# Overcoming Mass Transfer Limitations in Cross-Linked Polyethyleneimine-Based Adsorbents to Enable Selective $CO_2$ Capture at Ambient Temperature

**Supporting Information**

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**Table S1.** Sample sizes used for surface areas measurements, BET surface areas and $P/P_0$ range in which surface areas calculated.

| Sample | Mass (g) | $P/P_0$ range | Surface area ($m^2/g$) |
|---|---|---|---|
| 3:1 (V) | 0.0848 | 0.091 – 0.207 | 27.785 |
| 10:1 (V) | 0.2434 | 0.089 – 0.204 | 14.757 |
| 25:1 (V) | 0.0793 | 0.088 – 0.204 | 32.118 |
| 10:1 (R) | 0.0900 | 0.100 – 0.350 | 11.827 |

**Table S2.** Analysis settings for collection of low pressure $CO_2$ isotherms.

| **$CO_2$** | **Number of Data Points** | **Equilibrium threshold (mbar/min)** |
|---|---|---|
| **10:1 (V)** | | |
| 30 °C | 15 | 1.0 |
| 45 °C | 15 | 1.0 |
| 60 °C | 14 | 0.2 |
| **25:1 (V)** | | |
| 30 °C | 14 | 1.0 |
| 45 °C | 16 | 0.2 |
| 60 °C | 9 | 1.0 |
| 75 °C | 19 | 0.2 |
| **10:1 (R)** | | |
| 30 °C | 19 | 1.0 |
| 45 °C | 21 | 1.0 |
| 60 °C | 15 | 1.0 |
| **$N_2$** | | |
| 30 °C | 14 | 1.0 |

**Table S3.** Details of DVS experimental method, including operating conditions and programmed parameters. (TVSA = temperature and vacuum swing adsorption, sccm = standard cubic centimetres)

| Sample activation | | | | | | | |
|---|---|---|---|---|---|---|---|
| Material | | | | | T (°C) | Vacuum (Torr) | Time (h) |
| PEI-4BMFPT | | | | | 100 | $10^{-6}$ | 12 |
| Adsorption / desorption experiments | | | | | | | |
| T (°C) | RH range (%) | dm/dt (%/min) | Equilibrium time (min) | | Vapour flow (sccm)* | Regeneration method | Pressure control |
| | | | min | max | | | |
| 40 | 1-90 | 0.001 | 40 | 400 | 5-20 | TVSA | Dynamic mode |

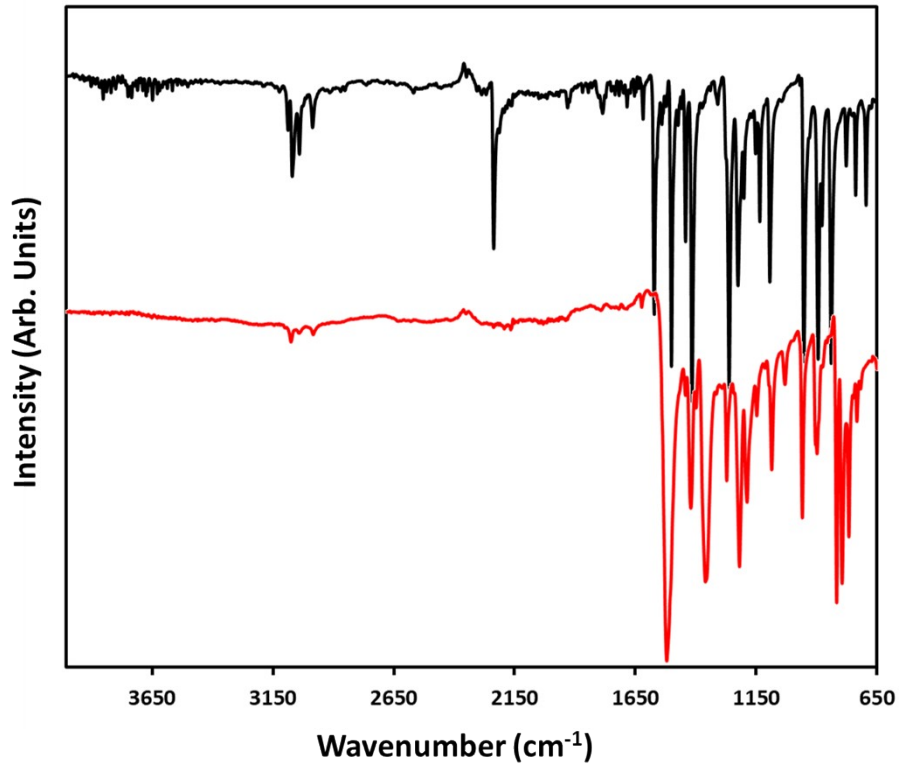


**Figure S1.** Stacked FTIR-ATR spectra of 4-(bromomethyl)-3-fluorobenzonitrile (black) and 2,4,6-tris-[4-(bromomethyl-3-fluoro)-phenyl]-1,3,5,-triazine (4BMFPT) (red).

**Figure S2.** 25:1 (V) (left) and 10:1 (R) (right).

**Table S4.** Elemental analysis data of all samples (wt%), C/N ratios and calculated amine:alkyl ratios.

| Sample | C | H | N | C/N | Amine:$CH_2$ |
|---|---|---|---|---|---|
| 1:1 (V) | 59.92 | 7.04 | 17.63 | 3.40 | 0.68:1 |
| 3:1 (V) | 58.52 | 5.80 | 16.26 | 3.60 | 0.57:1 |
| 5:1 (V) | 60.86 | 7.32 | 18.04 | 3.37 | 0.71:1 |
| 10:1 (V) | 52.52 | 8.56 | 18.91 | 2.78 | 1.25:1 |
| 25:1 (V) | 48.71 | 9.02 | 18.41 | 2.65 | 1.52:1 |
| 10:1 (R) | 57.42 | 8.50 | 21.02 | 2.73 | 1.33:1 |
| 10:1 (RH) | 55.82 | 7.97 | 20.71 | 2.70 | 1.42:1 |

The calculation of the amine/alkyl ratio was based on the following calculations. The C/N mol ratios of PEI ($C_2H_5N$) and 4BMFPT ($C_{24}Br_3F_3N_3H_{15}$) were calculated, thus PEI C/N = 2/1 = 2 and 4BMFPT C/N = 24/3 = 8.

