Electronic Supplementary Information

Building multiple adsorption sites in porous polymer networks for carbon capture applications

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1. Synthesis of PPN-6-SO_3NH_4

PPN-6-SO_3H was synthesized according to previously published procedure (*J. Am. Chem. Soc.* **2011**, *133*, 18126–18129).

Method 1: To an ice-bath-cooled PPN-6-SO_3H (150 mg) in flask, add ammonia hydroxide (20 mL), the resulting suspension was heated up 60 °C overnight. Then, it was cooled down, solid was collected, washed with water and methanol substantially, dried to produce PPN-6-SO_3NH_4 quantitatively.

Method 2: To an ice-bath-cooled PPN-6-SO_3H (150 mg) in methanol (20 mL), bubble ammonia gas for 10 min, the resulting suspension was heated up 60 °C overnight. Then, it was cooled down, solid was collected, washed with water and methanol substantially, dried to produce PPN-6-SO_3NH_4 quantitatively.

2. Low-Pressure Sorption Measurements

Low pressure (< 800 torr) gas sorption isotherms were measured using a Micrometrics ASAP 2020 surface area and pore size analyzer. Prior to the measurements, the samples were degassed for 10 h at 120 °C. UHP grade gases were used for all measurements. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the degassing process and isotherm measurement.

3. Langmuir Fit of isotherms

The isotherm of CO_2 was fitted to a dual site Langmuir model (**Fig. S1**), CH_4 and N_2 were fitted to a single site Langmuir model (**Fig. S2** & **S3**, respectively). The analytical functions were used afterwards to carry out further calculations such as IAST. The uptake data for N_2 have an unusual characteristic, which is caused by the very low uptake because the measurement instrument is working at its lower detection end. The Langmuir parameters are given in **Table 2** & **3**, respectively.

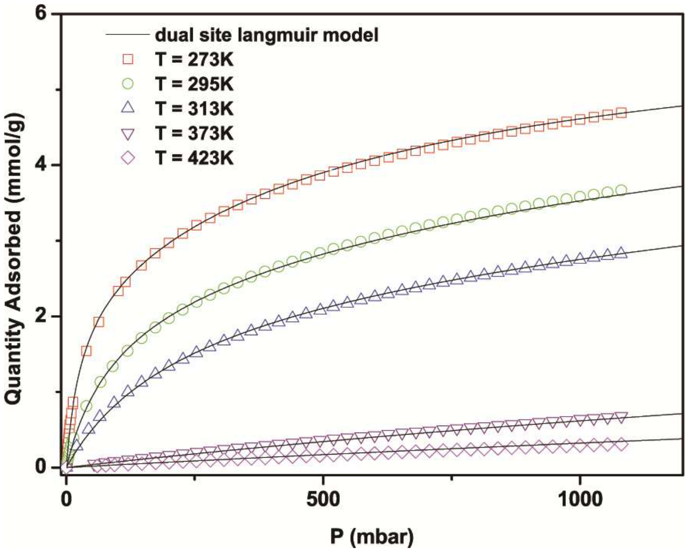


Fig. S1 Dual site Langmuir fit of CO_2 adsorption isotherms at different temperatures

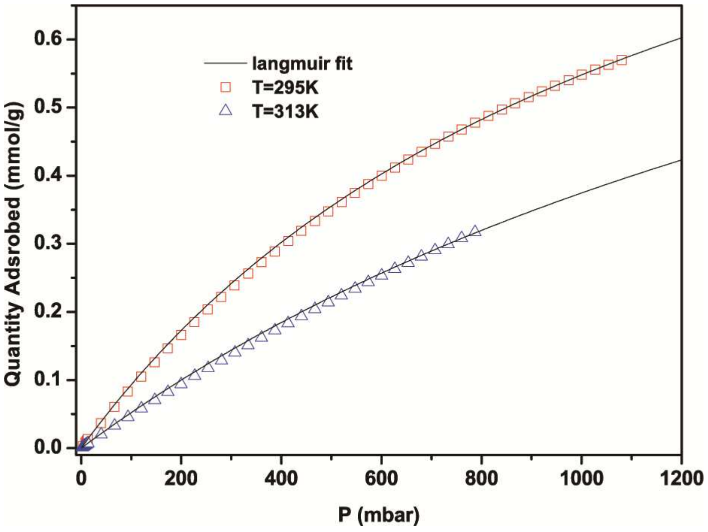


Fig. S2 Single site Langmuir fit of CH_4 adsorption isotherms at different temperatures

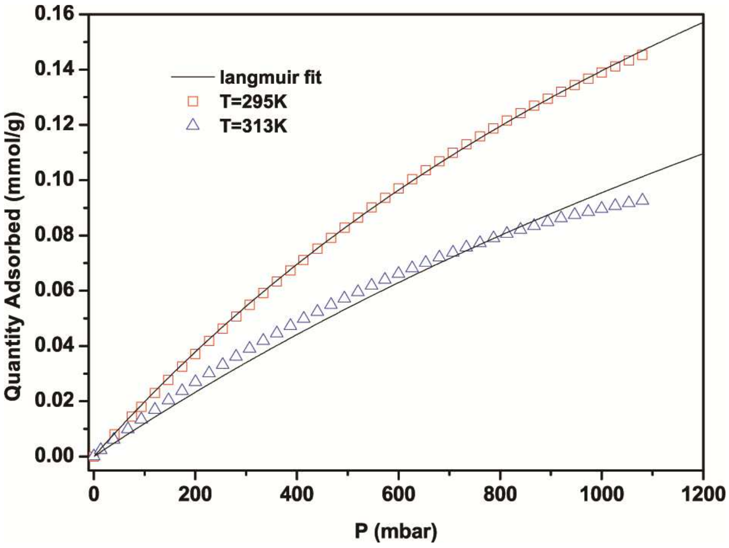


Fig. S3 Single site Langmuir fit of N_2 adsorption isotherms at different temperatures

Table S1 CO_2 – Langmuir parameters

$$q(T,p) = q_{sat,A} \cdot \frac{b_A \cdot p}{(1+b_A \cdot p)} + q_{sat,B} \cdot \frac{b_B \cdot p}{(1+b_B \cdot p)}, \quad b_i = b_i \cdot \exp\left(\frac{E_i}{R \cdot T}\right)$$

$q_{sat,A}$ [mmol/g]	$q_{sat,B}$ [mmol/g]	$b_{0,A}$ [pa]	$b_{0,B}$ [pa]	E_A [J/mol]	E_B [J/mol]
2.3369	3.8030	5.3411 E-11	1.7098 E-11	35646	31207

Table S2 CH_4, N_2 – Langmuir parameters

$$q(T,p) = q_{sat,A} \cdot \frac{b_A \cdot p}{(1+b_A \cdot p)}, \quad b_i = b_i \cdot \exp\left(\frac{E_i}{R \cdot T}\right)$$

	$q_{sat,A}$ [mmol/g]	$b_{0,A}$ [pa]	E_A [J/mol]
CH_4	1.1984	1.8621 E-10	26292
N_2	0.424	5.4206 E-10	22345

4. IAST adsorption selectivities

The adsorption selectivities, S_{ads}, for binary mixtures, defined by

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$

were calculated using the Ideal Adsorption Solution Theory (IAST) of Myers and Prausnitz [1].

