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Porous organic polymers with anchored aldehydes: A new platform for post-synthetic amine functionalization en route for enhanced CO_2 adsorption properties

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Materials and Methods

Instrumentation

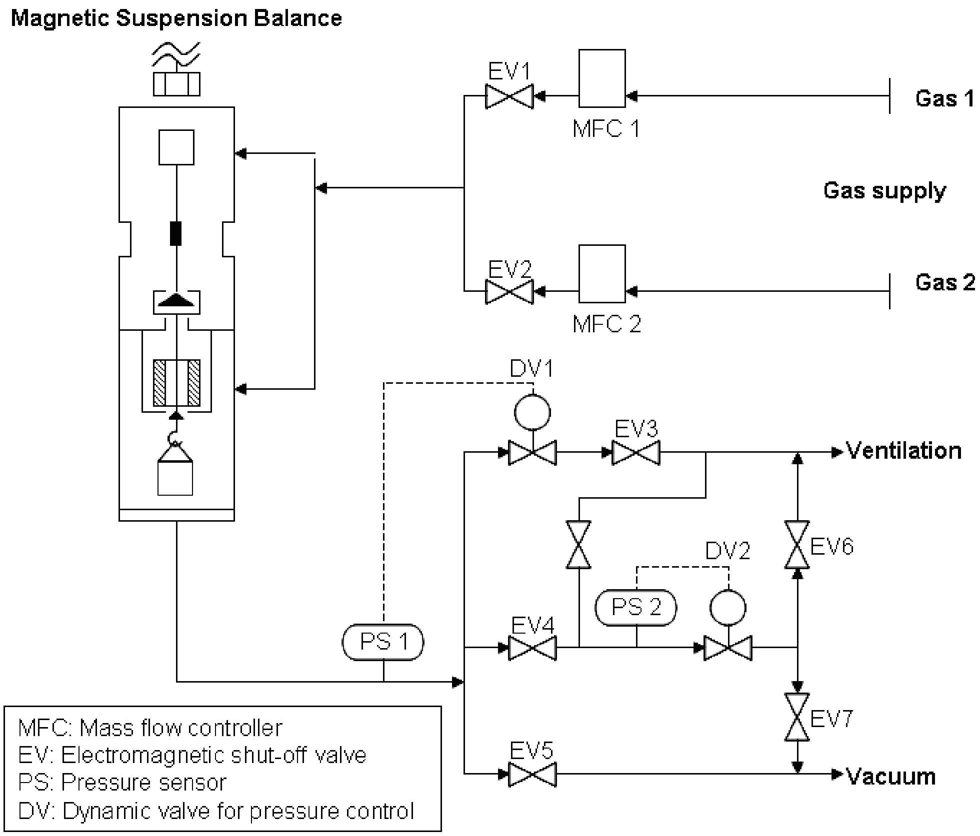
- **Thermogravimetric analysis (TGA)** measurements were performed on a TA Q500 apparatus, under air atmosphere (flow = 25 $cm^3.min^{-1}$, heating rate 5 $^oC.min^{-1}$).
- **Fourier-transform Infrared (FT-IR)** spectra (4000 – 600 cm^{-1}) were recorded on a Thermo Scientific Nicolet 6700 apparatus. The peak intensities are described in each of the spectra as very strong (vs), strong (s), medium (m), weak (w) and broad (br).
- **Low-pressure gas sorption measurements** were performed on a fully automated Autosorb 6B (for N_2 sorption screening) and Autosorb-iQ gas adsorption analyzer, (Quantachrome Instruments) at relative pressures up to 1 atm. The cryogenic temperatures were controlled using liquid nitrogen and argon baths at 77 K and 87 K, respectively. The bath temperature for the CO_2 sorption measurements was controlled using an ethylene glycol/H_2O re-circulating bath.
- **High pressure adsorption isotherms of CO_2, CH_4, N_2, H_2:** Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany) (Scheme S1), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flowmeters and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere and is able to perform adsorption measurements across a wide pressure range, i.e. from 0 to 20 MPa. The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount Ω. Correction for the buoyancy effect is required to determine the excess and absolute adsorbed amount using equation **1** and **2**, where

$V_{adsorbent}$ and V_{ss} and $V_{adorbed\ phase}$ refer to the volume of the adsorbent, the volume of the suspension system and the volume of the adsorbed phase, respectively.

$$\Omega = m_{absolute} - \rho_{gas}(V_{adsorbent} + V_{ss} + V_{adsorbed-phase}) \qquad \textbf{(1)}$$

$$\Omega = m_{excess} - \rho_{gas}(V_{adsorbent} + V_{ss}) \qquad \textbf{(2)}$$

The buoyancy effect resulted from the adsorbed phase maybe taken into account via correlation with the pore volume or with the theoritical density of the sample.



