

## Supporting Information

### **A robust doubly interpenetrated metal–organic framework constructed from a novel aromatic tricarboxylate for highly selective separation of small hydrocarbons**

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#### **General remark**

All reagents and solvents were used as received from commercial suppliers without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 MHz spectrometer. Tetramethylsilane (TMS) and deuterated solvents (CDCl<sub>3</sub>,  $\delta = 77.0$  ppm; DMSO-*d*<sub>6</sub>,  $\delta = 39.5$  ppm) were used as internal standards in <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments, respectively. The coupling constants were reported in Hertz. FTIR spectra were performed on a Bruker Vector 22 spectrometer at room temperature. The elemental analyses were performed with Perkin–Elmer 240 CHN analyzers from Galbraith Laboratories, Knoxville. Thermogravimetric analyses (TGA) were measured using a Shimadzu TGA-50 analyzer under a nitrogen atmosphere with a heating rate of 3 °C min<sup>-1</sup>. Powder X–ray diffraction (PXRD) patterns were recorded by a Rigaku Ultima IV diffractometer operated at 40 kV and 44 mA with a scan rate of 1.0 deg min<sup>-1</sup>. The crystallographic measurement was made on a Bruker SMART Apex II CCD–based X–ray diffractometer system equipped with a Mo–target X-ray tube ( $\lambda = 0.71073$  Å) operated at 2000 watts power (50 kV, 40 mA). The structure was solved by direct method and refined to convergence by least squares method on  $F^2$  using the SHELXTL software suit. A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To have a guest–free framework, the fresh sample was guest–exchanged with

dry acetone at least 10 times, filtered and vacuumed at 60 °C until the outgas rate was 5  $\mu\text{mHg min}^{-1}$  prior to measurements. A sample of 102.6 mg was used for the sorption measurements and was maintained at 77 K with liquid nitrogen, at 273 K with an ice–water bath. As the center–controlled air conditioner was set up at 23 °C, a water bath was used for adsorption isotherms at 296 K.

## Fits of pure-component isotherms

The measured experimental data on pure–component isotherms for  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_3\text{H}_8$  at 273 K, and 296 K in the **UTSA-35a** were first converted to absolute loadings using the Peng–Robinson equation of state for estimation of the fluid densities. The experimentally measured pore volume of 0.3133  $\text{cm}^3 \text{g}^{-1}$  was used for this purpose. Depending on the guest–host combination, the isotherm model of choice is either a 1-site Langmuir (SSL) model:

$$q = \frac{q_{\text{sat}} b p}{1 + b p}; \quad b = b_0 \exp\left(\frac{E}{RT}\right)$$

or a 2-site Langmuir (DSL) model

$$q \equiv q_A + q_B = \frac{q_{\text{sat},A} b_A p}{1 + b_A p} + \frac{q_{\text{sat},B} b_B p}{1 + b_B p}; \quad b_A = b_{A0} \exp\left(\frac{E_A}{RT}\right); \quad b_B = b_{B0} \exp\left(\frac{E_B}{RT}\right)$$

The selected isotherm models along with the fit parameters are specified in *Table S2*. *Figure S8* compares the experimental loadings with the isotherm fits for each hydrocarbon species. There is excellent agreement for each species over the entire range of pressures at both temperatures.

## Isosteric heats of adsorption

The isosteric heat of adsorption,  $Q_{\text{st}}$ , defined as

$$Q_{\text{st}} = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_q$$

was determined using the pure–component isotherm fits. The procedure for calculation of  $Q_{\text{st}}$  is the same as that described in the Supporting Information accompanying the paper by Mason et al.<sup>[1]</sup>  $Q_{\text{st}}$  is

a function of the loading. The loading dependences of  $Q_{st}$  for various hydrocarbons are compared in *Figure S9*.

## IAST calculations of adsorption selectivities

In order to determine the adsorption selectivities of different hydrocarbons  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_3H_6$ ,  $C_3H_8$  with respect to  $CH_4$ , 6-component mixture adsorption equilibrium was determined using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.<sup>[2]</sup> The bulk gas phase was assumed to be equimolar, with equal partial pressures of each of the six components. For each of the hydrocarbons, using the pure component isotherm fits, the adsorption selectivities were determined from

$$S_{ads} = \frac{q_{Hydrocarbon}/p_{Hydrocarbon}}{q_{CH_4}/p_{CH_4}}$$

The accuracy of the IAST calculations for estimation of the component loadings for several binary mixtures in a wide variety of zeolites, and MOF materials has been established by comparison with Configurational-Bias Monte Carlo (CBMC) simulations of mixture adsorption.<sup>[3-5]</sup>

## Breakthrough calculations

In order to demonstrate the feasibility of the use of **UTSA-35a** for separation of  $CH_4$  from other hydrocarbons in a PSA unit, we performed transient breakthrough calculations following the methodologies developed and described in earlier works.<sup>[6-8]</sup> *Figure S10* shows a schematic of a packed bed adsorber. Assuming plug flow of the gas mixture through the fixed bed maintained under isothermal conditions and negligible pressure drop, the partial pressures in the gas phase at any position and instant of time are obtained by solving the following set of partial differential equations for each of the species  $i$  in the gas mixture.

$$\frac{1}{RT} \varepsilon \frac{\partial p_i(t, z)}{\partial t} = -\frac{1}{RT} \frac{\partial (u(t, z) p_i(t, z))}{\partial z} - (1 - \varepsilon) \rho \frac{\partial q_i(t, z)}{\partial t}; \quad i = 1, 2, \dots, n \quad (1)$$

In the equation (1),  $t$  is the time,  $z$  is the distance along the adsorber,  $\rho$  is the framework density,  $\varepsilon$  is the bed voidage, and  $u$  is the superficial gas velocity. The molar loadings of the species  $i$ ,  $q_i(z, t)$  at any

position  $z$ , and time  $t$  are determined from IAST calculations. The adsorber bed is initially free of adsorbates, i.e. we have the initial condition

$$t = 0; \quad q_i(0, z) = 0$$

At time,  $t = 0$ , the inlet to the adsorber,  $z = 0$ , is subjected to a step input of the 6-component gas mixture and this step input is maintained till the end of the adsorption cycle when steady-state conditions are reached.