Table S3 Calculated IAST adsorption selectivity under mixed gas (15% CO_2 and 85% N_2) and 313 K

Total pressure (bar)	**Partial pressure CO_2 uptake (cm^3/g)***	**Partial pressure N_2 uptake (cm^3/g)***	**Selectivity (partial pressure)**	**IAST CO_2 uptake (cm^3/g)**	**IAST N_2 uptake (cm^3/g)**	**Selectivity (IAST)**
1E-4	1.871E-4	1.0442E-5	101.53566	1.87097E-4	1.04391E-5	101.5618
1E-3	0.00187	1.04395E-4	101.49581	0.00187	1.04111E-4	101.75744
0.01	0.01858	0.00104	101.10054	0.01855	0.00101	103.73475
0.02	0.03691	0.00208	100.66799	0.0368	0.00197	105.97698
0.04	0.07281	0.00413	99.82324	0.0724	0.00371	110.60787
0.06	0.10775	0.00617	99.00463	0.10689	0.00525	115.44053
0.08	0.14177	0.00818	98.21102	0.14034	0.0066	120.48304
0.1	0.17492	0.01017	97.44132	0.17281	0.00779	125.74371
0.2	0.3287	0.01983	93.91786	0.32238	0.01174	155.63233
0.3	0.46528	0.02902	90.86111	0.4546	0.01339	192.40446
0.4	0.58769	0.03776	88.18811	0.57335	0.01368	237.47368
0.5	0.69827	0.0461	85.83441	0.68127	0.0132	292.49614
0.6	0.79886	0.05405	83.74917	0.78021	0.0123	359.40181
0.7	0.89095	0.06165	81.89175	0.87152	0.01121	440.42817
0.8	0.97573	0.06892	80.22927	0.95621	0.01007	538.15772
0.9	1.05418	0.07587	78.73485	1.03509	0.00895	655.55874
1	1.12712	0.08253	77.3863	1.10882	0.00789	796.03141

* from Langmuir model fitted pure gas isotherms.

Table S4 Calculated IAST adsorption selectivity under mixed gas (50% CO_2 and 50% CH_4) and 295 K

Total pressure (bar)	**Partial pressure CO_2 uptake (cm^3/g)***	**Partial pressure CH_4 uptake (cm^3/g)***	**Selectivity (partial pressure)**	**IAST CO_2 uptake (cm^3/g)**	**IAST CH_4 uptake (cm^3/g)**	**Selectivity (IAST)**
1E-4	0.00146	4.85092E-5	30.05351	0.00146	4.84677E-5	30.07838
1E-3	0.01451	4.84925E-4	29.9132	0.0145	4.80803E-4	30.1611
0.01	0.13816	0.00483	28.59005	0.1378	0.00445	30.99088
0.02	0.26259	0.00963	27.27189	0.26131	0.00819	31.91878
0.04	0.47825	0.01911	25.0238	0.47422	0.01403	33.79474
0.06	0.65947	0.02845	23.17775	0.65219	0.01827	35.69979
0.08	0.81466	0.03766	21.63485	0.80406	0.02136	37.63625
0.1	0.94967	0.04672	20.32618	0.93591	0.02363	39.6061
0.2	1.4369	0.09012	15.94448	1.41139	0.02822	50.01161
0.3	1.75657	0.13053	13.45674	1.72502	0.02807	61.45856
0.4	1.9948	0.16827	11.85507	1.96057	0.02647	74.07298
0.5	2.18612	0.20357	10.73882	2.15109	0.02445	87.96323
0.6	2.34717	0.23668	9.91716	2.31241	0.0224	103.22993
0.7	2.48708	0.26778	9.28763	2.4532	0.02045	119.97036
0.8	2.61131	0.29707	8.79029	2.57865	0.01865	138.28086
0.9	2.72336	0.32468	8.38777	2.69209	0.01701	158.25746
1	2.82562	0.35077	8.05554	2.79583	0.01553	179.99754

* from Langmuir model fitted pure gas isotherms.

5. Breakthrough measurement

A mass Spectrometer (Hiden Analytics, QGA-gas analysis system, Software: MASsoft 7) was used to measure the concentration in the exhaust gas of the breakthrough column. The measurement setup (**Fig. S4**) has two gas inlets free connectable to different gas tanks. Two magnet vents (BROOKS mass flow controller 5850E) with integrated flow measuring system are connected to a flow controller (Read out and control, Electronics 0154) which is used to assure a constant gas flow. The gas flow can be directed ether through a bypass tube or through the breakthrough column. The gas composition is measured by a mass spectrometer before the gas is released to an exhaust gas system. The adsorption column and a heat coil in front of the column is temperated in an oil/water- bath. The temperature of the gas stream is measured (with a thermo couple type K connected to a hand reader/ data logger testo 175 with a temperature accuracy of +/- 0.1°C) in the outlet of the column, 0.3 cm within the packed material. The pressure is measured as difference pressure to the environment (Dwyer digital manometer series 490, accuracy of +/- 1mbar). The flow can be switched from the regular outlet to a highly accurate manual bubble flow meter.

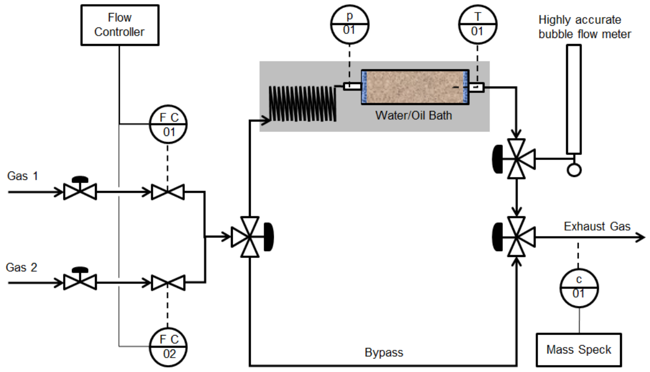


Fig. S4 Breakthrough measurement setup

The Measurement is carried out in three basic steps (**Fig. S5**). The material in the column is in-situ activated by heating in an oil bath and introducing a constant helium flow, at the same time the whole system is flushed with helium. Vacuum is not needed for activation because the constant helium flow lowers the partial pressure of all other components in the system to zero and therefor introduces a "quasi vacuum" for any coordinated guest molecule in the adsorption material. In the next step a test gas flow is run through the bypass until the concentration and flow rate is in equilibrium. The Breakthrough starts with switching the test gas flow from the bypass to the breakthrough. At the beginning of the breakthrough the composition at the gas outlet will be pure helium. After filling the free volume and the adsorption capacity of the material with the test gas the breakthrough can be detected. After reaching complete equilibrium in concentration the flow rate will be measured with the manual bubble flow.

1. Activation and flushing of the system with helium
2. Test gas flow over bypass until concentration equilibrium.
3. Start Breakthrough: Change from Bypass to Adsorption Column, After Breakthrough manual Flow measurement with bubble flow meter

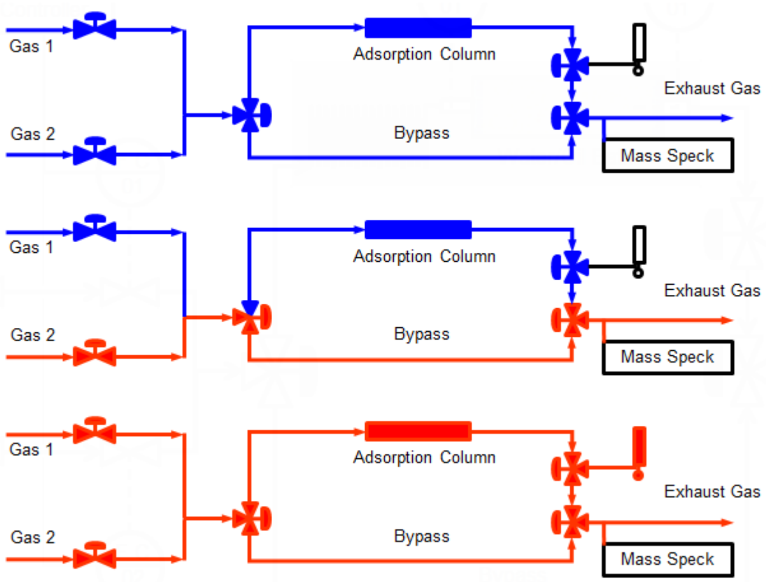


Fig. S5 Breakthrough measurement illustration

Equation 1 has been used to calculate the amount of CO_2 adsorbed on the material. The Integral evaluates the total volume of gas that remains in the system (red colored area in Fig. S6). Part of the volume is adsorbed in the material and another part fills the free volume. That why the free volume has to be subtracted from the integral. (EV = Empty Volume)

$$V_{ads} = \int_{t0}^{t1} \left(x_{0,CO_2} - x\right) dt \cdot \dot{V} - V_{EV} \cdot x_{0,CO_2} = V_{CO_2} - V_{CO_2,EV}$$ **Equation 1**