The following equations are set out:

$2x + 8y =$ (C/N mole ratio of product)

$x + y = 1$

Taking 10:1 (R) as an example:

| **CHN (wt%)** | **Mol ratio of C and N** |
|---|---|
| C = 57.42<br>N = 21.02 | C = 57.42/12 = 4.79<br>N = 21.02/14 = 1.5<br>C/N ratio = 3.19 |
| **Calculation of x and y** | **Calculation of PEI (amine) : 4BMFPT (1 x alkyl group)** |
| $2x + 8y = 3.19$<br>$x + y = 1 \therefore y = 1-x$<br><br>$2x + 8 (1 – x) = 3.19$<br>$2x + 8 – 8x = 3.19$<br>$-6x = -4.81$<br>$x = 0.80$<br>$y = 0.20$ | x:y<br>PEI (amine) : 4BMFPT<br>0.80:0.20<br><br>PEI (amine) : 1/3 4BMFPT ($\therefore$ 1 x alkyl group)<br>0.80:0.60<br>= 1.33:1 |

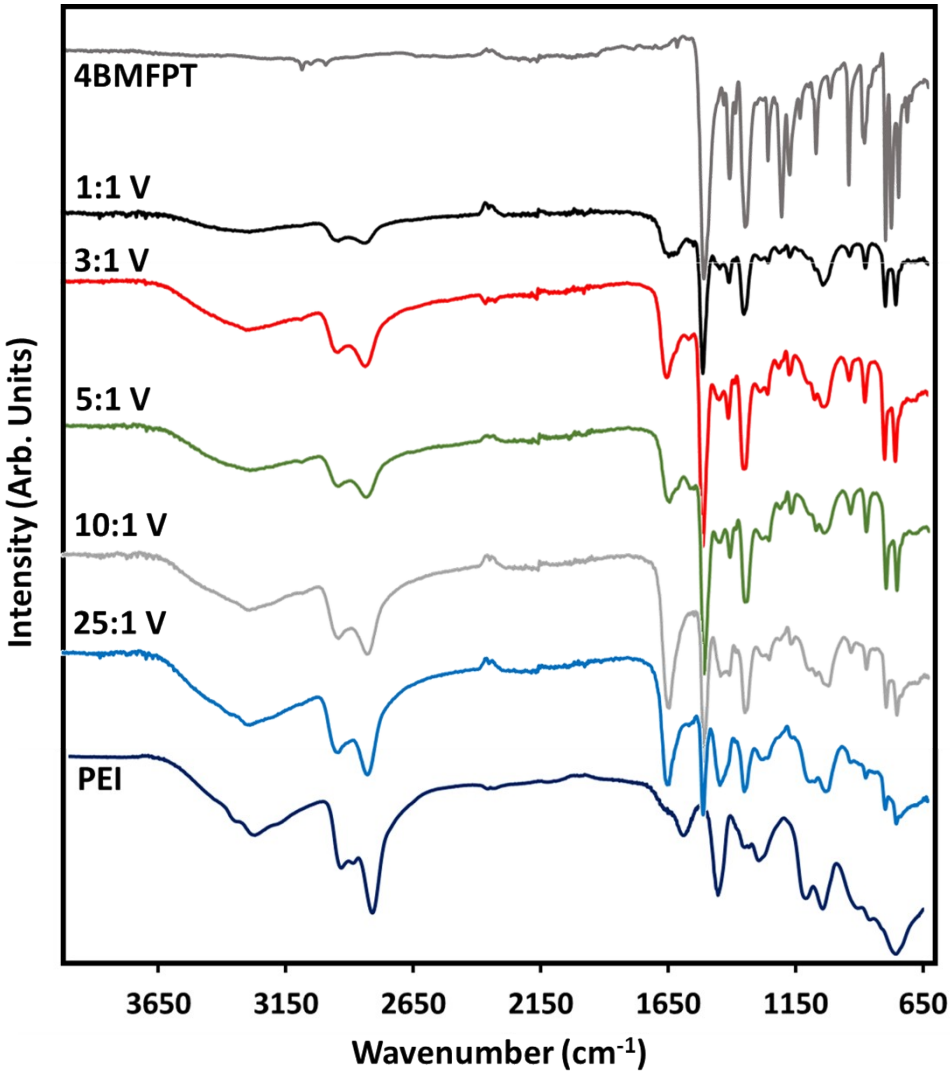


**Figure S3.** FTIR-ATR spectra of starting materials and PEI:4BMFPT cross-linked products.

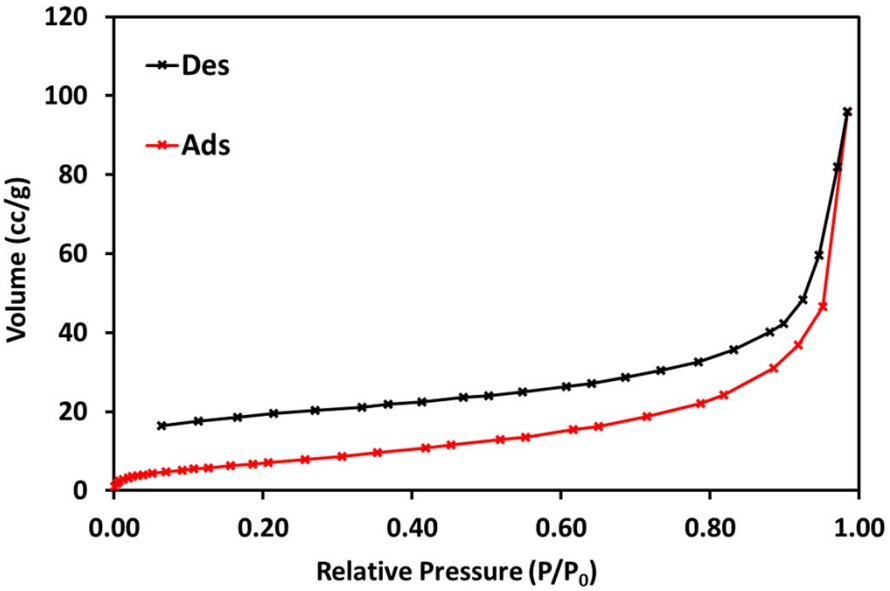


**Figure S4.** $N_2$ adsorption − desorption isotherm of 3:1 (V) at 77 K.

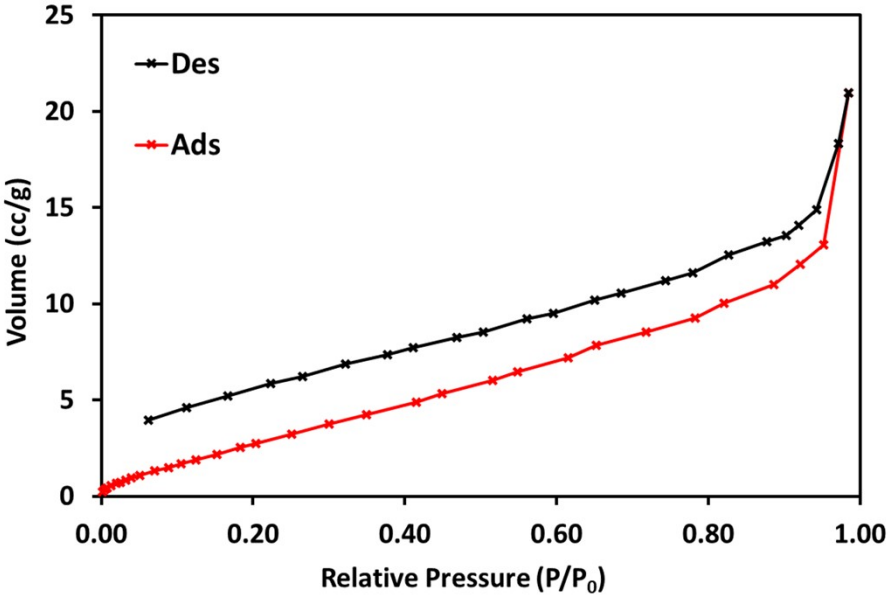


**Figure S5.** $N_2$ adsorption − desorption isotherm of 10:1 (V) at 77 K.

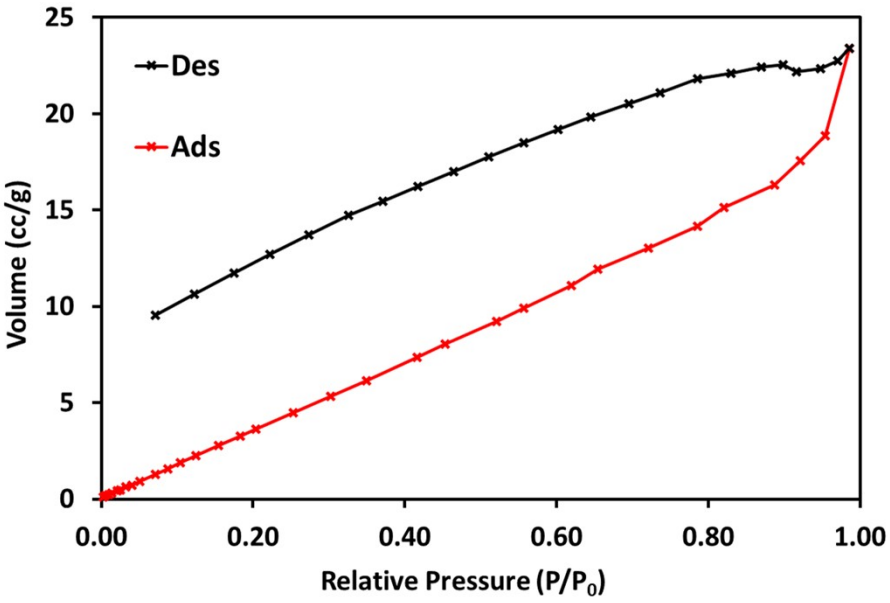