Scheme S1 *Representation of the Rubotherm gravimetric-densimetric apparatus.*

These volumes are determined using the helium isotherm method by assuming that helium penetrates in all open pores of the materials without being adsorbed. The density of the gas is determined using Refprop equation of state (EOS) database and checked experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. Simultaneous measurement of adsorption capacity and gas phase density as a function of pressure and temperature is therefore possible.

The pressure is measured using two Drucks high pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to each adsorption experiment, about 200 mg of sample is outgassed at 473 K at a residual pressure 10^{-6} mbar. The temperature during adsorption measurements is held constant by using a thermostated circulating fluid.

- **Toth Model for single gas adsorption fitting:** In the current work, the Toth model was used to fit the pure gas isotherms because of its suitable behavior at both low and high pressure and its simple formulation as expressed by equation **3**.[1]

$$n = n_s \frac{KP}{(1+(KP)^m)^{1/m}} \qquad \textbf{(3)}$$

where n is the amount adsorbed, n_s is the amount adsorbed at saturation, P is the equilibrium pressure, K is the equilibrium constant, and m is a parameter indicating the heterogeneity of the adsorbent.

- **Prediction of multicomponent gas adsorption Ideal Adsorption Solution Theory (IAST):** The Ideal Adsorption Solution Theory (IAST) proposed by Mayer and Prausnitz[2] uses pure gases adsorption isotherms to predict the mixture adsorption equilibrium at the temperature of interest. For IAST application, the main condition to be fulfilled is the availability of (i) good quality single component adsorption data of different gases, and (ii) excellent curve fitting model for such data.[3] In the current work, MSL and DSL models was used to fit the pure gas isotherms as mentioned earlier

The most important equations used in the IAST calculation are listed hereafter:

$$f_i = x_i f_i^0(\pi) \qquad \textbf{(4)}$$

$$\frac{\pi A}{RT} = \int_0^{f_i^0} n_i \, d \ln f_i \qquad \textbf{(5)}$$

$$\frac{1}{n_t} = \sum_i \frac{x_i}{n_i^0} \qquad \textbf{(6)}$$

$$S_{CO_2-i} = \frac{x_{CO_2}/x_i}{y_{CO_2}/y_i} \qquad \textbf{(7)}$$

where f_i is the fugacity of component i in the gas phase; f_i^0 is the standard-state fugacity, i.e. the fugacity of pure component i at the equilibrium spreading pressure of the mixture, π; x_i and y_i are the mole fractions of component i in the adsorbed and gas phase, respectively; A is the surface area of the adsorbent, n_i is the number of moles adsorbed of pure component i (i.e., the pure-component isotherm), and n_i^0 is the number of moles adsorbed of pure component i at the standard-state pressure

Equation **4** is the central equation of IAST, specifying the equality of the chemical potential of component i in the gas and the adsorbed phase (which is assumed to be ideal in the sense of Raoult's law). Equation **5** allows the calculation of the spreading pressure from the pure-component adsorption isotherm. The total amount adsorbed of the mixture, n_t and the selectivity of CO_2 with respect to i, S_{CO_2-i} are given by equations **6** and **7**, respectively. The selectivity S_{CO_2-i} reflects the efficiency of CO_2 separation.

- **NMR spectra** were recorded at room temperature with Bruker Avance 400MHz spectrometer using $CDCl_3$ as a solvent.

- **Elemental analysis** was performed with a Thermo Scientific Flash 2000 instrument.