The adsorbed molar amount can be evaluated from ideal gas law by using the thermodynamic conditions of the gas where the flow is measured by **Equation 2**:

$$n_{ads} = \frac{V_{CO_2} \cdot p_0}{R \cdot T} - \frac{V_{CO_2,EV} \cdot p_{EV}}{R \cdot T}$$ **Equation 2**

$x_{0,CO2}$ = mol fraction of CO_2 in the test gas, $\dot{V}$ = total input volume flow of the test gas, V_{EV}=empty volume of the system (macro pores in between particles and empty volume in tubes)

p_0 =environmental pressure, p_{EV}=pressure in the column during breakthrough, T = temperature where the volume flow has been measured (room temperature), R = gas constant. These relationships can be used as long the dead volume is measured at the same condition (temperature and pressure) as the actual breakthrough experiment.

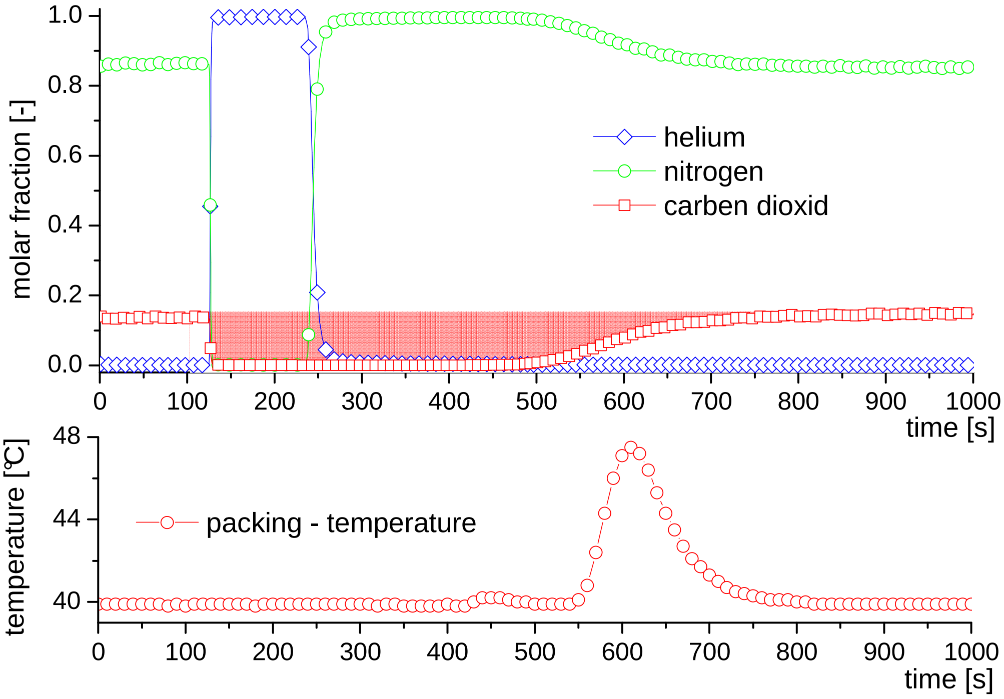


Fig. S6 Example breakthrough curve (Test gas: CO_2/N_2 15%/85%, Temperature: 40°C, Pressure 1bar)

Measurement of the dead volume:

The dead volume has been measured with filling the system with helium and afterwards measuring the breakthrough of argon. In this case the gas framework interaction is assumed to be zero and the integrated area will be equal to the free space in the system. This measurement has been done for every temperature two times.

Temperature	vol. measurement 01	vol. measurement 02	middle value
22°C	20.8783 cm^3	21.0572 cm^3	20.9678 cm^3
40°C	19.5975 cm^3	19.7250 cm^3	19.6613 cm^3

Possible sources of errors:

- Thermodynamic state (temperature)
  The Temperature influences the breakthrough results in two different ways. The adsorption capacity of the adsorbents is highly dependent on especially the temperature. The wrong measured temperature in the adsorption bed would lead to the right measured uptake but at a different temperature. A different error will occur when the flow temperature at the bubble flow meter is measured wrong; the wrong temperature would lead in this case to an error in the calculated amount of mole introduced into the system. Because of these sources of errors the bed temperature were measured in situ during breakthrough measurements. The Flow temperature was not measured in situ but test measurements have shown that the low flow rate and the external measuring method with the bubble flow meter result in a flow temperature equal to the room temperature which was stable at 22°C.
- Thermodynamic state (pressure)
  For dense packed column of adsorption material certain pressure drops might occur even at very low volume flows. When the breakthrough experiment is started the volume amount which fills the free/dead volume is dependent on the pressure in the system. A bigger volume is necessary to fill a system to higher pressure. Therefor the pressure is measured directly in front of the heat coil which is sitting in front of the packed column. The pressure drops where found to be in a range between 1 and 100 mbar depending on the gas mixture the used volume flow and of course the packing of the column. Especially for the start of the breakthrough experiment it is necessary that the pressure dos not have to build up before an actual volume flow starts, because this is causing a big time delay and causes in a wrong result from the integration. To overcome this problem we have set the system with inert gas under pressure before starting the breakthrough measurement.
- Mass Spectrometer
  The quantitative measurement of concentrations using Mass Spectroscopy is challenging. The instrument is calibrated for the measurement of Nitrogen and Carbon Dioxide mixtures in 15 to 85%. To compensate the deviation at different concentrations measurements with known gas mixtures have been carried out (Fig. S7 left), to calculate the difference between mass spectrometer and real concentration (Fig. S7 left). The correction was afterwards applied to all measurements. Unknown errors can occur when more than two compound gas mixtures are analyzed by the mass spectrometer. But we have to keep in mind that the error caused by the mass spectrometer is only taken place as long a transition state in the concentration of a mixture is measured. That means as long we integrate an area where is no CO_2 concentration measured in the outlet the mass spec is causing any errors in the evaluation.

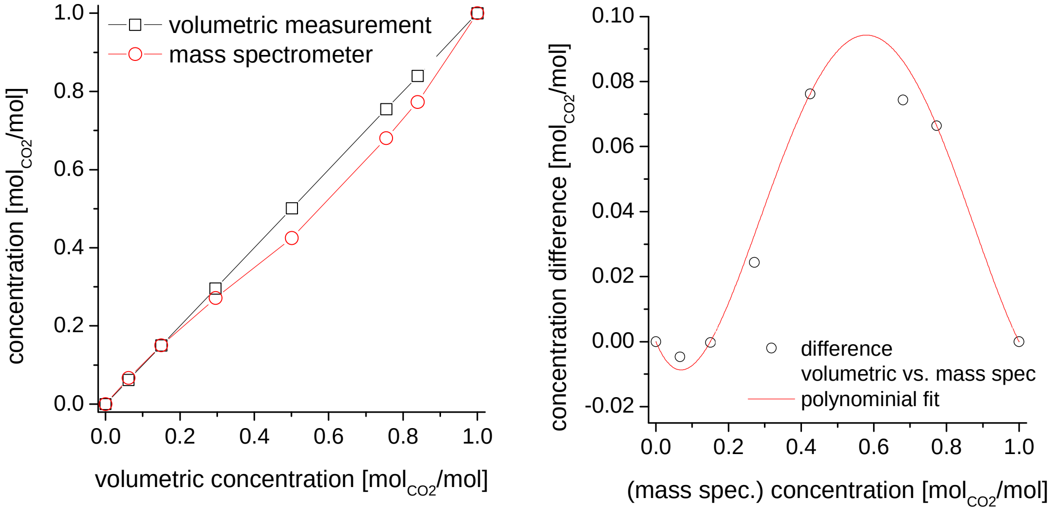


Fig. S7 CO2/N2 Mixture: Left: comparison of the CO_2 concentration measured by the mass spectrometer and the volumetric measurement. Right: deviation of the mass spectrometer, Polynomial Fit: $y = 1.516 \cdot x^4 - 3.523 \cdot x^3 + 2.274 \cdot x^2 - 0.267 \cdot x.$,
The shown example calibration has been made for all appearing gas mixtures.