**Figure S6.** $N_2$ adsorption − desorption isotherm of 25:1 (V) at 77 K.

**Table S5.** $CO_2$ adsorption capacity after 120 mins, after 10 minutes and % of final capacity reached after 10 mins under 1 atm, 90% $CO_2$/Ar.

| Sample | Amine:$CH_2$ (1/3 Triazine) | Uptake at 120 mins (mmol/g) | | | Uptake at 10 mins (mmol/g) | | | Percentage of final capacity at 10 mins (%) | | | $CO_2$ uptake at 0.1 bar $CO_2$, 30 °C (mmol/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 30 °C | 60 °C | 90 °C | 30 °C | 60 °C | 90 °C | 30 °C | 60 °C | 90 °C | |
| 1:1 (V) | 0.68:1 | 1.17 | 0.86 | 0.53 | 0.79 | 0.76 | 0.56 | 67.49 | 89.12 | 105.62 | - |
| 3:1 (V) | 0.57:1 | 1.44 | 1.07 | 0.68 | 1.24 | 1.02 | 0.68 | 85.80 | 94.87 | 100.44 | - |
| 5:1 (V) | 0.71:1 | 1.28 | 0.97 | 0.65 | 1.07 | 0.85 | 0.58 | 84.04 | 87.80 | 89.97 | - |
| 10:1 (V) | 1.25:1 | 1.73 | 1.95 | 1.46 | 0.68 | 1.60 | 1.36 | 39.49 | 81.88 | 93.54 | 1.15 |
| 25:1 (V) | 1.52:1 | 1.90 | 2.45 | 1.80 | 0.73 | 1.93 | 1.67 | 38.26 | 78.66 | 92.35 | 0.90 |
| 10:1 (R) | 1.33:1 | 2.31 | 2.09 | 1.45 | 1.38 | 1.89 | 1.35 | 59.51 | 90.34 | 95.50 | 1.06 |
| 10:1 (RH) | 1.42:1 | 2.09 | 1.79 | 1.21 | 1.06 | 1.59 | 1.11 | 50.52 | 89.05 | 91.88 | - |

