Supporting Information

Pristine and Carboxyl-Functionalized Tetraphenylethylene-Based Ladder Networks for Gas Separation and Volatile Organic Vapor Adsorption

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Scheme 1. Detailed procedure for synthesis of MP1 and MP2
**Materials:** Bis(3,4-dimethoxyphenyl)methanone was synthesized according to the previous literature.\(^1\) Titanium tetrachloride (TiCl\(_4\)), anhydrous tetrahydrofuran (THF), potassium carbonate (K\(_2\)CO\(_3\)), dichloromethane, diethyl ether, methanol, boron tribromide (BBr\(_3\)), N,N-dimethylacetamide (DMAc), hydrochloride acid (HCl), potassium hydroxide (KOH), ethanol were obtained from Sigma-Aldrich and used as received.

*Synthesis of 1, 1, 2, 2-tetrakis(3,4-dimethoxyphenyl)ethane* (intermediate ii). 200 mL of anhydrous tetrahydrofuran were added to a 500 mL three-neck round bottle flask and cooled using an ice-bath. To it, TiCl\(_4\) (6.00 mL, 54.0 mmol) was added dropwise under argon atmosphere. Zn dust (4.4 g, 68 mmol) and dry pyridine (0.2 g, 2.5 mmol) were thereafter added and the resulting black suspension was warmed to room temperature and then refluxed for 2 h. A solution of tetramethoxybenzophenone (6.00 g, 19.9 mmol) in tetrahydrofuran (50 mL) was added dropwise to the black reaction mixture in 0.5 h and the resulting mixture was refluxed for additional 12 h. The resultant mixture was cooled to room temperature and quenched with 10% aqueous K\(_2\)CO\(_3\) (50 mL). The organic layer was separated and the aqueous suspension was extracted with dichloromethane (4 x 50 mL). The combined organic layers were dried over anhydrous MgSO\(_4\), filtered and evaporated to afford a pale yellow solid, which was purified by crystallization from a 1:1 mixture of dichloromethane and methanol to give 1, 1, 2, 2-tetrakis(3,4-dimethoxyphenyl) ethane in 92% yield. mp: 168 - 170 °C; \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\): 3.54 (s, 12 H), 3.82 (s, 12 H), 6.57-5.65 (m, 12 H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta\): 55.83, 55.89, 110.43, 114.97, 124.05, 136.91, 139.15, 147.59, 148.15.

*Synthesis of 4,4',4",4"''-(ethene-1,1,2,2-tetrayl)tetrakis(benzene-1,2-diol).* 1, 1, 2, 2-tetrakis (3,4-dimethoxyphenyl) ethane (1.14 g, 2.00 mmol) was dissolved in dichloromethane (30 mL) and cooled using an ice bath. To it, BBr\(_3\) (1.51 g, 4 mmol) was added dropwise and the system
was stirred further for 12 h to form a clear light yellow solution. The solution was poured into 100 mL ice-water and stirred for 1 h. The aqueous phase was separated and extracted with diethyl ether (3 × 50 mL); the organic phase was combined and washed with water twice and dried with magnesium sulfate. Most of the diethyl ether was removed by rota-evaporation. The remaining solvent was added dropwise to a large quantity of dichloromethane and an off-white solid (736 mg, yield: 80%) was collect by filtration and dried in under vacuum at 40 °C for 24 h before use. mp: 108.8 °C; \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 8.64 (s, 4H), 8.48 (s, 4H), 6.43 (d, 4H, \(J = 8.10\) Hz), 6.33 (s, 4H), 6.20 (d, 4H, \(J = 8.15\) Hz). \(^{13}\)C NMR (125 MHz, DMSO-\(d_6\)): \(\delta\) 144.6, 143.8, 138.0, 136.4, 122.6, 118.6, 115.2; Anal. for \(\text{C}_{26}\text{H}_{20}\text{O}_8\): Calcd. for C, 67.82; H, 4.38; Found: C, 65.51; H, 4.43; HRMS for \([\text{C}_{26}\text{H}_{21}\text{O}_8]^+\): Calcd. for 461.1231. Found: 461.1231.