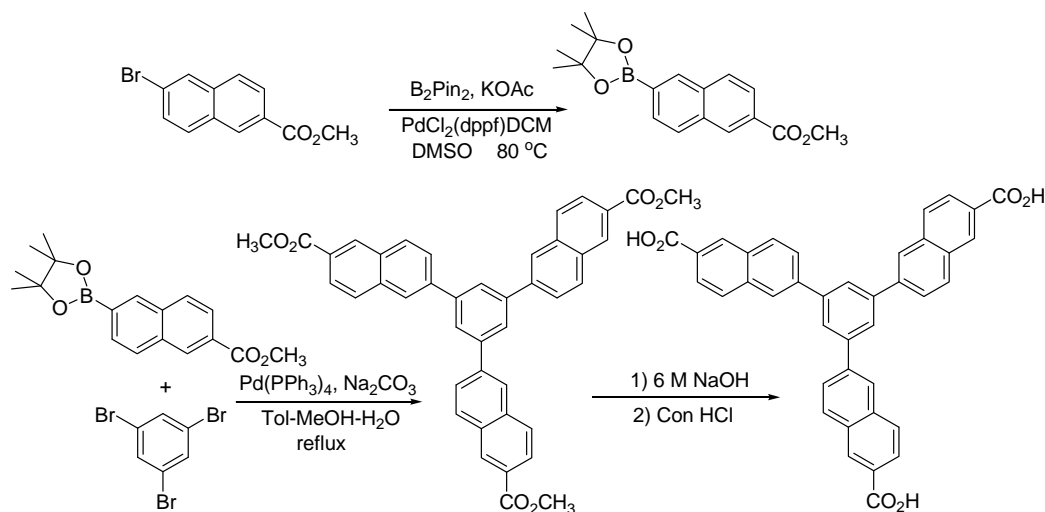
$$t \geq 0; \quad p_i(0, t) = p_{i0}; \quad u(0, t) = u_0$$

where  $u_0$  is the superficial gas velocity at the inlet to the adsorber. Invoking the constraint of negligible pressure drop, the overall material balance is obtained by summing equation (1) over the six component species.

$$\frac{1}{RT} p_i \frac{\partial(u(t, z))}{\partial z} = -(1 - \varepsilon) \rho \frac{\partial q_i(t, z)}{\partial t} \quad (2)$$

Equation (2) allows the calculation of the gas velocity  $u$  along the length of the adsorber. In the breakthrough calculation the following parameter values were used:  $L = 0.12$  m;  $\varepsilon = 0.75$ ;  $u = 0.00225$  m s<sup>-1</sup> (at inlet). The framework density of **UTSA-35a** is 1046 kg m<sup>-3</sup>.

### Synthesis and characterization of the organic building block (**H<sub>3</sub>BTN**)



**Scheme S1.** Synthetic route to the organic building block **H<sub>3</sub>BTN**.

**Methyl 6-(pinacolboronyl)-2-naphthoate:** A mixture of methyl 6-bromo-2-naphthoate (15.00 g, 56.58 mmol, Alfa), B<sub>2</sub>Pin<sub>2</sub> (15.80 g, 62.22 mmol, Aldrich), KOAc (16.66 g, 169.76 mmol, Aldrich) and

PdCl<sub>2</sub>(dppf)·CH<sub>2</sub>Cl<sub>2</sub> (1.38 g, 1.69 mmol, Alfa) in dry DMSO (340 mL) was heated with stirring at 80 °C for 12 h under a nitrogen atmosphere. After removal of the solvents, CH<sub>2</sub>Cl<sub>2</sub> (400 mL) and H<sub>2</sub>O (200 mL) were added. The organic layer was separated and the aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL × 2). The combined organic phase was washed with brine (150 mL), dried over anhydrous MgSO<sub>4</sub>, filtered and concentrated to dryness. The residue was purified by silica gel column chromatography using hexane/ethyl acetate as eluent to give methyl 6-(pinacolboryl)-2-naphthoate as a pure white solid in 91% yield (16.07 g, 51.48 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.0 MHz) δ (ppm): 8.60 (s, 1H), 8.40 (s, 1H), 8.06 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.91-7.94 (m, 3H), 4.00 (s, 3H), 1.42 (s, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.4 MHz) δ (ppm): 167.03, 135.72, 134.64, 133.88, 131.06, 130.69, 128.74, 128.23, 128.16, 125.07, 84.12, 52.31; selected FTIR (neat, cm<sup>-1</sup>): 2976, 1709, 1598, 1485, 1437, 1379, 1338, 1287, 1268, 1230, 1177, 1129, 1095, 1080, 963, 917, 854, 842, 821, 779, 757, 703, 686, 672.