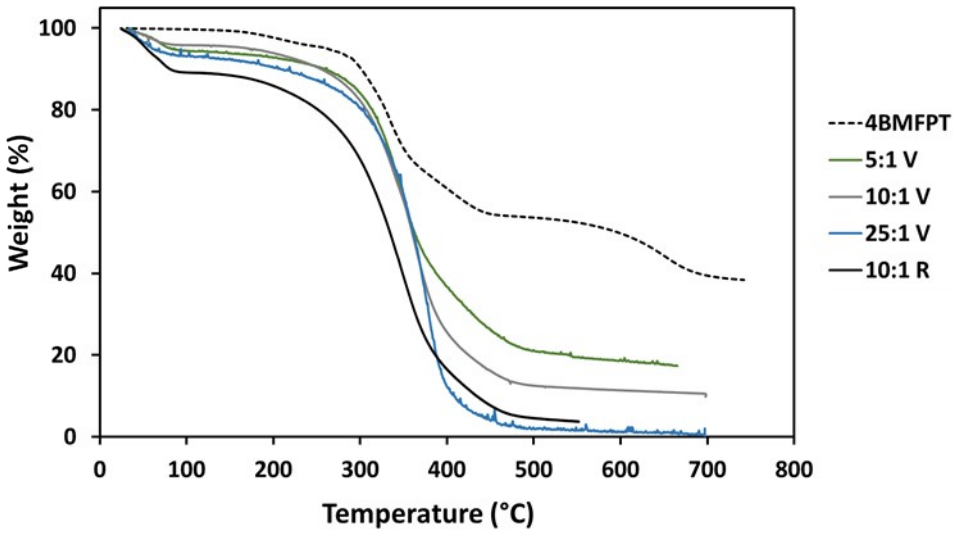


**Figure S7.** TGA thermal decomposition of selected materials in an argon atmospheres with a ramp rate of 10 °C/min.

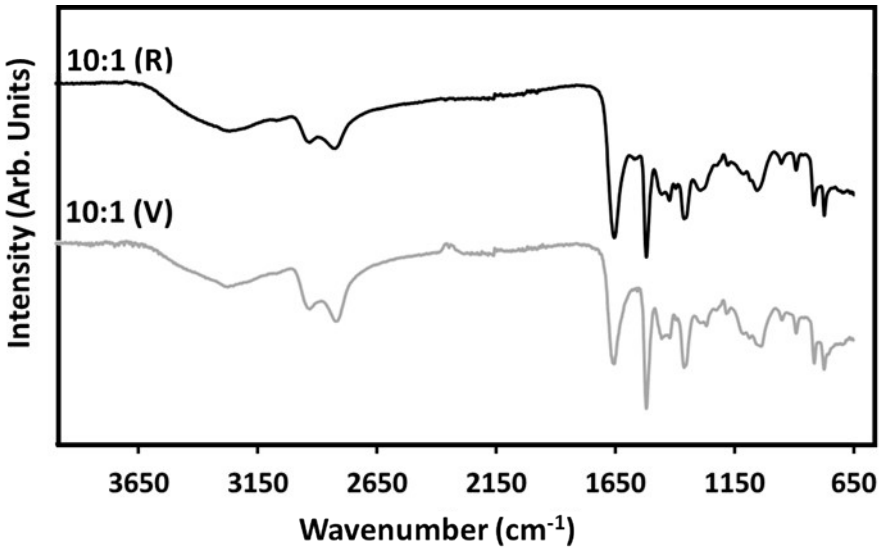


**Figure S8.** FTIR-ATR spectra of 10:1 (V) and 10:1 (R).

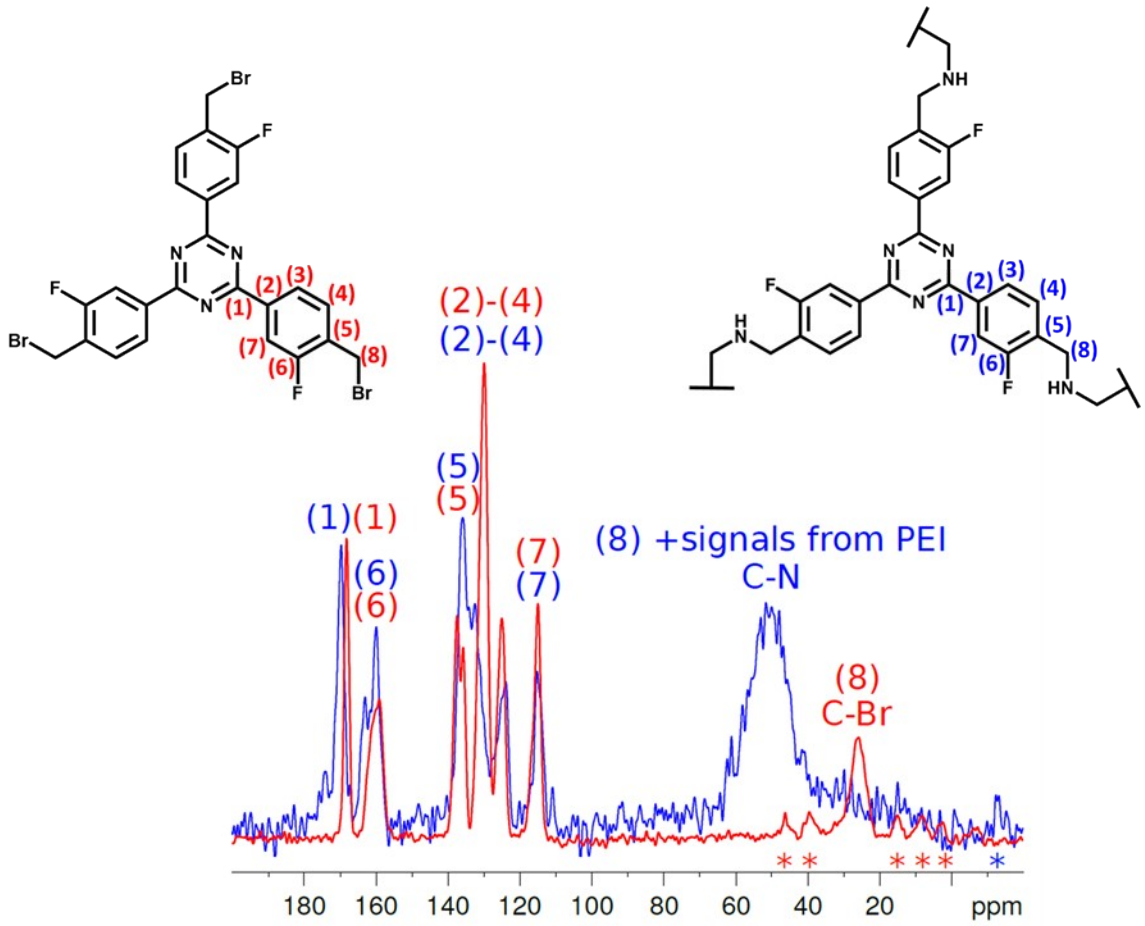


**Figure S9.** $^{13}$C CP-MAS NMR spectra of 4BMFPT (red) against 10:1 (R) (blue), using a MAS rate of 12300 Hz for 10:1 (R) and 15000 Hz on 4BMFPT.

Spinning sidebands are indicated by asterisks (*). Spectrum of 4BMFPT was acquired in 3k transients, over a signal averaging time of 3.5 hours. Spectrum of 10:1 (R) was acquired in 15k transients, over a signal averaging time of 17 hours.

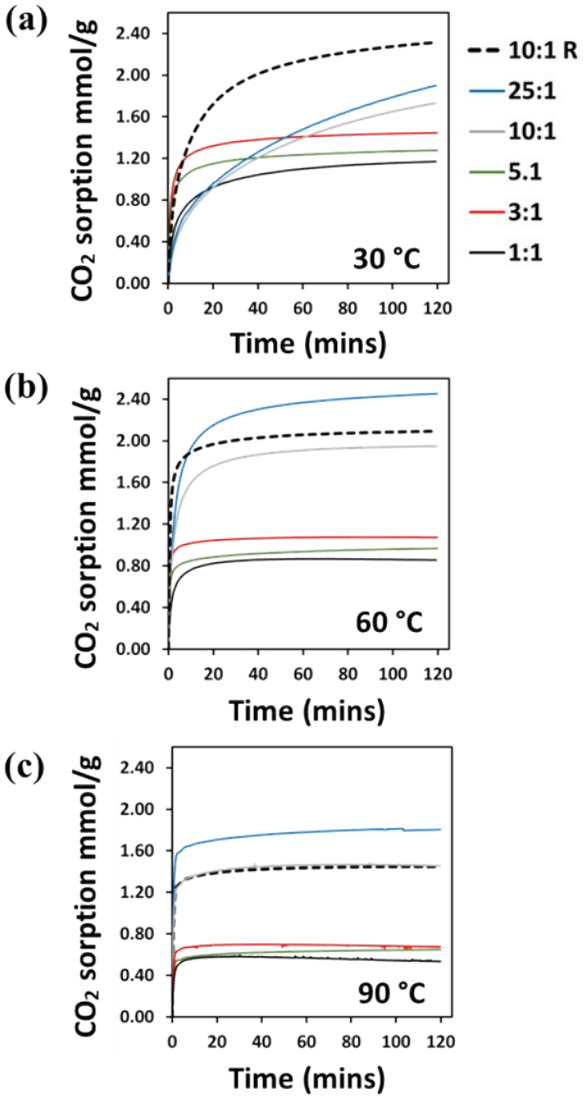


**Figure S10.** TGA-$CO_2$ sorption (mmol/g) of PEI-4BMFPT 1:1 (V), 3:1 (V), 5:1 (V), 10:1 (V), 25:1 (V) and 10:1 (R) at: (a) 30 °C; (b) 60 °C; (c) 90 °C, under 1 atm, 90% $CO_2$/Ar.

