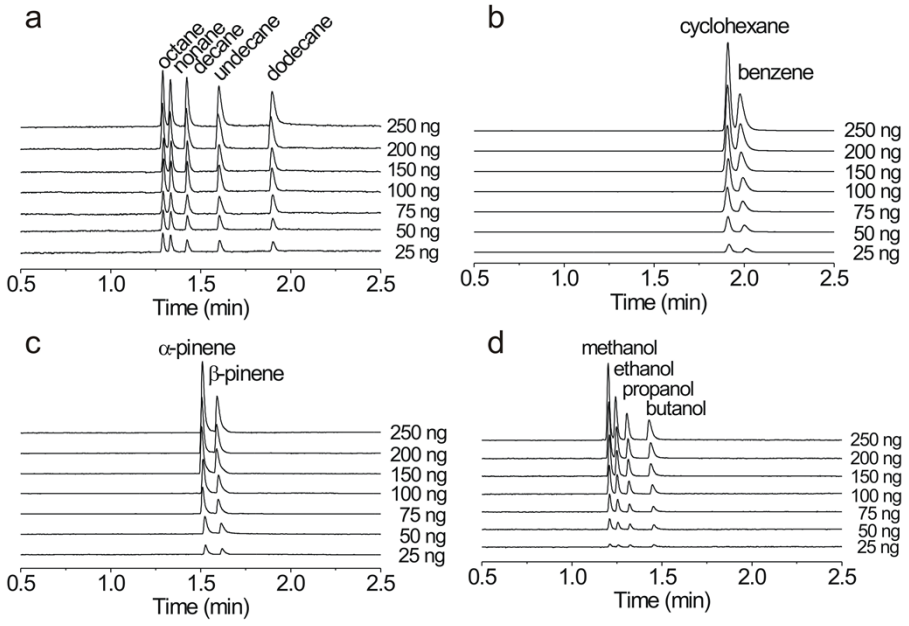

Fig. S11 Effect of analytes mass on the separation of (a) alkanes, (b) cyclohexane and benzene, (c) α-pinene and β-pinene, and (d) alcohols on the TpBD coated capillary column (20-m long × 0.25 mm i.d.). Separation conditions are the same as Fig. S10.

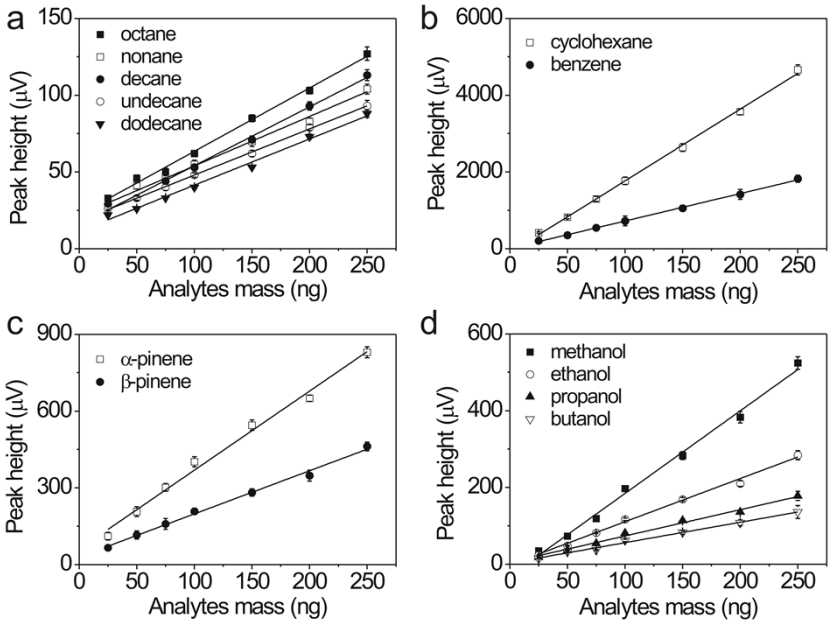

Fig. S12 Effect of analytes mass on the peak height for the separation of (a) alkanes, (b) cyclohexane and benzene, (c) α-pinene and β-pinene, and (d) alcohols on the TpBD coated capillary column (20-m long × 0.25 mm i.d.). Separation conditions are the same as Fig. S10. Errors bar shows the standard deviation for triplicate determinations.