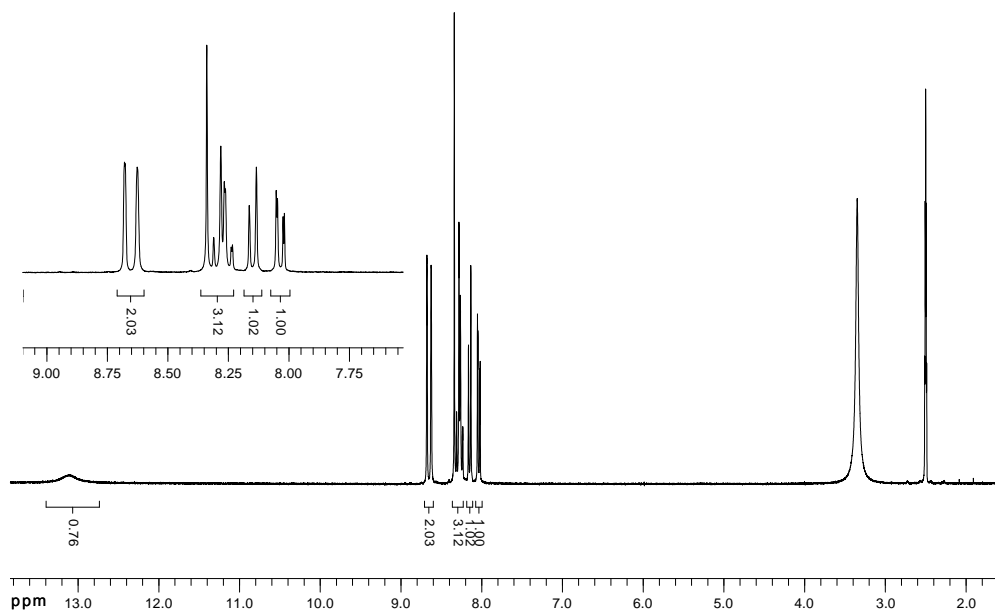
**1,3,5-tri(6-methoxycarbonylnaphthalen-2-yl)benzene:** To a mixture of 1,3,5-tribromobenzene (3.00 g, 9.53 mmol, Aldrich), methyl 6-(pinacolboryl)-2-naphthoate (11.90 g, 38.12 mmol), Na<sub>2</sub>CO<sub>3</sub> (12.12 g, 114.35 mmol, Alfa), and Pd(PPh<sub>3</sub>)<sub>4</sub> (1.10 g, 0.95 mmol, TCI) were added degassed toluene–methanol–water mixed solvents (200/60/60 mL). The resulting reaction mixture was stirred for 48 h under reflux under a nitrogen atmosphere. After removal of the solvents, the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 × 3 mL), washed with brine (80 mL), dried over anhydrous MgSO<sub>4</sub>, filtrated, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography using dichloromethane as eluent to give 1,3,5-tri(6-methoxycarbonylnaphthalen-2-yl)benzene as a white solid in 88% yield (5.27 g, 8.36 mmol). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.0 MHz) δ (ppm): 8.68 (s, 3H), 8.23 (s, 3H), 8.08-8.15 (m, 9H), 7.94-8.01 (m, 6H), 4.03 (s, 9H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.4 MHz) δ (ppm): 166.99, 142.04, 140.37, 135.66, 131.76, 130.75, 130.03, 128.35, 127.54, 126.31, 126.09, 125.85, 125.82, 52.35; selected FTIR (neat, cm<sup>-1</sup>): 2951, 1716, 1630, 1591, 1482, 1435, 1388, 1333, 1279, 1246, 1206, 1181, 1135, 1097, 1047, 993, 958, 910, 868, 804, 783, 769, 746, 700, 673.

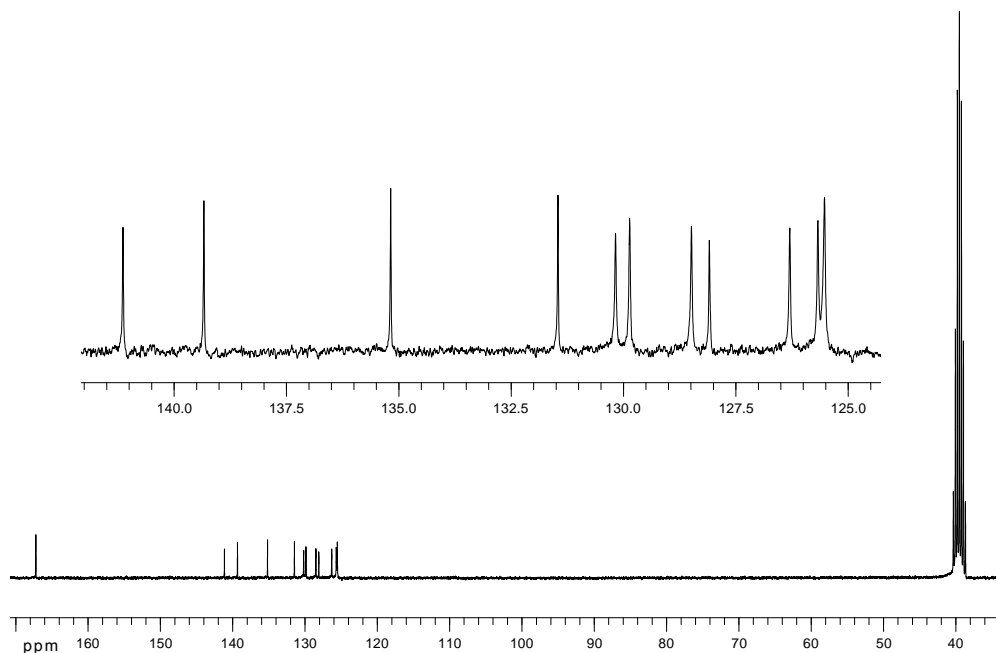
**1,3,5-tri(6-hydroxycarbonylnaphthalen-2-yl)benzene (H<sub>3</sub>BTN):** To 1,3,5-tri(6-methoxycarbonylnaphthalen-2-yl)benzene (5.00 g, 7.93 mmol) in MeOH/THF (100/50 mL) was added 6 M NaOH aqueous solution (60 mL, 360 mmol). The resulting mixture was refluxed overnight. After removal of the solvents, the residue was dissolved in water and filtered. The filtrate was neutralized with concentrated HCl (36%) in ice-water bath. The precipitation was collected by filtration, washed with water and dried in *vacuo* at 90 °C to give the organic building block H<sub>3</sub>BTN as an off-white solid in

99% yield (4.61 g, 7.83 mmol).  $^1\text{H}$  NMR (DMSO- $d_6$ , 300.0 MHz)  $\delta$  (ppm): 13.13 (s, 3H), 8.66 (d,  $J = 15.6$  Hz, 6H), 8.35 (s, 3H), 8.24-8.32 (m, 6H), 8.16 (d,  $J = 8.7$  Hz, 3H), 8.03-8.06 (m, 3H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 75.4 MHz)  $\delta$  (ppm): 167.21, 141.15, 139.35, 135.19, 131.47, 130.19, 129.88, 128.50, 128.10, 126.31, 125.68, 125.54; selected FTIR (neat,  $\text{cm}^{-1}$ ): 1679, 1625, 1575, 1512, 1481, 1438, 1401, 1239, 1201, 1131, 957, 909, 870, 806, 770, 749, 715.