Experimental Methods

Synthetic reactions were performed under argon atmosphere in oven-dried glassware. All reagents were obtained from commercial vendors and used as received, unless otherwise stated. Tetrahydrofuran (THF, ReagentPlus®, >99%, Sigma-Aldrich) was freshly distilled over $LiAlH_4$. Anhydrous N,N-dimethylformamide, (DMF, 99.8%, Sigma Aldrich) was stored over CaH_2. Other reagents: 1,3-dibromo-5-trimethylsilylbenzene, (>97%, TCI Japan); solution of lithium diisopropylamide (LDA, 2M in tetrahydrofuran/heptane/ethylbenzene, Sigma Aldrich); 1,3,5-triethynylbenzene, (TEB, 98%, Alfa Aesar); copper(I) iodide (CuI, 98%, Acros Organics); bis(triphenylphosphine)palladium(II) dichloride, (98%, Sigma Aldrich); triethylamine (Chromanorm®, HPLC grade, VWR); methanol (MeOH, HPLC grade, Fisher); absolute ethanol (EtOH, HPLC grade, Sigma Aldrich); ethylenediamine, (EDA, 99%, Acros Organics).

- *Preparation of 2,6-dibromo-4-trimethylsilylbenzaldehyde,*[4] Under argon atmosphere, the mixture of 1,3-dibromo-5-trimethylsilylbenzene (10 mmol, 3.08 g, 1 *eq*.) in dry THF (20 ml) was cooled to – 70 °C, and 2 M solution of LDA (12 mmol, 6 ml, 1.2 *eq*.) was added dropwise for 30 min and the mixture was stirred for 30 min at the same temperature. Dry DMF (12 mmol, 1 ml, 1.2 *eq*.) was then added dropwise for 5 min, and stirring was continued for 30 min at the same temperature. Then, to the cold mixture a diluted sulfuric acid was added (2 drops of conc. acid in 60 ml of water). The mixture was subsequently diluted with 50 ml of diethyl ether and the phases were separated. The water phase was further extracted with 30 ml of diethyl ether and the combined organic extracts were dried with Na_2SO_4. The reaction mixture was then filtered and concentrated using rotary evaporator. Residual oil was subjected to column chromatography (100% hexane to 95:5 hexane : EtOAc) to give 2.93 g (85%) of the yellow oil, that solidified upon standing. Rf=0.5 (95:5 Hexane : EtOAc). ^1H NMR ($CDCl_3$, 400 MHz): δ = 10.2 (1H, s, CHO), 7.70 (2H, s, $H_{ar.}$), 0.31 (9H, s, TMS) ppm (in agreement with the reported data[5]). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 191.4 (CHO), 150.5 (C4), 138.1 (C3), 132.7 (C1), 124.8 (C2), -1.420 (TMS) ppm.

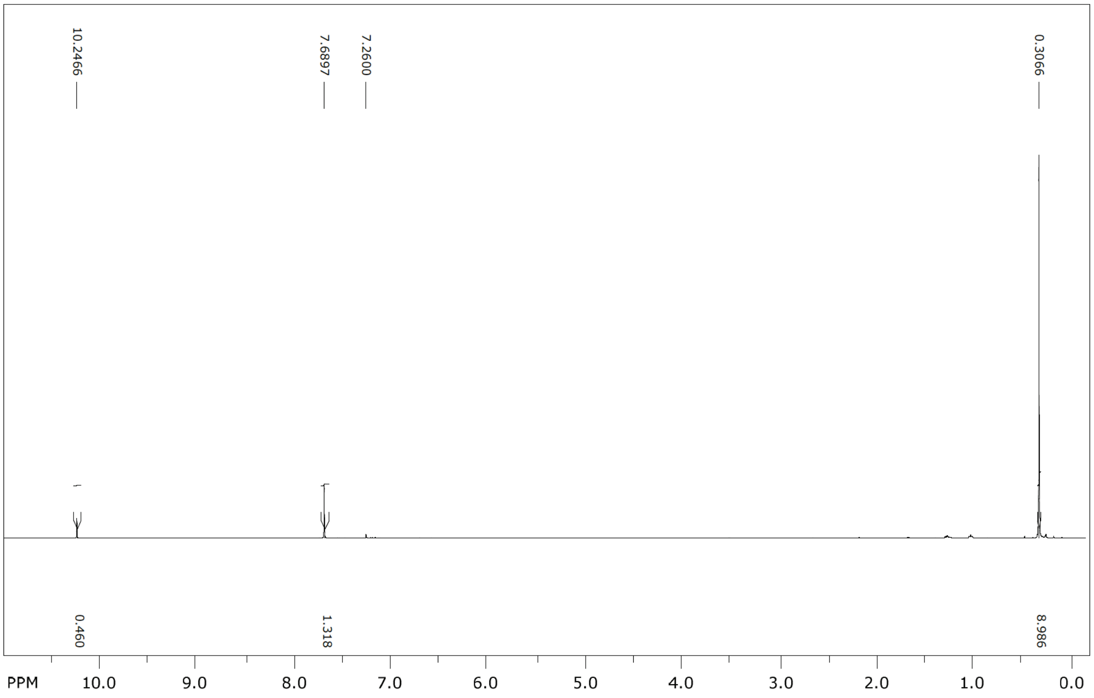


Fig. S1 *^{1}H NMR spectrum of 2,6-dibromo-4-trimethylsilylbenzaldehyde (CDCl$_3$, 400 MHz).*