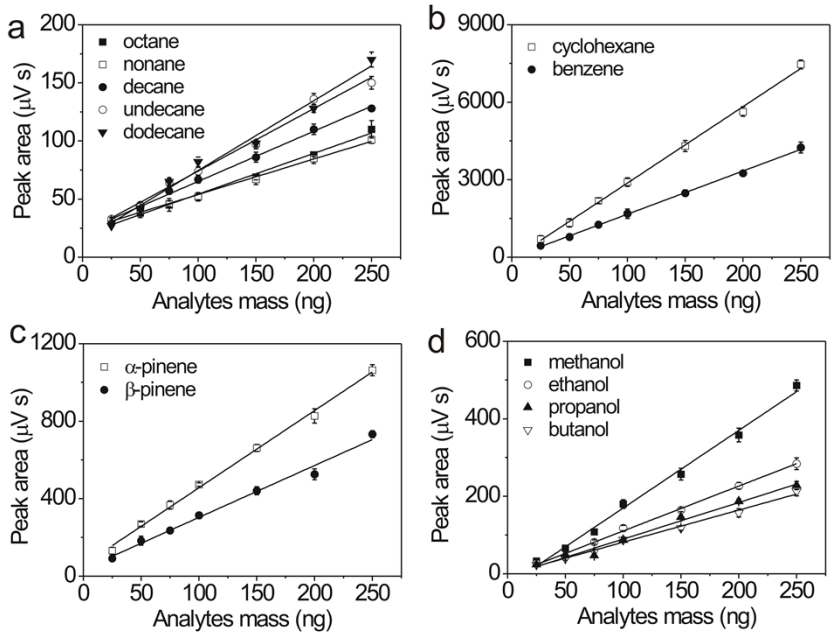

Fig. S13 Effect of analytes mass on the peak area for the separation of (a) alkanes, (b) cyclohexane and benzene, (c) α-pinene and β-pinene, and (d) alcohols on the TpBD coated capillary column (20-m long × 0.25 mm i.d.). Separation conditions are the same as Fig. S10. Errors bar shows the standard deviation for triplicate determinations.

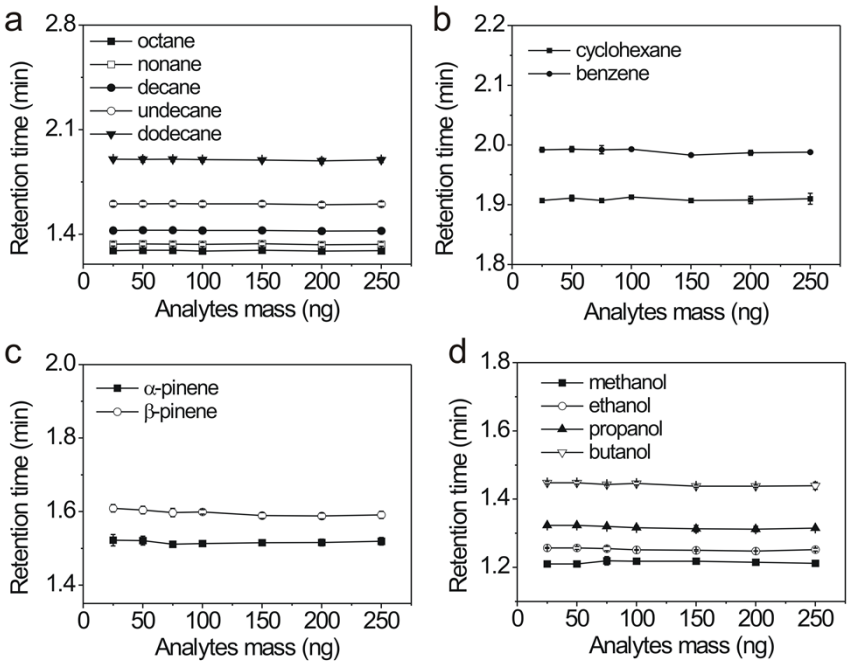

Fig. S14 Effect of analytes mass on the retention time for the separation of (a) alkanes, (b) cyclohexane and benzene, (c) α-pinene and β-pinene, and (d) alcohols on the TpBD coated capillary column (20-m long × 0.25 mm i.d.). Separation conditions are the same as Fig. S10. Errors bar shows the standard deviation for triplicate determinations.