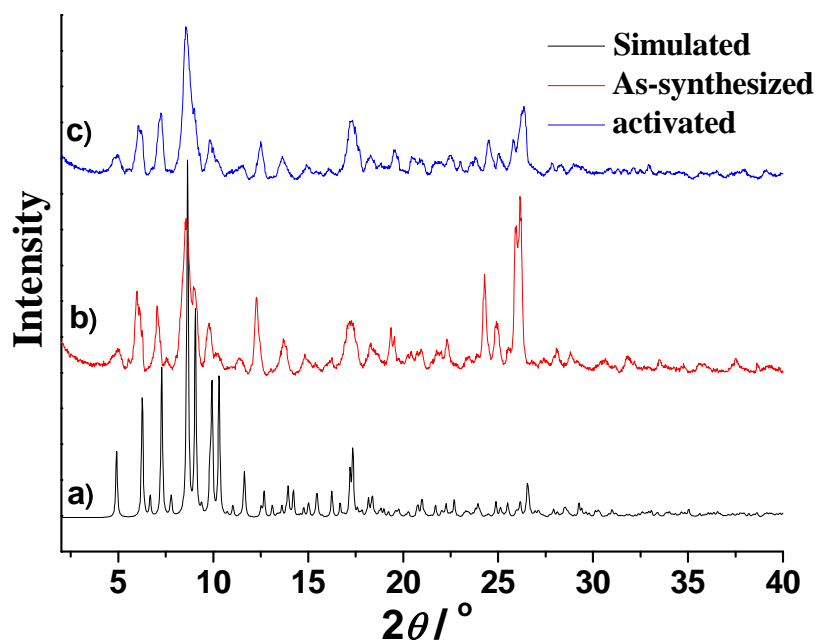
## Synthesis and characterization of UTSA-35

A mixture of the organic linker H<sub>3</sub>BTN (10 mg, 17.0  $\mu\text{mol}$ ) and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (20 mg, 64.8  $\mu\text{mol}$ ) was dissolved in DMF (1.5 mL) and heated in a disposable scintillation vial (20 mL) at 100 °C for 24 h. The block-shaped crystals were collected in 66% yield. **UTSA-35** was best formulated as Cd<sub>3</sub>(BTN)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>(DMF)<sub>6</sub> on the basis of the single-crystal structure determination, TGA, and microanalysis. Selected FTIR (neat,  $\text{cm}^{-1}$ ): 1645, 1543, 1478, 1437, 1386, 1253, 1214, 1093, 918, 874, 816, 780, 751, 704; TGA data: Calcd. weight loss for 6DMF and 3H<sub>2</sub>O: 24.6%, Found: 24.9%; Anal. for C<sub>96</sub>H<sub>90</sub>N<sub>6</sub>O<sub>21</sub>Cd<sub>3</sub>: C, 57.62; H, 4.53; N, 4.20, Found: C, 57.55%; H, 4.62%; N, 4.11%.

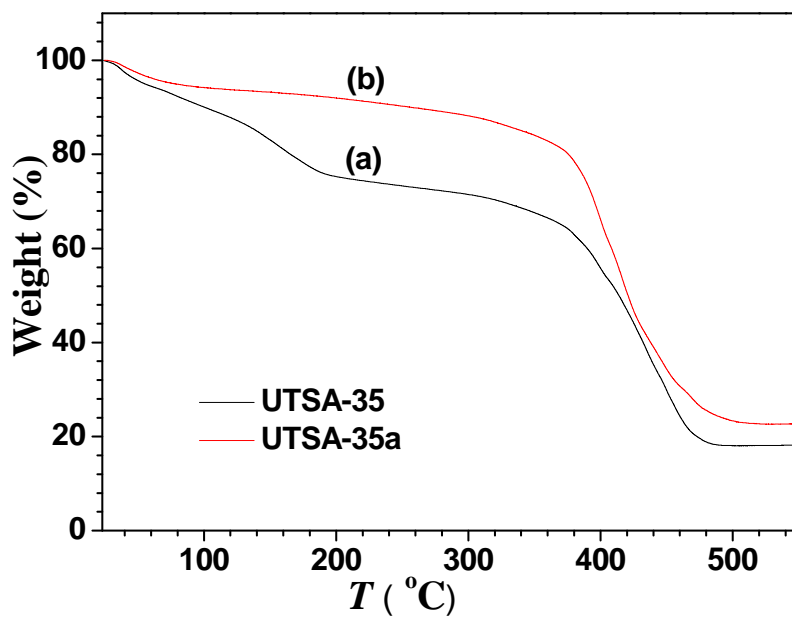




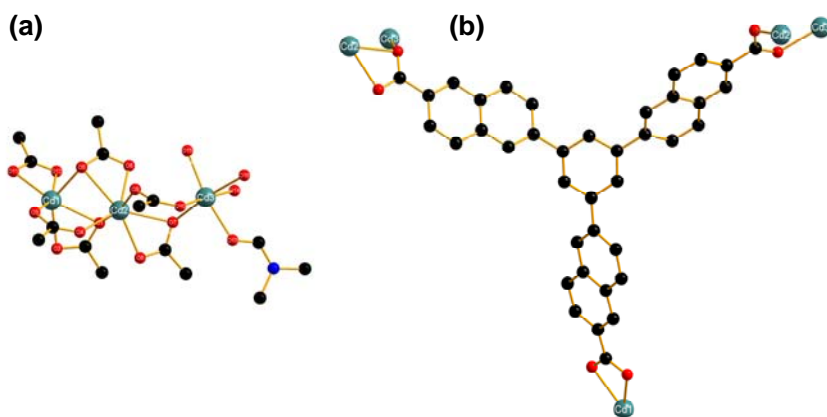
**Figure S0.** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300.0 MHz) and <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75.4 MHz) spectra of the organic linker H<sub>3</sub>BTN.