**Synthesis of the network polymer-MP1.** 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetrakis(benzene-1,2-diol) (460 mg, 1.00 mmol) and 2,3,5,6-tetrafluoroterephthalonitrile (400 mg, 2.00 mmol) were dissolved in anhydrous DMAc (2.7 mL). The solution was heated to 80 °C and fine \(\text{K}_2\text{CO}_3\) (690 mg, 5.00 mmol) powder was added. The reaction system was then heated to 120 °C and kept for 6 h. The system was then poured into 2N HCl (30 mL) and stirred for 1 h at room temperature. The solid was collected by filtration, washed with water, acetone, THF and acetone to remove trace insoluble inorganic materials. The product (700 mg, yield: 99%) was obtained as a yellow powder after drying in vacuum oven at 80 °C for 24 h. \(^{13}\)CP-MAS (100 MHz, ppm): \(\delta\) 140, 128, 118, 108, 94; \(T_d\) onset = 450 °C; FT-IR (film, \(\nu\), cm\(^{-1}\)): 2242 (m, C≡N), 1594 (m, aromatic C-H vibration), 1500, 1453, 1410, (s, asymetric vibration of C=C of benzene), 1251 (s, vibration of C-O-C), 1000 (s, vibration of C-F bond); Anal for \(\text{C}_{42}\text{H}_{12}\text{N}_4\text{O}_8\). Calcd. for. C, 71.19; H, 1.70; N, 7.91; Found: C, 67.95; H, 1.85; N, 8.04; \(S_{\text{BET}} = 1020\) m\(^2\) g\(^{-1}\).
**Synthesis of the network polymer-MP2.** Ball-milled MP1 fine powder (500 mg, 0.706 mmol repeat unit) was dispersed in 10 mL ethanol and stirred at room temperature for 10 min. To it, KOH (4.10 g, 70.6 mmol) dissolved in water (10 mL) was added dropwise. The system was refluxed for 48 h and then poured into 300 mL water and acidified with HCl (4N). The solid was collected by filtration and dried in vacuum oven at 40 °C for 24 h. $^{13}$CP-MAS (100 MHz, ppm): $\delta$ 164.7, 140, 128, 118; T_d onset = 320 °C; FT-IR (film, $\nu$, cm$^{-1}$): 3500 - 3100 (br, vibration of COOH), 1671, 1600 (s, vibration of C=O), 1502, 1440 (s, asymmetric vibration of C=C of benzene), 1251 (s, vibration of C-O-C), 1000 (s, vibration of C-F bond); Anal. for. C$_{42}$H$_{16}$O$_{16}$, Calcd. for. C, 64.29; H, 2.05; Found: C, 63.93; H, 2.93; N, 1.87; $S_{BET} = 150 \text{ m}^2 \text{ g}^{-1}$.

**Isosteric Heat of Adsorption:**

The isosteric heat of adsorption ($Q_{st}$) of CO$_2$ for MP1 and MP2 were calculated according to the Clausius-Clapeyron equation from the measured absolute isotherms at 273 and 298 K, respectively:

$$\ln p = \frac{Q_{st}}{RT} + C$$

where $p$ is the equilibrium pressure, $Q_{st}$ is the isostatic heat of adsorption, $R$ is the ideal gas constant, $T$ is the testing temperature, $C$ is a constant. By measuring two temperatures of adsorption, the $Q_{st}$ can be obtained using the following equation:

$$Q_{st} = R \times \frac{(T_2 - T_1)}{T_1 \times T_2} \times \ln \frac{P_1}{P_2}$$
Figure S1. The heat of sorption of CO\textsubscript{2} for MP1 and MP2 with different CO\textsubscript{2} capacities.

**CO\textsubscript{2}/N\textsubscript{2} and CO\textsubscript{2}/CH\textsubscript{4} Selectivity Calculation by Ideal Adsorbed Solution Theory (IAST)**

The ideal adsorbed solution theory (IAST) calculation for N\textsubscript{2} can be performed using a single-site Langmuir model to fit the adsorption isotherms.

\[
q = \frac{q_{\text{sat}} b p}{1 + b p}
\]

The ideal adsorbed solution theory (IAST) calculations of MP1 and MP2 for CO\textsubscript{2} and CH\textsubscript{4} can be carried out using a dual-site (site A and site B) Langmuir model to fit the adsorption isotherms; the double Langmuir model follows: \cite{2}

\[
q = q_A + q_B = \frac{q_{\text{sat}, A} b_A P}{1 + b_A p} + \frac{q_{\text{sat}, B} b_B P}{1 + b_B p}
\]

where \( q_A \) and \( q_B \) are the molar adsorption capacity of the site A and site B (mmol g\textsuperscript{-1}); \( q_{\text{sat}, A} \) and \( q_{\text{sat}, B} \) are saturated adsorption capacity of site A and site B, \( b_A \) and \( b_B \) are the Langmuir constant of site A and site B (bar\textsuperscript{-1}); \( p \) is feeding gas pressure (bar).