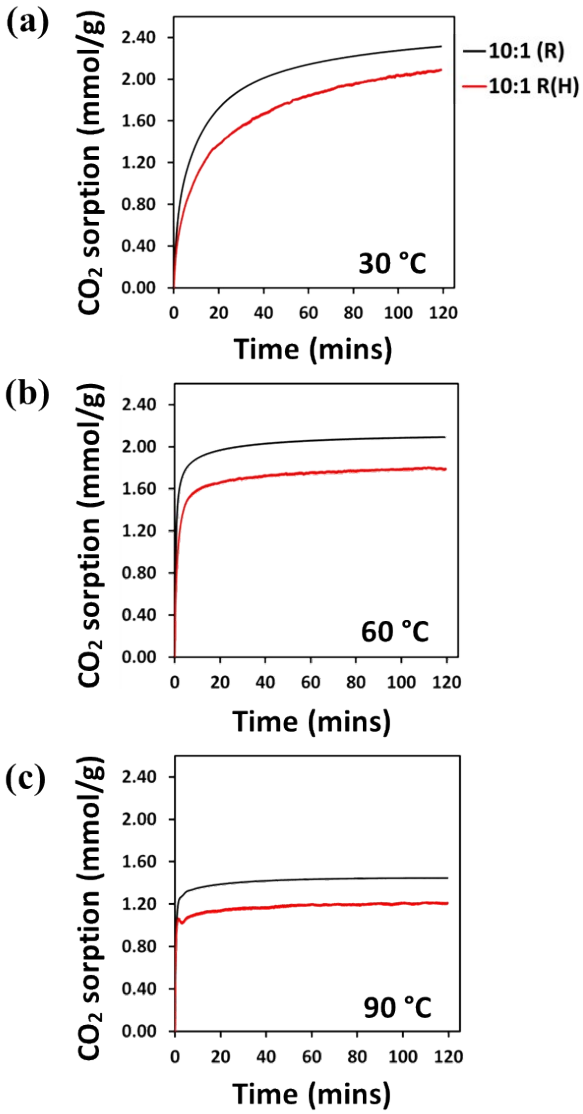


**Figure S11.** TGA-$CO_2$ sorption (mmol/g) of PEI-4BMFPT 10:1 (R) (fluorinated, black) and PEI-4BMPT 10:1 (RH), (non-fluorinated, red) at: (a) 30 °C; (b) 60 °C; (c) 90 °C, under 1 atm, 90% $CO_2$/Ar.

NOTE: Synthesis of 2,4,6-tris-[4-(bromomethyl)-phenyl]-1,3,5,-triazine (4BMPT) same as for 4BMFPT except for the use of 4-(bromomethyl)-benzonitrile in place of 4-(bromomethyl)-3-fluorobenzonitrile. 4BMPT: 4.802 g of product were recovered (Yield: 96.0 %). Analysis found (calculated for $C_{24}H_{15}N_3Br_3$): C, 48.05 (49.26); H, 2.93 (2.59); N, 7.01 (7.18).