**Figure S1.** PXRD patterns of as-synthesized UTSA-35 (b) and activated UTSA-35a (c) along with the simulated XRD pattern from its single-crystal X-ray structure (a).

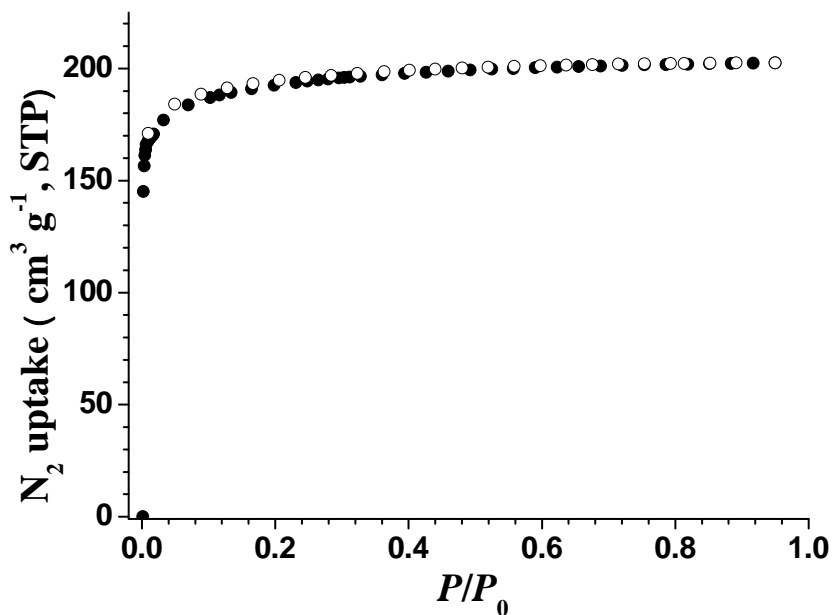


**Figure S2.** TGA curves of as-synthesized UTSA-35 (a) and activated UTSA-35a (b).

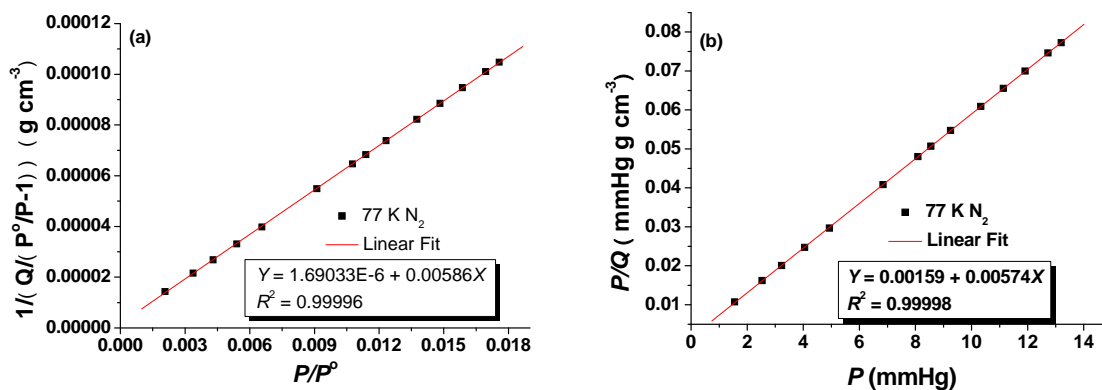


**Figure S3.** The tricadmium-carboxylate cluster (a) and the different coordination modes ( $\eta^2$ ,  $\mu_2-\eta^1:\eta^1$ ,  $\mu_2-\eta^2:\eta^1$ ) of three carboxylate groups of the organic linker (b).





**Figure S4.** N<sub>2</sub> sorption isotherm of **UTSA-35a** at 77 K. Solid symbols: adsorption, open symbols: desorption.



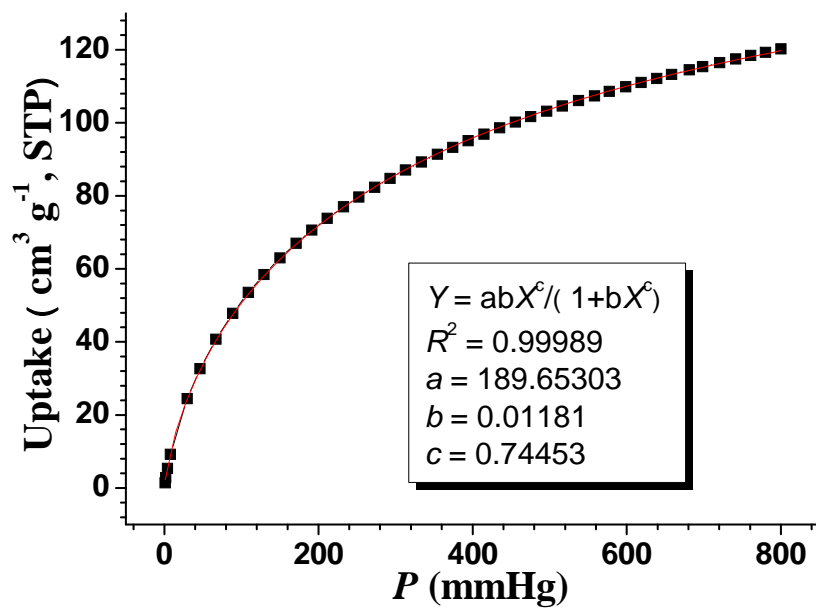
$$S_{\text{BET}} = (1/(1.69033 \times 10^{-6} + 0.00586))/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 742.7 \text{ m}^2 \text{ g}^{-1}$$

$$S_{\text{Langmuir}} = (1/0.00574)/22414 \times 6.023 \times 10^{23} \times 0.162 \times 10^{-18} = 758.4 \text{ m}^2 \text{ g}^{-1}$$