Breakthrough measurements:

All measurements have been executed at least two times. These are the results for CO_2-uptake by resulting by integration of the breakthrough curves:

CO2 Partial Presure	CO2 Uptake at 295K	CO2 Uptake at 313K
[mbar]	[mmol/g]	[mmol/g]
150	1.7004	1.1225
150	1.712	1.1809
500	2.9508	2.1204
500	2.9448	2.1503
1000	3.6854	2.751
1000	3.6761	2.7611
1000	-	2.7705

Here we present for each condition the breakthrough curve:

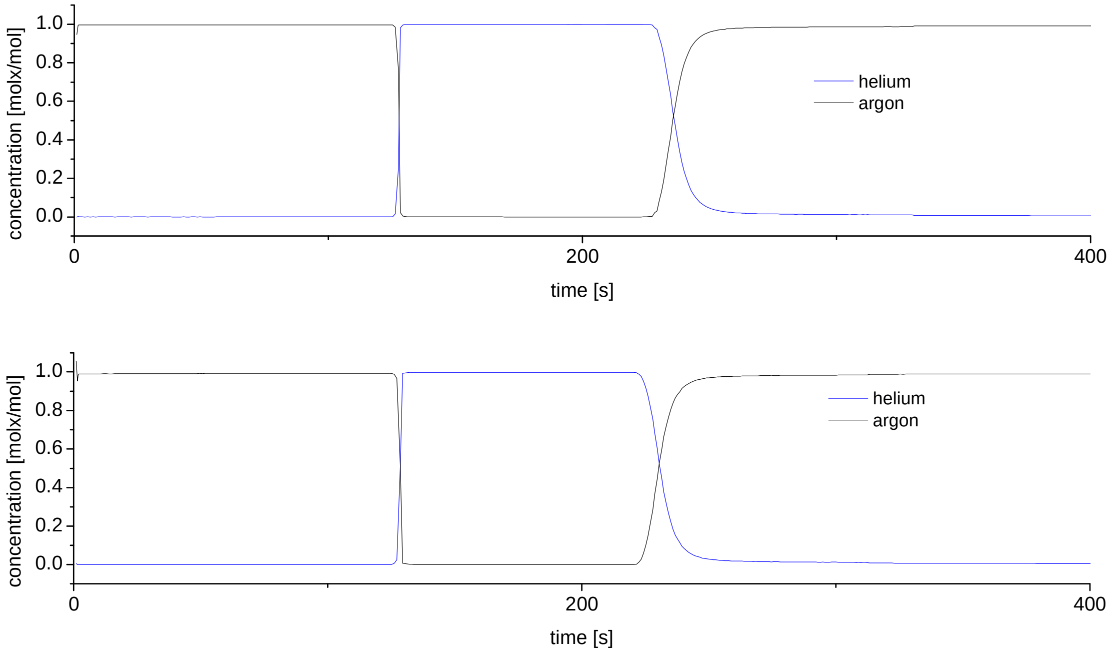


Fig. S8 breakthrough for calculation of empty volume : Top: T=295K, volume flow = 11.40ccm/min. Bottom: T=313Kvolume flow = 11.35ccm/min.

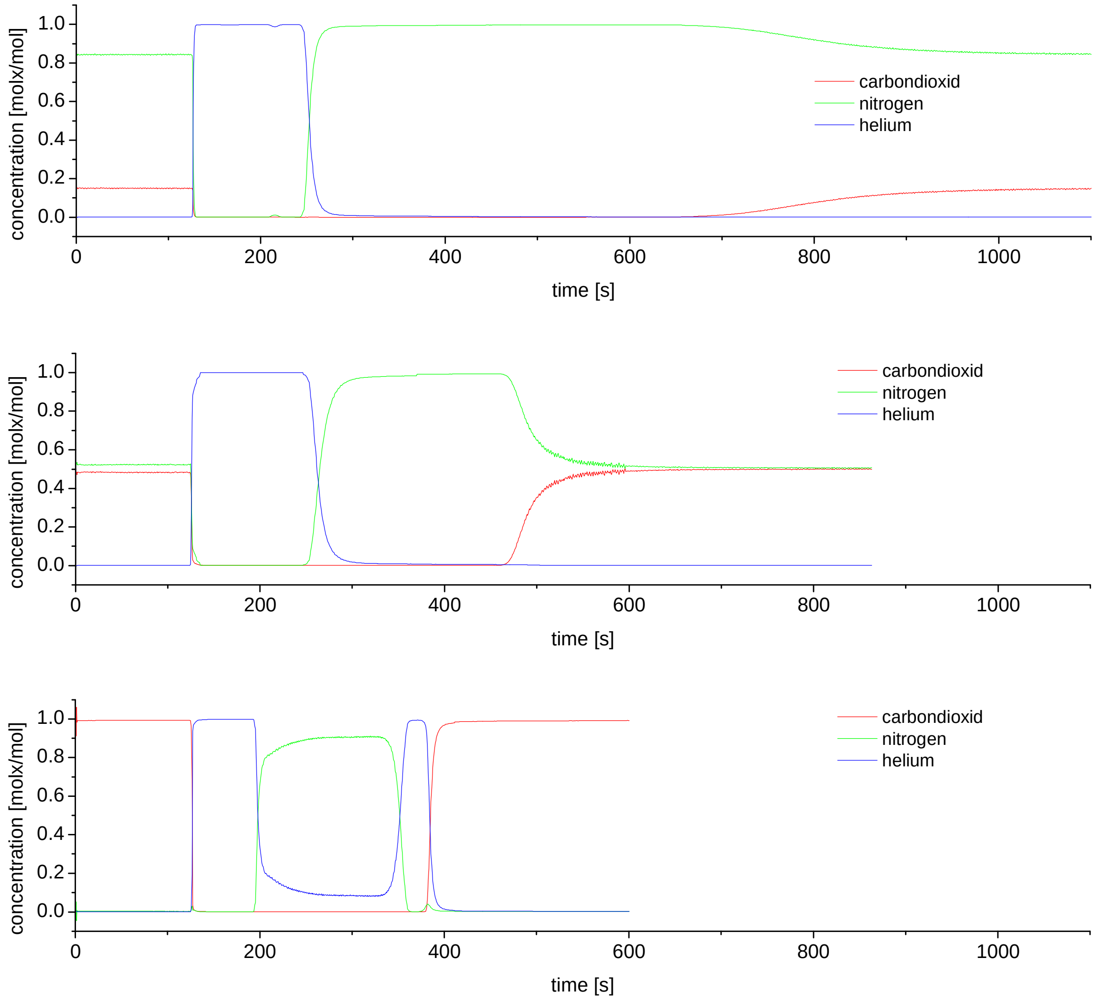


Fig. S9 Breakthrough at **295K**, : Top: 15%CO2/85%N2 mixture, volume flow = 10.19ccm/min. Middle: 50%CO2/50%N2 mixture, volume flow = 11.47ccm/min. Bottom: 100%CO2, volume flow = 11.95ccm/min (the measured concentration of nitrogen is caused by the stopping flow of CO2. The mass spectrometer sucks air from the environment if no volume flow is coming from the system.)