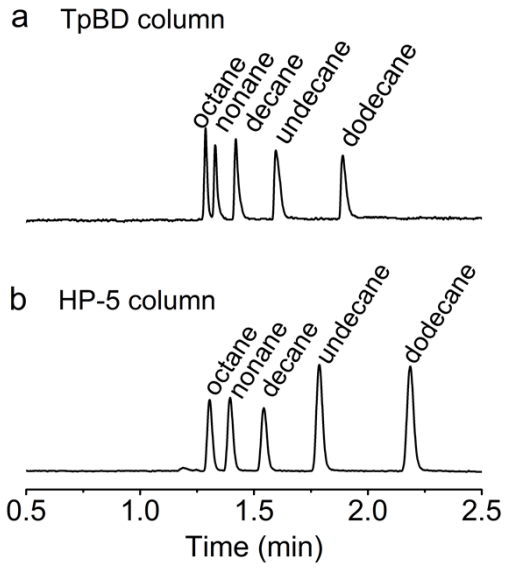

Fig. S15 GC separation of alkanes: (a) TpBD coated column (20-m long × 0.25 mm i.d.) with an optimized temperature program of 20 ^{o}C min^{-1} from 40 ^{o}C to 80 ^{o}C at a constant N_2 pressure of 80 KPa; (b) HP-5 column (20-m long × 0.25 mm i.d.) with an optimized temperature of 150 ^{o}C at a constant N_2 pressure of 60 KPa. The injected analyte mass is 50 ng.

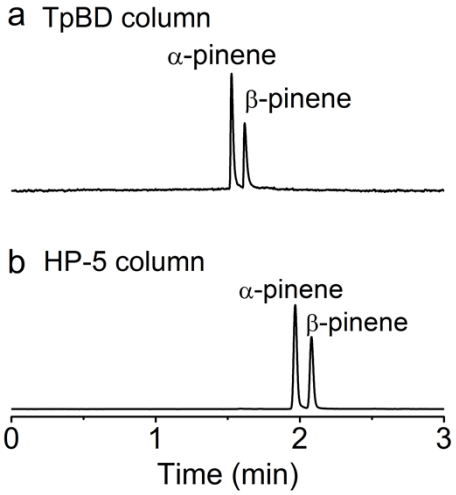

Fig. S16 GC separation of α-pinene and β-pinene: (a) TpBD column (20-m long × 0.25 mm i.d.) with an optimized temperature program of 65 ^{o}C for 0.5 min and then 10 ^{o}C min^{-1} to 100 ^{o}C at a constant N_2 pressure of 60 KPa; (b) HP-5 column (20-m long × 0.25 mm i.d.) with an optimized temperature of 150 ^{o}C at a constant N_2 pressure of 40 KPa. The injected analyte mass is 50 ng.

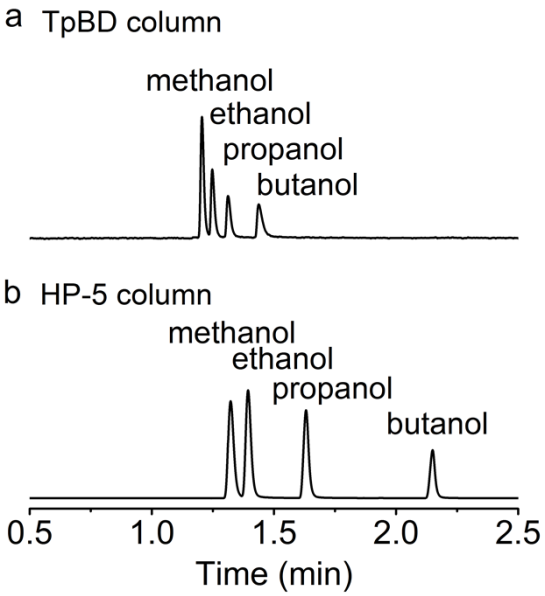

Fig. S17 GC separation of alcohols: (a) TpBD column (20-m long × 0.25 mm i.d.) with an optimized temperature program of 23 ^{o}C min^{-1} from 95 ^{o}C to 150 ^{o}C at a constant N_2 pressure of 80 KPa; (b) HP-5 column (20-m long × 0.25 mm i.d.) with an optimized temperature program of 40 ^{o}C for 1 min and then 20 ^{o}C min^{-1} to 150 ^{o}C at a constant N_2 pressure of 40 KPa. The injected analyte mass is 50 ng.