The fitting parameters obtained from the dual-site Langmuir model given in Table S1 were used for the calculation of IAST selectivity. The IAST gives an analytic relationship of two functions \( q_1(p) \) and \( q_2(p) \) for two different gases by:
\[
\int_0^{p_1} x_t q_1(p) d\ln p = \int_0^{p_2} x_t q_2(p) d\ln p
\]

where \(p_t\) is the total pressure of the gas mixture, \(y_i\) the mole fraction of component \(i\) in the gas phase and \(x_i\) the mole fraction of component \(i\) in the network phase. Integration of the above equation with two single-site Langmuir functions leads to:

\[
q_{sat1} \ln(1+b_1 \frac{P_i y_1}{x_1}) = q_{sat2} \ln(1+b_2 \frac{P_i y_2}{x_2})
\]

In which, \(q_{sat1}, q_{sat2}, b_1\) and \(b_2\) were obtained from the fitting curve of IAST curve, where

\[
x_1 + y_1 = 1
\]

where \(x_1, x_2, p_t\) values can be calculated using the software Mathematica 9 (Wolfram, UK); the selectivity can be obtained via:

\[
S = \frac{x_1}{x_2} / \frac{y_1}{y_2}
\]

**Table S1. Fitting Parameters of IAST Plots.**

| Polymer | Gas | \(q_{sat,A}\) mmol g\(^{-1}\) | \(b_A\) bar\(^{-1}\) | \(q_{sat,B}\) mmol g\(^{-1}\) | \(b_B\) bar\(^{-1}\) |
|---------|-----|-------------------------------|------------------|-------------------------------|------------------|
| MP1     | N\(_2\) | 4.731                         | 0.0650           | -                             | -                |
| 273 K    | CH\(_4\) | 1.203                         | 0.8640           | 8.752                         | 0.0615           |
|          | CO\(_2\) | 1.336                         | 8.156            | 6.981                         | 0.7801           |
| MP1     | N\(_2\) | 116.6                         | 0.0014           | -                             | -                |
| 298 K    | CH\(_4\) | 1.410                         | 0.2201           | 1.961                         | 0.2201           |
|          | CO\(_2\) | 0.987                         | 3.130            | 6.741                         | 0.3731           |
| MP2     | N\(_2\) | 2.357                         | 0.075            | -                             | -                |
| 273 K    | CH\(_4\) | 0.556                         | 1.723            | 32.54                         | 0.008            |
|          | CO\(_2\) | 2.642                         | 4.445            | -                             | -                |
| MP2     | N\(_2\) | 143.5                         | 6.411            | -                             | -                |
| 298 K    | CH\(_4\) | 5.300                         | 0.0186           | 0.7814                        | 0.5575           |
|          | CO\(_2\) | 2.248                         | 0.7111           | 0.6508                        | 7.013            |
Details of the Breakthrough Experiments

The breakthrough separation experiments were conducted using a custom-made set-up as illustrated in Figure S2:

![Figure S2. Schematic set-up for breakthrough experiments.](image)

The absolute adsorbed amount of gas $i$ ($q_i$) was calculated from the breakthrough curve by the equation:

$$q_i = \frac{F_i \times t_0 - V_{\text{dead}} - \int_{0}^{t_0} F_e \Delta t}{m}$$

where $F_i$ is the flow rate of the specific gas ($\text{cm}^3 \text{ min}^{-1}$); $t_0$ is the adsorption time (min); $V_{\text{dead}}$ is the dead volume of the system ($\text{cm}^3$); $F_e$ is the flow rate of the specific gas ($\text{cm}^3 \text{ min}^{-1}$); $m$ is the mass of the tested adsorbent (g).

The selectivity of the breakthrough experiment was determined by $\alpha_{i/j} = (q_i/y_i)/(q_j/y_j)$, where $y_i$ is the mole fraction of gas $i$ in the gas mixture.
The breakthrough experiments were performed as follows: MP1 and MP2 were grounded to small particles using a ball mill, and then filled into a quartz tube (5.8 mm, I. D. × 150 mm) with silica wool filling the void space. The MP1 and MP2 in the tube were activated at 200 °C for 1 h with a helium flow rate of 10 mL min⁻¹. The test temperature was 25 °C. Then, the flow of helium was turned off and a gas mixture of N₂/CO₂ (85/15) at a flow rate of 10 mL/min was sent to the column. The effluent gas mixture from the column was monitored by a mass spectroscopy. The dead time (dead volume) was determined after adsorption saturated using the same column. All breakthrough experiments were repeated three times by regeneration of the samples.

References

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(2) Myers, A. L; Prausnitz, J. M., Thermodynamics of Mixed-Gas Adsorption. *AIChE J.* **1965**, *11*, 121-127.