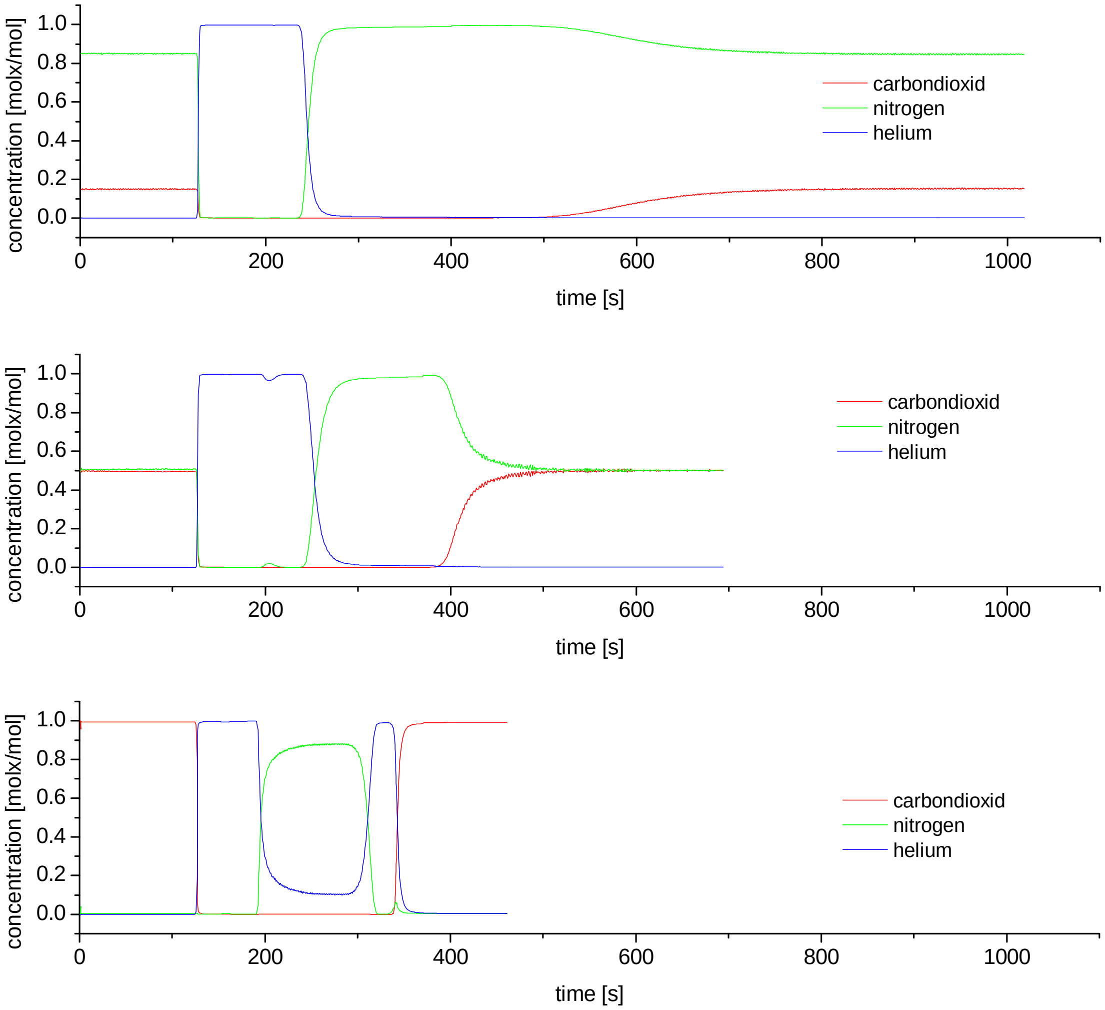


Fig. S10 Breakthrough at **313K**, : Top: 15%CO2/85%N2 mixture, volume flow = 10.41ccm/min. Middle: 50%CO2/50%N2 mixture, volume flow = 11.54ccm/min. Bottom: 100%CO2, volume flow = 11.82ccm/min (the measured concentration of nitrogen is caused by the stopping flow of CO2. The mass spectrometer sucks air from the environment if no volume flow is coming from the system.)

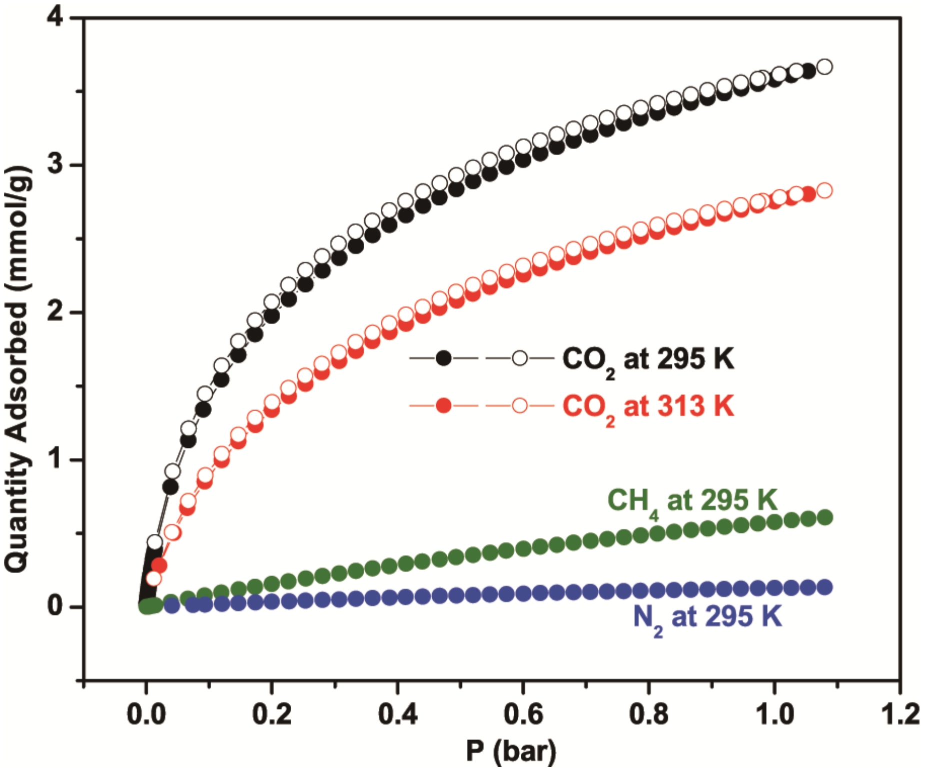
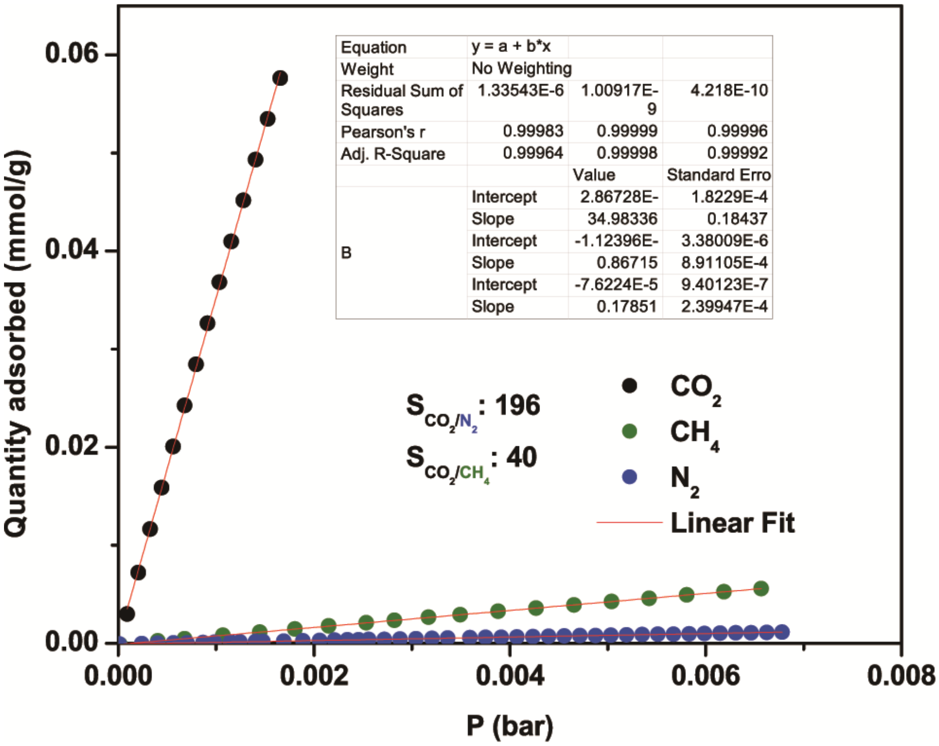
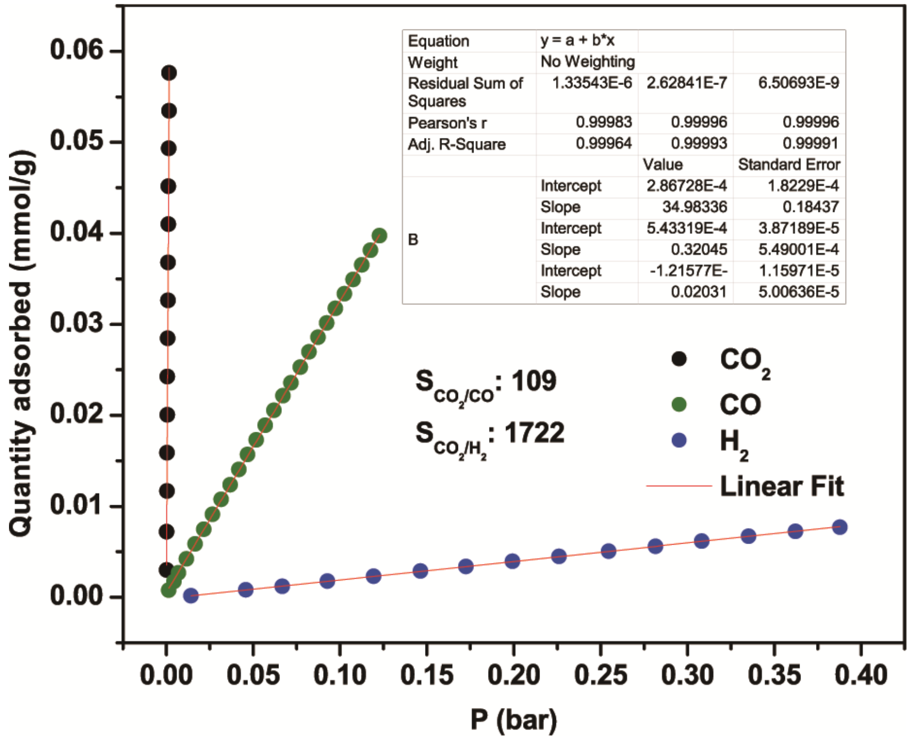