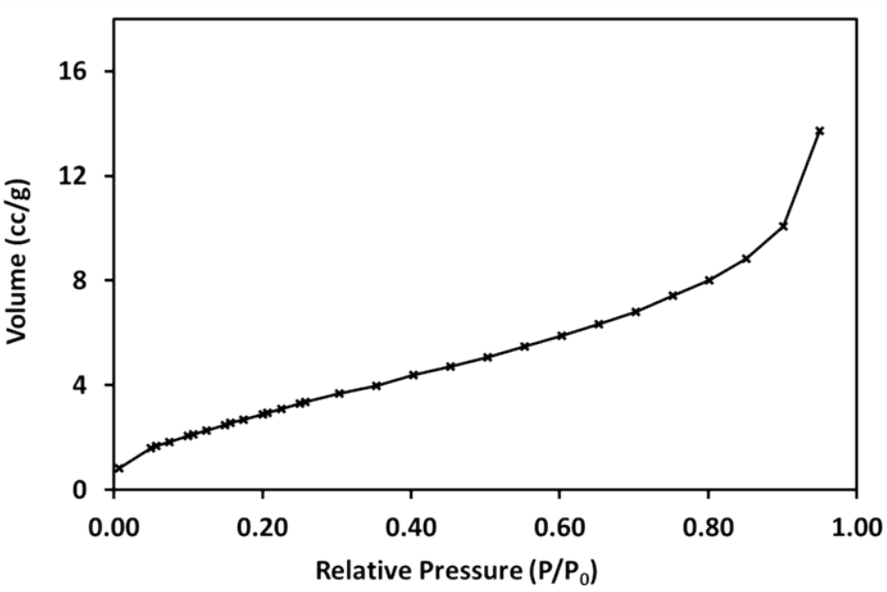


**Figure S12.** $N_2$ adsorption isotherm of 10:1 (R) at 77 K.

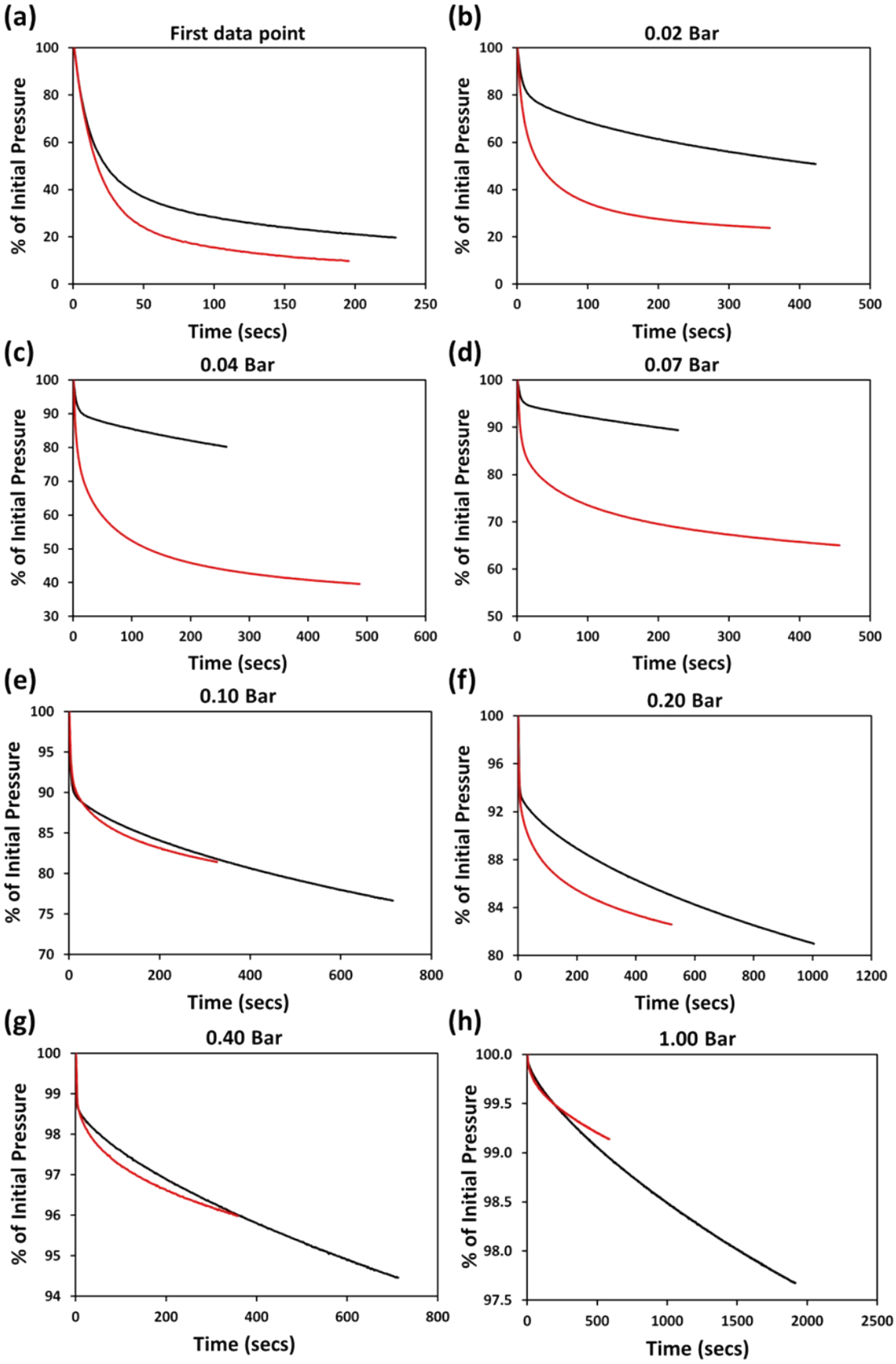


**Figure S13.** Percentage decrease in initial cell pressure at selected data collection points:

(a) Initial data point (0.002 - 0.005 bar); (b) 0.02 bar; (c), 0.04 bar; (d) 0.07 bar; (e) 0.10 bar; (f) 0.20 bar; (g) 0.40 bar; (h) 1.00 bar; for isotherms collected on 10:1 (R) at 30 °C (black), and 60 °C (red).