Table S1 Precision for five replicate separations on the TpBD coated capillary column.

analyte	chromatogram	RSD (%) (n = 5)		
		retention time	peak area	peak height
octane	Fig. S10a	0.1	3.8	1.7
nonane		0.1	3.4	6.6
decane		0.1	4.2	4.2
undecane		0.1	4.5	4.6
dodecane		0.2	4.7	5.1
cyclohexane	Fig. S10b	0.1	1.9	4.3
benzene		0.1	3.4	3.3
α-pinene	Fig. S10c	0.1	5.6	3.8
β-pinene		0.2	3.5	4.8
methanol	Fig. S10d	0.1	4.0	5.2
ethanol		0.1	3.7	1.7
propanol		0.1	3.6	2.4
butanol		0.2	1.6	2.4

Table S2 Values of ΔH, ΔS and ΔG (mean ± s, n=3) for alkanes, cyclohexane and benzene, α-pinene and β-pinene, and alcohols on the TpBD coated capillary column.

analytes	ΔH (KJ mol^{-1}) [a]	ΔS (J mol^{-1} K^{-1}) [a]	ΔG (kJ mol^{-1}) [b]	R^2
octane	-18.4 ± 0.9	-48.3 ± 1.5	-2.3 ± 0.4	0.991
nonane	-26.6 ± 1.7	-71.7 ± 3.5	-2.7 ± 0.5	0.983
decane	-45.1 ± 2.9	-123.9 ± 5.6	-3.8 ± 1.0	0.984
undecane	-51.9 ± 1.3	-137.9 ± 3.2	-5.9 ± 0.6	0.997
dodecane	-58.7 ± 1.2	-151.7 ± 2.8	-8.2 ± 0.3	0.998
cyclohexane	-8.2 ± 0.6	-15.3 ± 0.6	-3.1 ± 0.4	0.981
benzene	-14.8 ± 0.7	-29.7 ± 0.5	-4.9 ± 0.5	0.991
α-pinene	-28.8 ± 1.2	-68.5 ± 3.7	-5.9 ± 0.1	0.993
β-pinene	-38.2 ± 1.1	-92.7 ± 3.3	-7.3 ± 0.1	0.997
methanol	-43.6 ± 1.2	-102.3 ± 3.2	-5.4 ± 0.1	0.997
ethanol	-50.5 ± 1.8	-115.9 ± 5.0	-7.3 ± 0.1	0.995
propanol	-52.8 ± 3.6	-117.9 ± 9.7	-8.8 ± 0.4	0.981
butanol	-60.3 ± 2.9	-133.2 ± 7.9	-10.6 ± 0.1	0.991

[a] Calculated from the van't Hoff plots in a temperature range of 40-80^{o}C for alkanes, cyclohexane and benzene, α-pinene and β-pinene, and 80-120 ^{o}C for alcohols.

[b] 60^{o}C for alkanes, cyclohexane and benzene, α-pinene and β-pinene, and 100 ^{o}C for alcohols.

Table S3 Comparison of the column efficiency (plates m^{-1}) of TpBD coated column and HP-5 column for the separation of alkanes, cyclohexane and benzene, α-pinene and β-pinene, and alcohols under the separation conditions as shown in Fig. S15-17.

	TpBD coated column	HP-5 column
octane	4058	3704
nonane	3689	3729
decane	3413	3878
undecane	2837	3436
dodecane	2534	3145
α-pinene	3067	3059
β-pinene	2153	2968
methanol	3018	2731
ethanol	2759	2542
propanol	2161	2677
butanol	2017	2534