Fig. S11 CO_2 sorption isotherms at 295 K and 313 K, (●)/desorption (○); 295 K N_2 and CH_4 adsorption isotherms at 295 K.



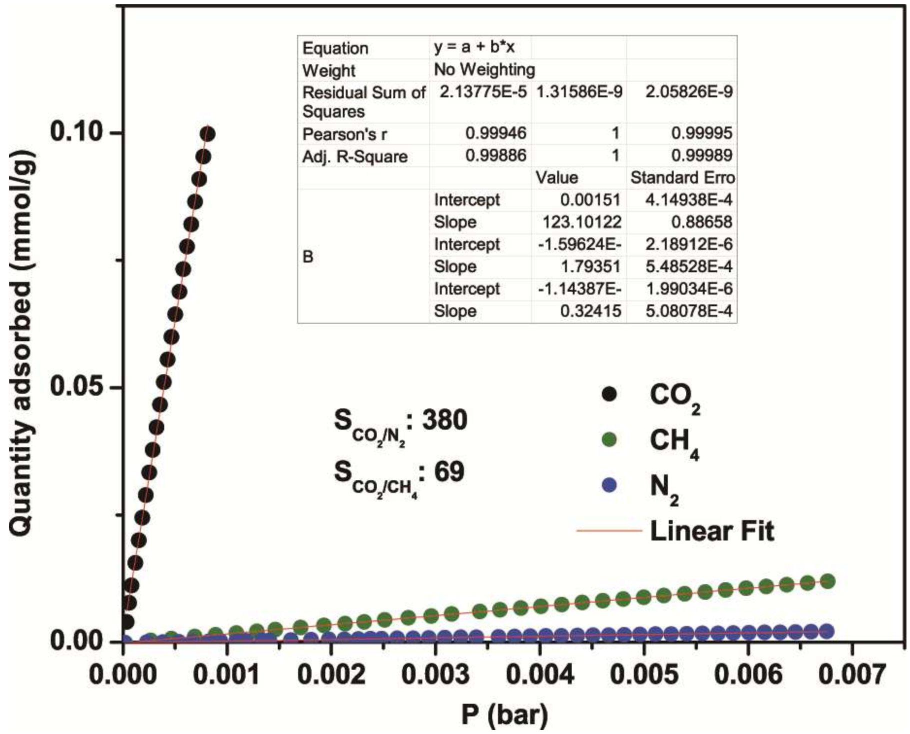
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.33543E-6	1.00917E-9	4.218E-10
Pearson's r	0.99983	0.99999	0.99996
Adj. R-Square	0.99964	0.99998	0.99992
		Value	Standard Erro
B	Intercept	2.86728E-	1.8229E-4
	Slope	34.98336	0.18437
	Intercept	-1.12396E-	3.38009E-6
	Slope	0.86715	8.91105E-4
	Intercept	-7.6224E-5	9.40123E-7
	Slope	0.17851	2.39947E-4

Fig. S12 Adsorption selectivity of CO_2 over N_2 and CO_2 over CH_4 as calculated from initial slope ratios at 295 K



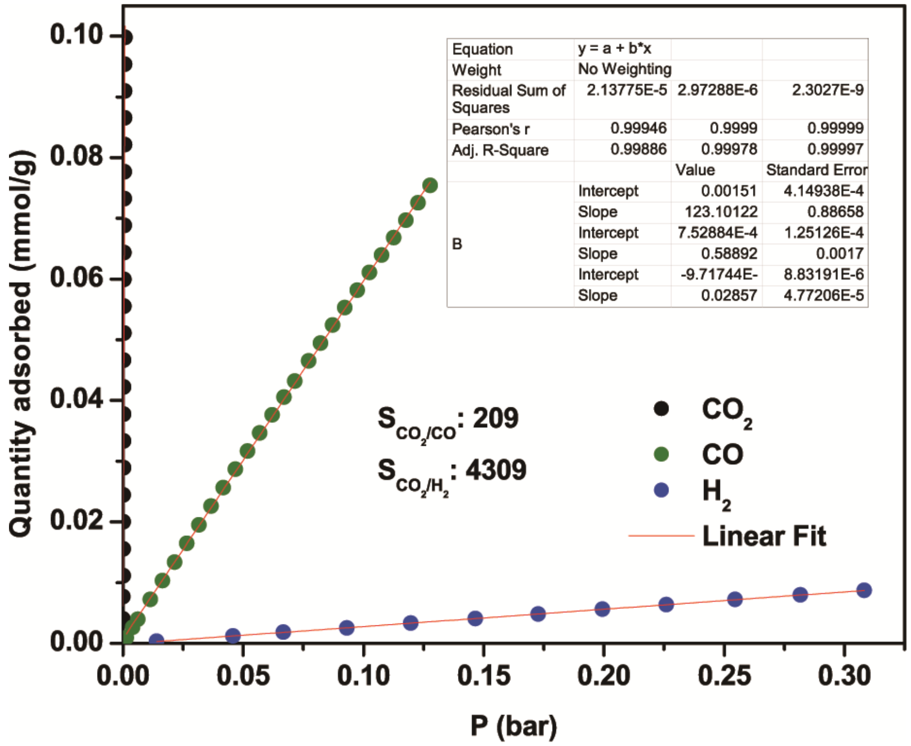
Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	1.33543E-6	2.62841E-7	6.50693E-9
Pearson's r	0.99983	0.99996	0.99996
Adj. R-Square	0.99964	0.99993	0.99991
		Value	Standard Error
B	Intercept	2.86728E-4	1.8229E-4
	Slope	34.98336	0.18437
	Intercept	5.43319E-4	3.87189E-5
	Slope	0.32045	5.49001E-4
	Intercept	-1.21577E-	1.15971E-5
	Slope	0.02031	5.00636E-5