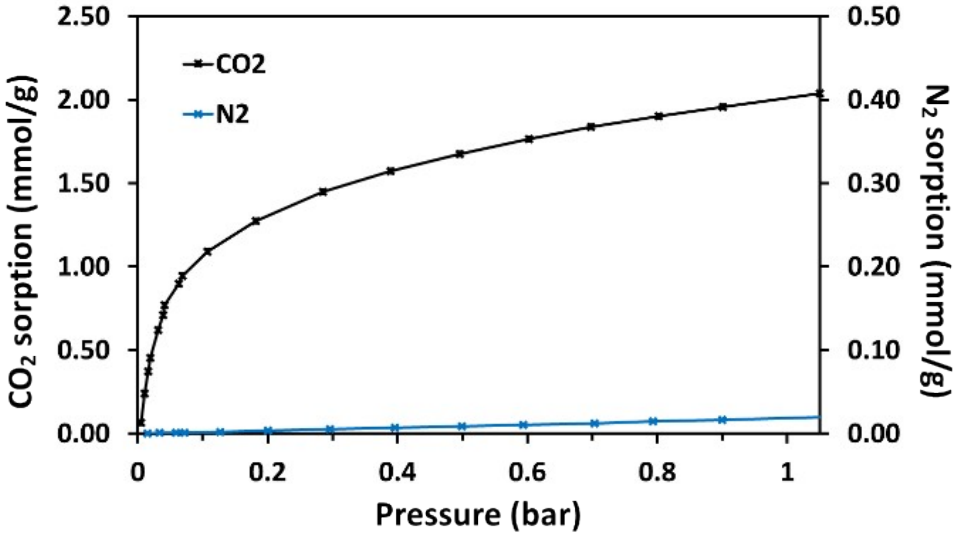


**Figure S14.** Single-component $CO_2$ and $N_2$ sorption isotherm of 10:1 (R) at 30 °C from 0.1 – 1 bar, ($N_2$ on secondary axis).

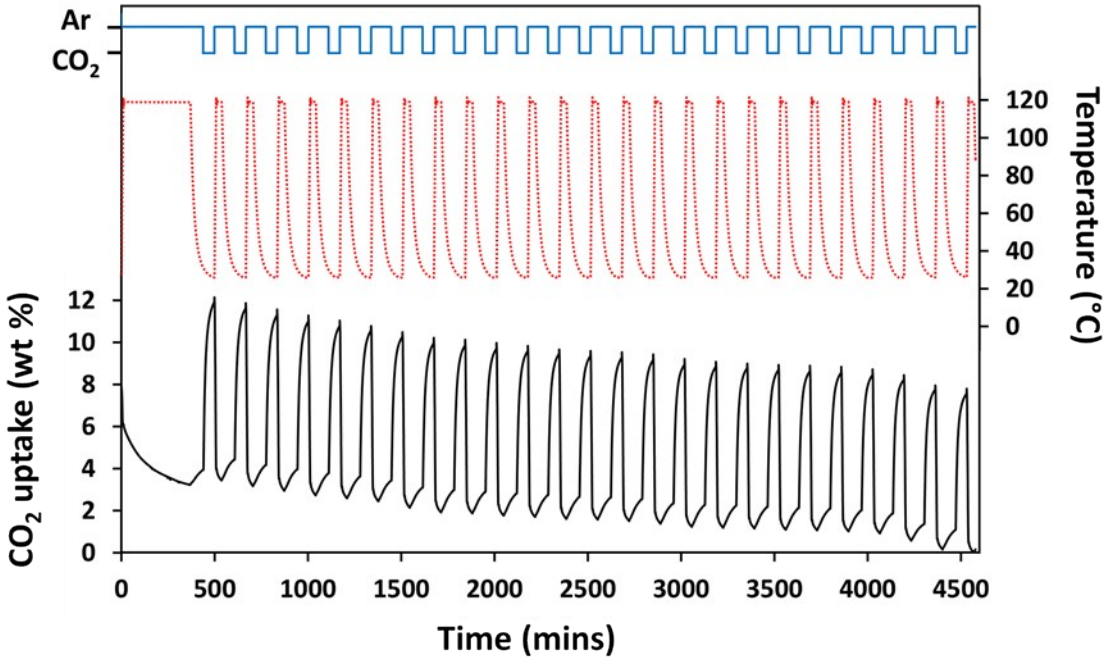


**Figure S15.** $CO_2$ uptake of 10:1 (R) under temperature swing adsorption–desorption cycles in 1 atm pure, dry $CO_2$.