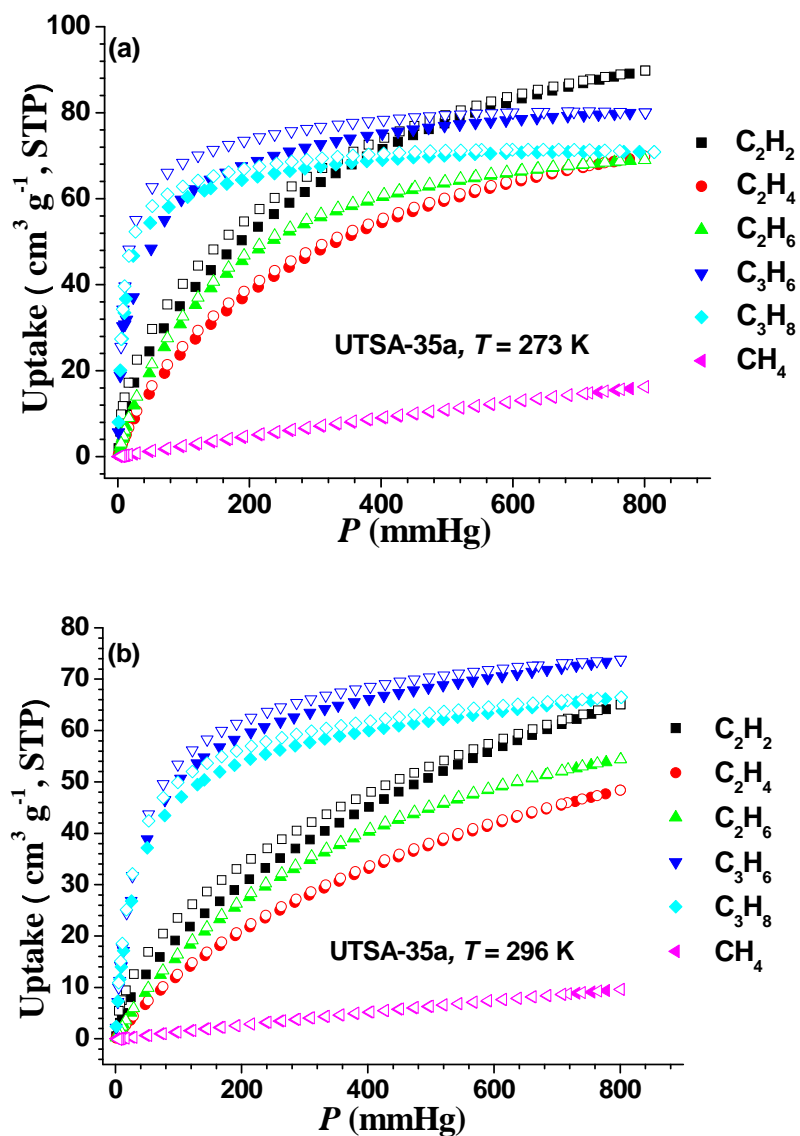
$$\text{BET constant} = 1 + 0.00586/(1.69033 \times 10^{-6}) = 3467.8$$

$$\text{Langmuir constant} = 0.00574/0.00159 = 3.6 \text{ mmHg}^{-1} = 2.7 \times 10^{-2} \text{ Pa}^{-1}$$

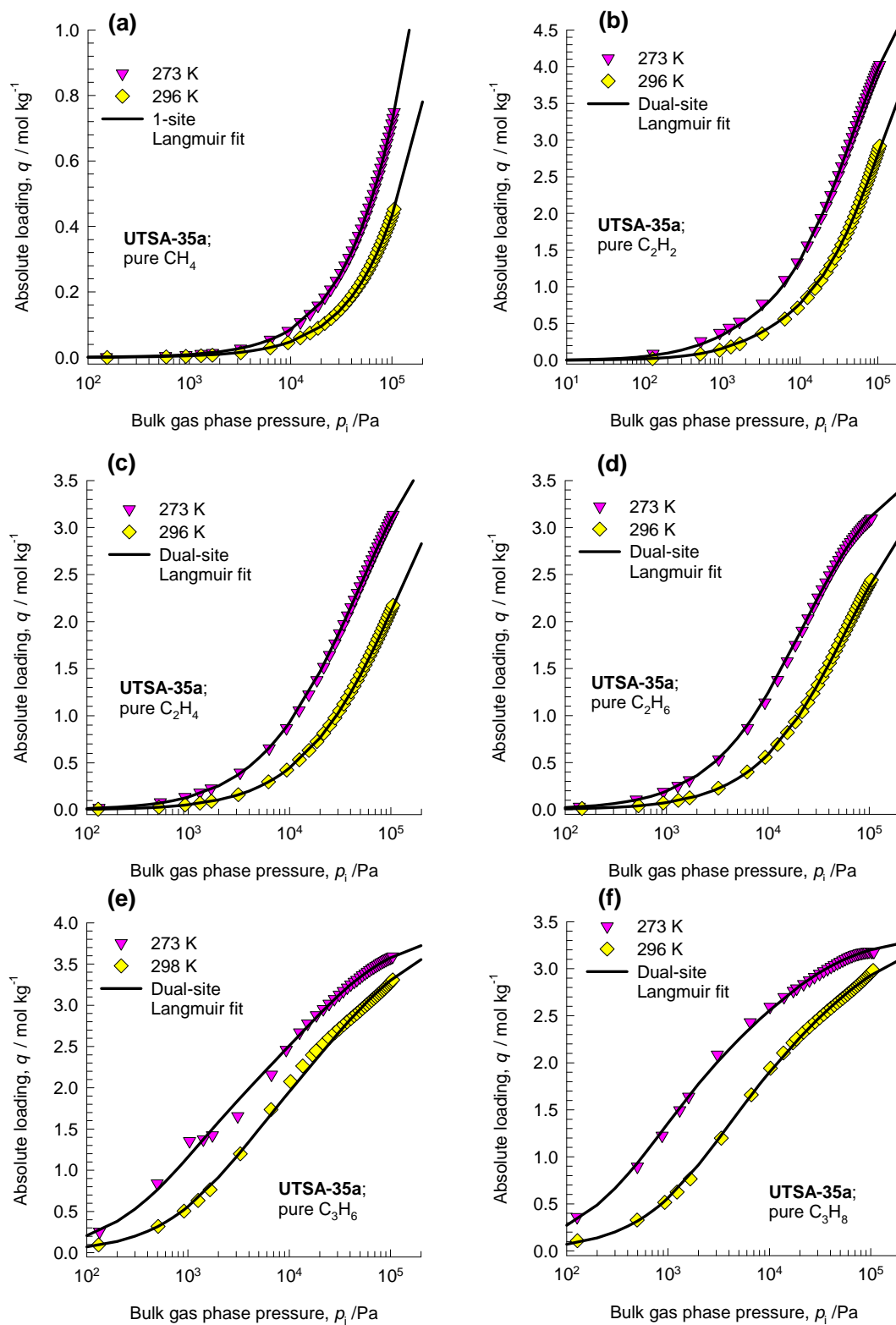
**Figure S5.** The BET (a) and Langmuir (b) surface areas of **UTSA-35a** obtained from N<sub>2</sub> adsorption isotherm at 77 K.