Fig. S13 Adsorption selectivity of CO_2 over CO and CO_2 over H_2 as calculated from initial slope ratios at 295 K



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2.13775E-5	1.31586E-9	2.05826E-9
Pearson's r	0.99946	1	0.99995
Adj. R-Square	0.99886	1	0.99989
		Value	Standard Erro
B	Intercept	0.00151	4.14938E-4
	Slope	123.10122	0.88658
	Intercept	-1.59624E-	2.18912E-6
	Slope	1.79351	5.48528E-4
	Intercept	-1.14387E-	1.99034E-6
	Slope	0.32415	5.08078E-4

Fig. S14 Adsorption selectivity of CO_2 over N_2 and CO_2 over CH_4 as calculated from initial slope ratios at 273 K



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	2.13775E-5	2.97288E-6	2.3027E-9
Pearson's r	0.99946	0.9999	0.99999
Adj. R-Square	0.99886	0.99978	0.99997
		Value	Standard Error
B	Intercept	0.00151	4.14938E-4
	Slope	123.10122	0.88658
	Intercept	7.52884E-4	1.25126E-4
	Slope	0.58892	0.0017
	Intercept	-9.71744E-	8.83191E-6
	Slope	0.02857	4.77206E-5

Fig. S15 Adsorption selectivity of CO_2 over CO and CO_2 over H_2 as calculated from initial slope ratios at 273 K

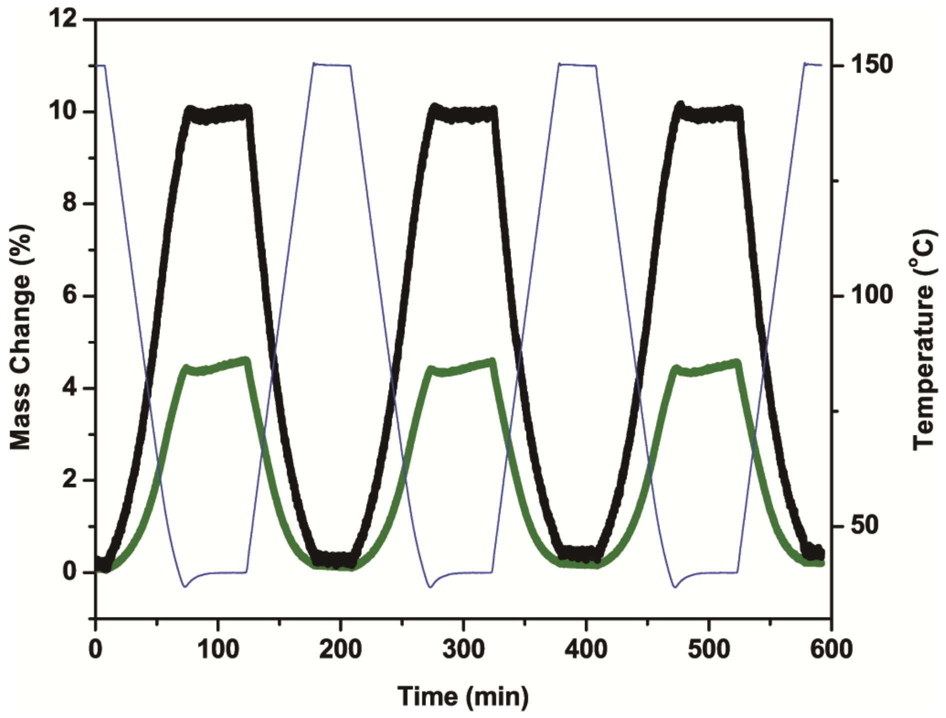


Fig. 16 Tepmerature dependent gravimetric adsroption studies of PPN-6-SO_3NH_4 using TGA. Experimetnal mass changes are shown as a function of temperature in pure CO_2 (black line) and 15% CO_2 balanced with N_2 (green line). Flow rates are 20mL/min and temperatures are plotted as blue line. The sample mass at 150 °C under each gas was normalized to be 0%.

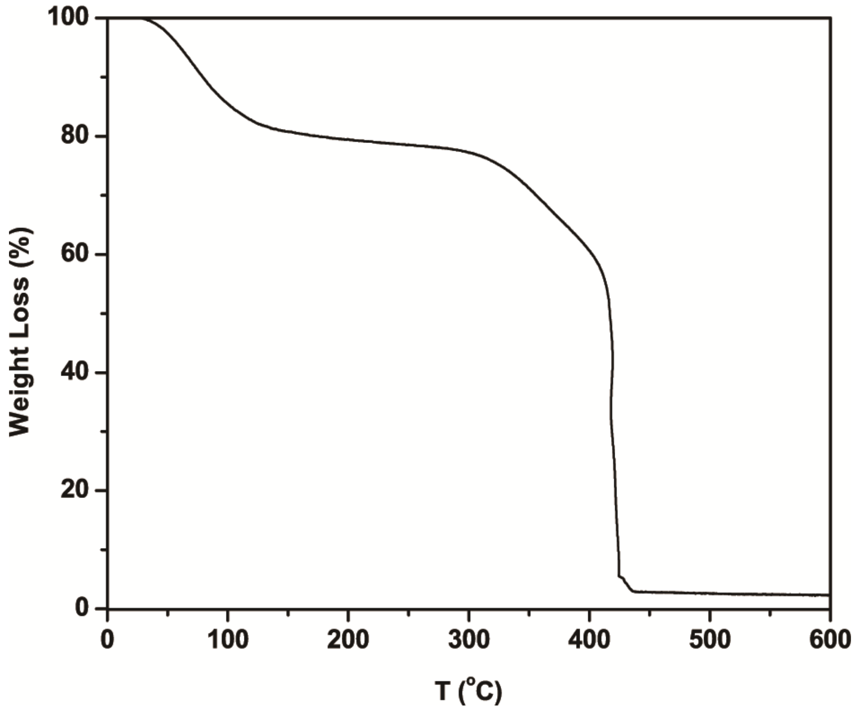


Fig. S17 TG analysis of PPN-6-SO_3NH_4 in nitrogen atmosphere, data were collected on a SHIMADZU TGA-50 Thermogravimetric Analyzer, with a heating rate of 3 °C min^{-1}