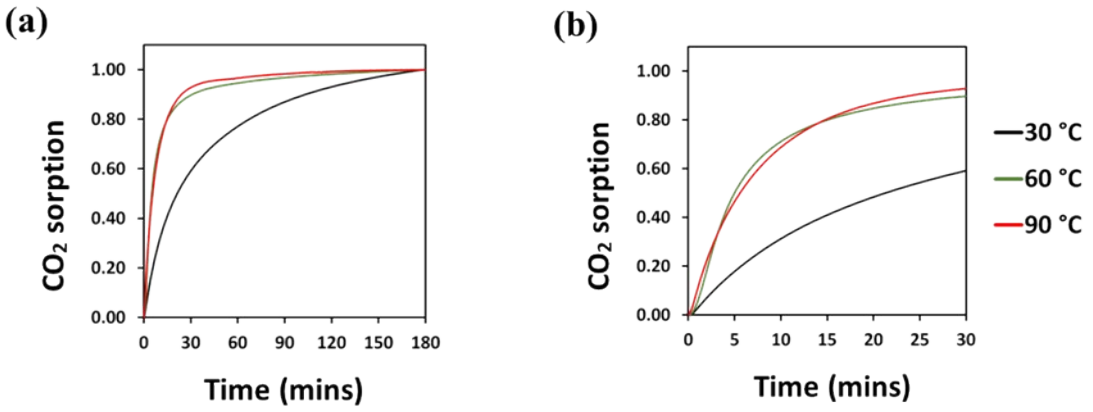


**Figure S16.** Normalised TGA-$CO_2$ sorption of 10:1 (R), in 1 atm 10% $CO_2/N_2$ over (a) 180 minutes and (b) first 30 minutes.

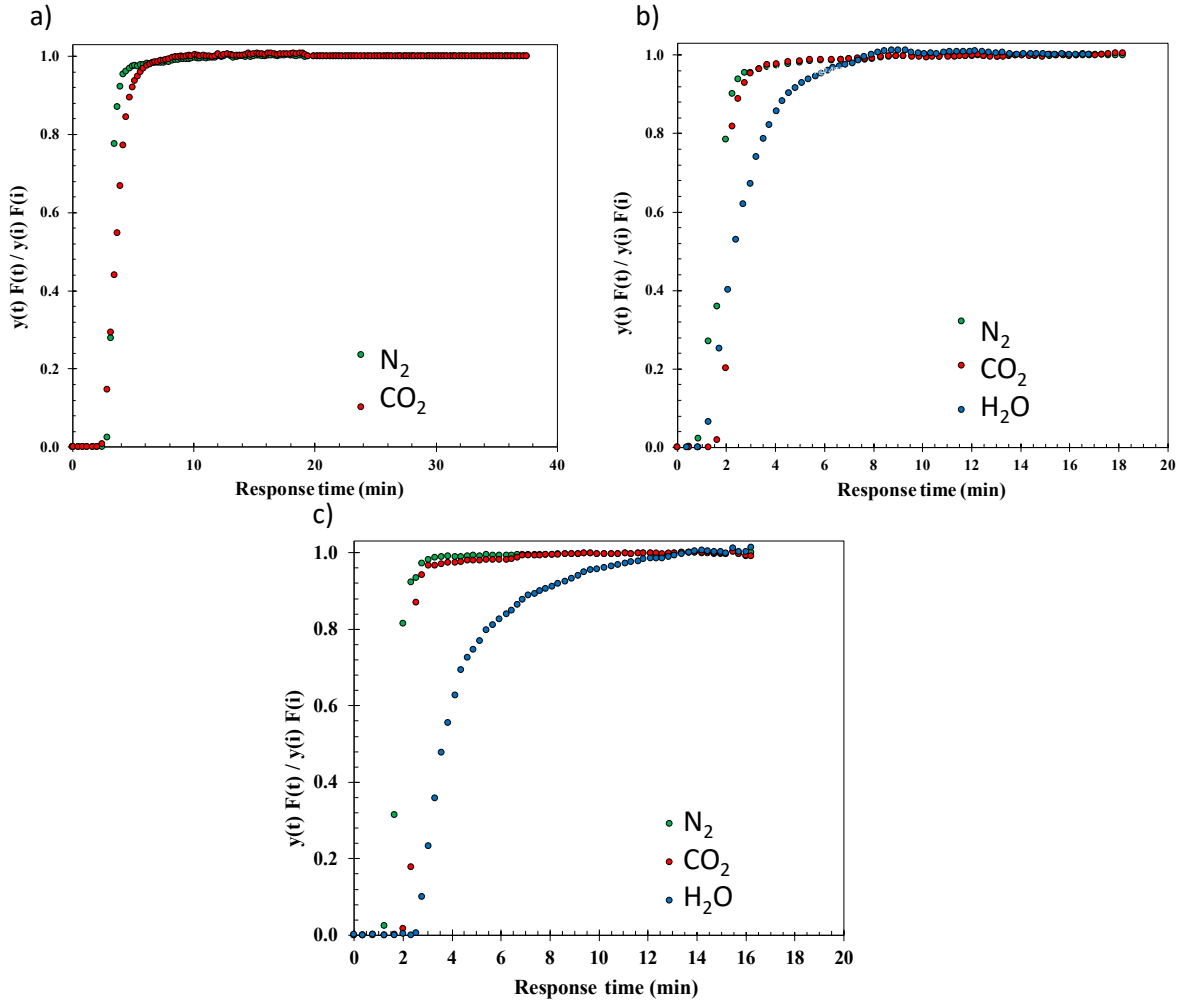


**Figure S17.** Normalized breakthrough curves of blank experiment at 40 °C, 1 atm 14 % $CO_2$, (a) dry experiment, (b) wet pre-saturation with 5% $H_2O$ and (c) wet co-adsorption with 5% $H_2O$.