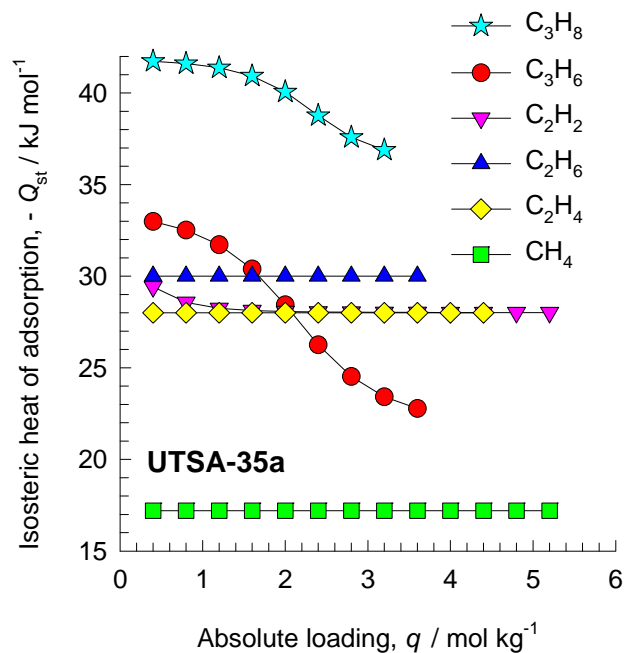
**Figure S6.** Fitting the hydrogen isotherm data with Langmuir–Freudlium equation, from which the maximum H<sub>2</sub> adsorption amount of 189.7 cm<sup>3</sup> g<sup>-1</sup> (STP) (1.7 wt%) at 77 K can be predicted.



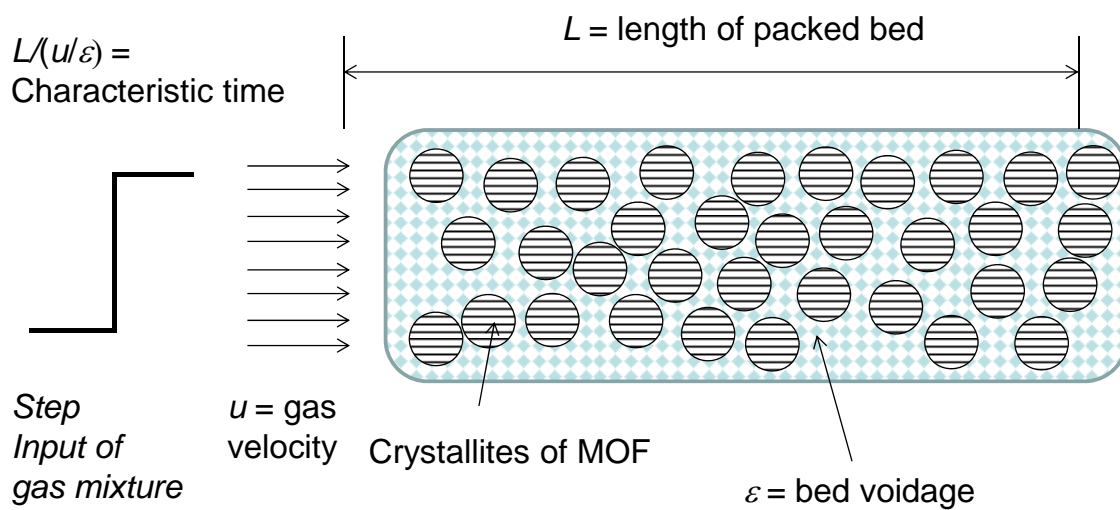
**Figure S7.** Single-component sorption isotherms of various hydrocarbons in UTSA-35a at 273 K (a), and 296 K (b). Solid symbols: adsorption, open symbols: desorption.



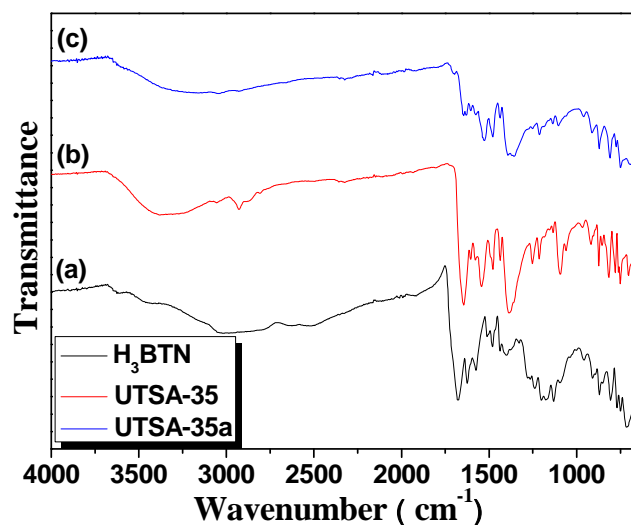
**Figure S8.** Comparison of the experimentally determined absolute loadings with the Langmuir isotherm fits. The continuous solid lines are the Langmuir fits using the parameters in Table S2.