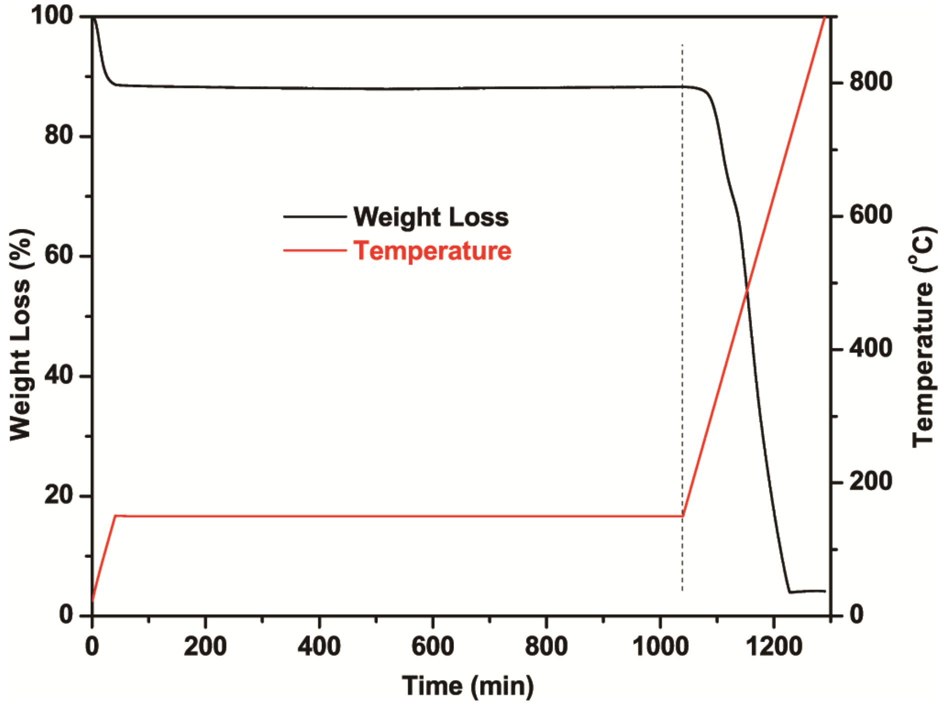


Fig. S18 TG analysis of PPN-6-SO_3NH_4 in air, the temperature was kept at 150 °C for 999 min (red line), data were collected on a SHIMADZU TGA-50 Thermogravimetric Analyzer, with a heating rate of 3 °C min^{-1}

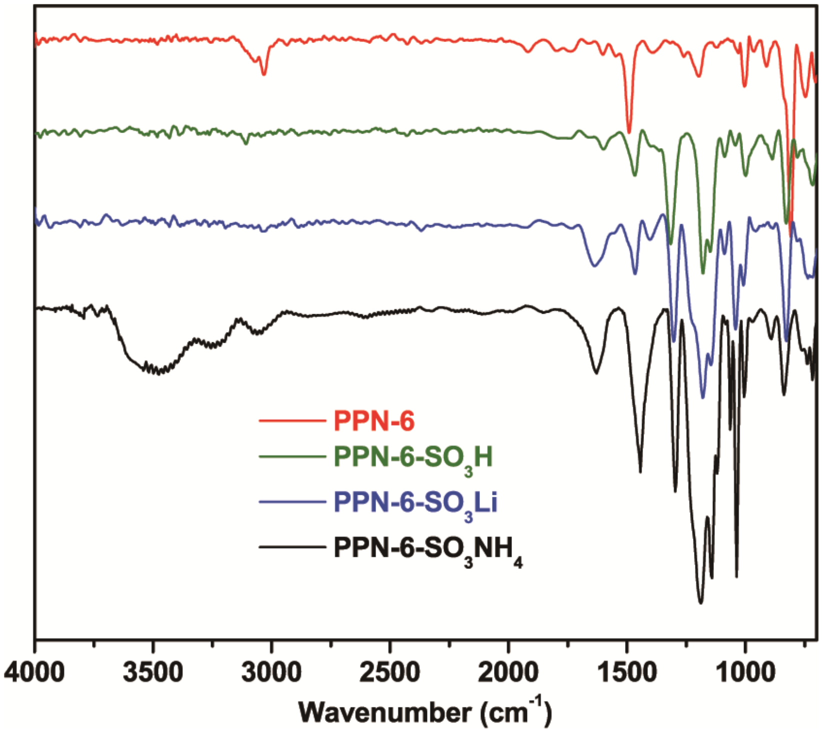


Fig. S19 Infrared spectroscopy of PPN-6, PPN-6-SO_3H, PPN-6-SO_3Li, PPN-6-SO_3NH_4, data were collected on a SHIMADZU IRAffinity-1 FTIR Spectrophotometer

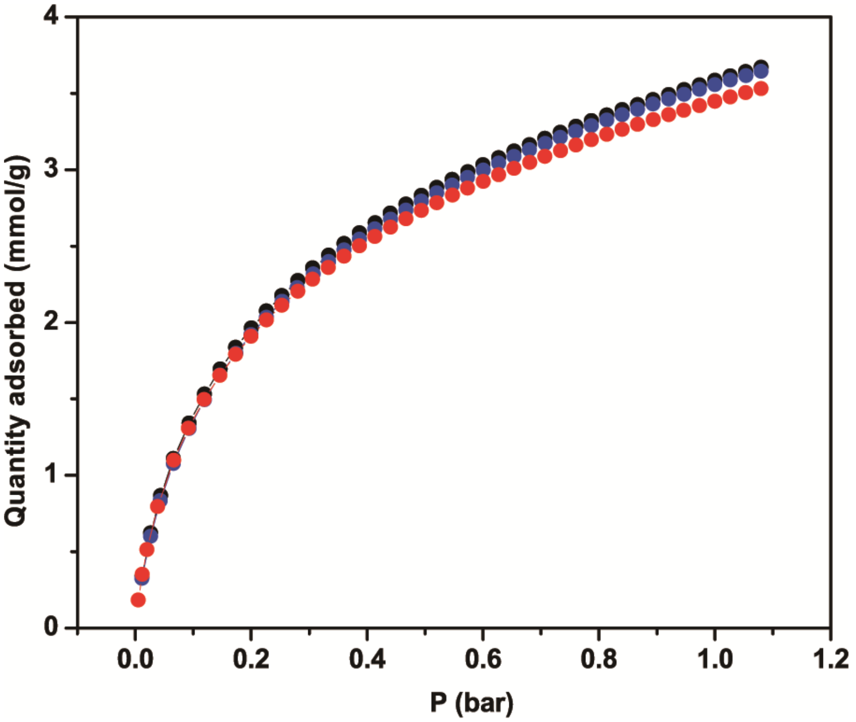


Fig. S20 CO_2 adsorption isotherms for PPN-6-SO_3NH_4 at 295 K, as-synthesized (black); after exposed to air for three months (blue); after stirred in water at 60 °C overnight (red), all the samples dried under vacuum at 120 °C for 10 h before measurements.

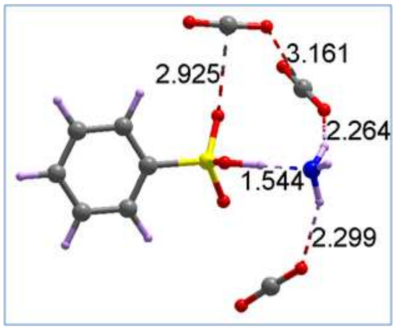


Fig. S21 Simulated interaction between PPN-6-SO_3NH_4 and CO_2 in gas phase at room temperature, carbon (gray); hydrogen (purple); sulphur (yellow); oxygen (red); nitrogen (blue), the unit for these numbers is angstrom.

Table S5. Elemental Analysis data of **PPN-6**, **PPN-6-SO_3H**, and **PPN-6-SO_3NH_4***

	PPN-6		**PPN-6-SO_3H**		**PPN-6-SO_3NH_4**	
	Exp.	Cal.** ($C_{25}H_{16}$)	Exp.	Cal.*** ($C_{25}H_{16}O_6S_2$)	Exp.	Cal.**** ($C_{25}H_{22}N_2O_6S_2$)
C%	93.51	94.90	62.29	63.01	58.46	58.81
H%	5.25	5.06	3.97	3.38	4.48	4.34
N%	0.17	0.00	0.18	0.00	5.71	5.49
S%	NA	0.00	11.86	13.46	11.08	12.56
Br%	NA	0.00	0.00	0.00	0.00	0.00
O%	NA	0.00	20.27	20.15	18.75	18.80
Li%	NA	0.00	NA	0.00	NA	0.00
Residue%	1.07	0.00	1.43	0.00	1.52	0.00

* Measured by Atlantic Microlab, Inc., sample was dried at 100^{0}C under vacuum for 10 h before measurement

**Assuming default diamondoid structure

***Assuming benzene ring/sulfonic acid (2/1)

**** Assuming complete conversion from sulfonic acid to its ammonium salt

1. A. L. Myers and J. M. Prausnitz, *A.I.Ch.E.J.*, 1965, **11**, 121-130.