**Figure S9.** Comparison of the loading dependences of the isosteric heats of adsorption of different hydrocarbons in **UTSA-35a**.



**Figure S10.** Schematic of a packed bed adsorber.



**Figure S11.** FTIR spectra of the organic building block H<sub>3</sub>BTN (a), as-synthesized UTSA-35 (b) and activated UTSA-35a (c).

**Table S1.** Crystal data and structure refinement for UTSA-35

Empirical formula	C <sub>84</sub> H <sub>62</sub> Cd <sub>3</sub> N <sub>2</sub> O <sub>17</sub>
Formula weight	2001.00
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>
Unit cell dimensions	<i>a</i> = 14.306(2) Å $\alpha$ = 90° <i>b</i> = 19.509(3) Å $\beta$ = 99.6290(9)° <i>c</i> = 36.482(5) Å $\gamma$ = 90°
Volume (Å <sup>3</sup> )	10039(2)
Z, Calculated density (Mg m <sup>-3</sup> )	4, 1.324
Absorption coefficient (mm <sup>-1</sup> )	0.683
<i>F</i> (000)	3440
Crystal size (mm)	0.37 × 0.20 × 0.17
$\theta$ range for data collection	2.55 to 25.66°
Limiting indices	-17 ≤ <i>h</i> ≤ 17, -23 ≤ <i>k</i> ≤ 23, -44 ≤ <i>l</i> ≤ 44
Reflections collected / unique	32711 / 18251 ( <i>R</i> <sub>int</sub> = 0.0513)
Completeness to $\theta$ = 25.66°	95.8 %
Max. and min. transmission	0.8928 and 0.7862
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	18251 / 0 / 907
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.022
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0594, <i>wR</i> <sub>2</sub> = 0.1586
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.1090, <i>wR</i> <sub>2</sub> = 0.1744
Largest diff. peak and hole (e.Å <sup>-3</sup> )	1.979 and -0.901
CCDC No.	868753

**Table S2.** Isotherm fit parameters for **UTSA-35a**.

Adsorbate	Site A			Site B		
	$q_{\text{sat,A}}$ mol kg <sup>-1</sup>	$b_{A0}$ Pa <sup>-1</sup>	$E_A$ kJ mol <sup>-1</sup>	$q_{\text{sat,B}}$ mol kg <sup>-1</sup>	$b_{B0}$ Pa <sup>-1</sup>	$E_B$ kJ mol <sup>-1</sup>
CH <sub>4</sub>	4	$1.12 \times 10^{-9}$	17.2			
C <sub>2</sub> H <sub>2</sub>	5.05	$9.7 \times 10^{-11}$	28	0.5	$1.04 \times 10^{-9}$	31
C <sub>2</sub> H <sub>4</sub>	4	$8.33 \times 10^{-11}$	28	0.5	$6.08 \times 10^{-10}$	28
C <sub>2</sub> H <sub>6</sub>	3.65	$8.45 \times 10^{-11}$	30	0.1	$9.02 \times 10^{-10}$	30
C <sub>3</sub> H <sub>6</sub>	1.8	$3.78 \times 10^{-9}$	21.5	2.1	$3.28 \times 10^{-10}$	34
C <sub>3</sub> H <sub>8</sub>	1.11	$9.37 \times 10^{-12}$	36	2.25	$1.22 \times 10^{-11}$	42

### Notation

$b_i$	dual-site Langmuir constant for species $i$ , Pa <sup>-1</sup>
$L$	length of packed bed adsorber, m
$n$	number of components in mixture, dimensionless
$p_i$	bulk gas pressure of species $i$ , Pa
$q_i$	component molar loading of species $i$ , mol kg <sup>-1</sup>
$q_t$	total mixture loading, mol kg <sup>-1</sup>
$q_{i,\text{sat}}$	saturation loading of species $i$ , mol kg <sup>-1</sup>
$t$	time, s
$T$	temperature, K
$u$	superficial gas velocity, m s <sup>-1</sup>

### Greek letters

$\varepsilon$	voidage of packed bed, dimensionless
$\tau$	dimensionless time
$\tau_{\text{break}}$	breakthrough time, dimensionless

### Subscripts

$i$	referring to component $i$
A	referring to site A
B	referring to site B

## Reference

- [1] Mason, J. A., Sumida, K., Herm, Z. R., Krishna, R. & Long, J. R. Evaluating Metal–Organic Frameworks for Post-Combustion Carbon Dioxide Capture *via* Temperature Swing Adsorption. *Energy Environ. Sci.* **3**, 3030–3040 (2011).
- [2] Myers, A. L. & Prausnitz, J. M. Thermodynamics of mixed gas adsorption. *A.I.Ch.E.J.* **11**, 121–130 (1965).
- [3] Krishna, R. & van Baten, J. M. Using molecular simulations for screening of zeolites for separation of CO<sub>2</sub>/CH<sub>4</sub> mixtures. *Chem. Eng. J.* **133**, 121–131 (2007).
- [4] Krishna, R. & van Baten, J. M. In Silico Screening of Zeolite Membranes for CO<sub>2</sub> Capture. *J. Membr. Sci.* **360**, 323–333 (2010).
- [5] Krishna, R. & van Baten, J. M. In silico screening of metal–organic frameworks in separation applications. *Phys. Chem. Chem. Phys.* **13**, 10593–10616 (2011).
- [6] Krishna, R. & Long, J. R. Screening metal–organic frameworks by analysis of transient breakthrough of gas mixtures in a fixed bed adsorber. *J. Phys. Chem. C* **115**, 12941–12950 (2011).
- [7] Krishna, R. & van Baten, J. M. A comparison of the CO<sub>2</sub> capture characteristics of zeolites and metal–organic frameworks. *Sep. Purif. Technol.* **87**, 120–126 (2012).
- [8] Krishna, R. & Baur, R. Modelling issues in zeolite based separation processes. *Sep. Purif. Technol.* **33**, 213–254 (2003).