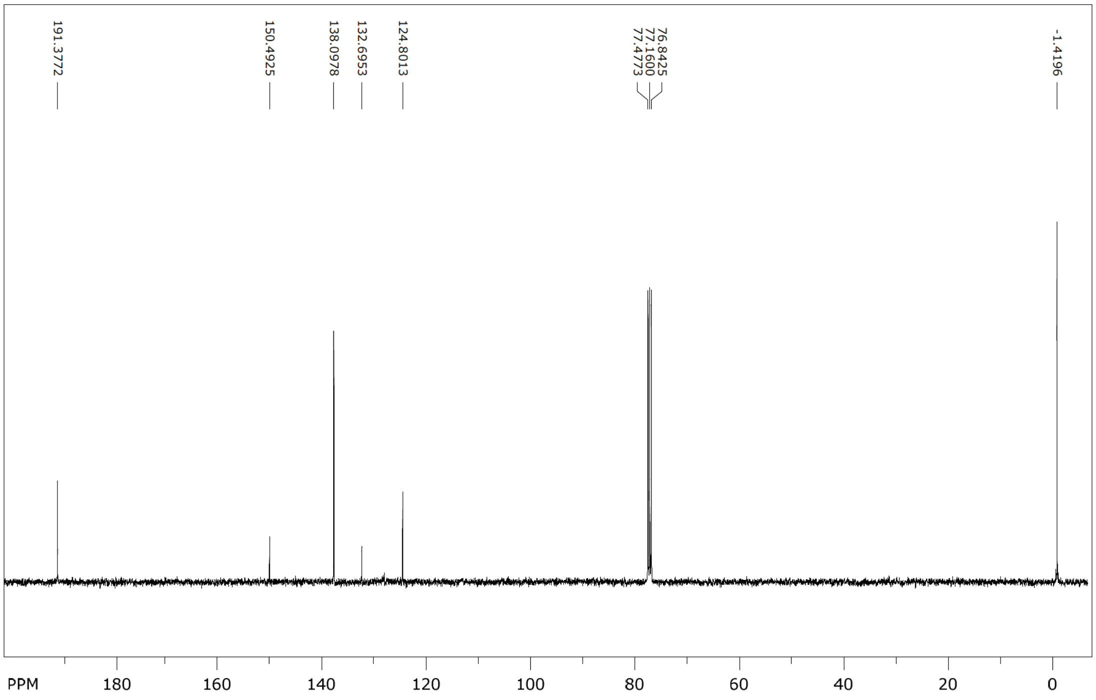


Fig. S2 *^{13}C NMR spectrum of 2,6-dibromo-4-trimethylsilylbenzaldehyde (CDCl$_3$, 100 MHz).*

- *Preparation of* $\{[(C_2)_3\text{-}C_6H_3]_2[(CH_3)_3Si\text{-}C_6H_2\text{-}CHO]_3\}_n$ *(**1**):* A mixture of dry DMF/triethylamine (4:1, 25 mL) in a round-bottom flask (100 mL), sealed with septum, was evacuated/backfilled three times, then bubbled with argon for 30 min. Then 2,6-dibromo-4-trimethylsilylbenzaldehyde (3 mmol, 1 g, 1 *eq*.), 1,3,5-triethynylbenzene (3 mmol, 450 mg, 1 *eq*.), bis(triphenylphosphine)palladium(II) dichloride (0.142 mmol, 100 mg, 0.048 *eq*.) and CuI (0.22 mmol, 42 mg, 0.075 *eq*.) were added together, the flask was then evacuated/backfilled with argon and the mixture was stirred at 80 °C for 29 h. Dark precipitate formation was observed. The mixture was diluted with methanol, filtered, and then the solid was thoroughly washed with chloroform, water, methanol and acetone. It was further purified by refluxing in ethanol for 24 h to remove any residual starting material. The product was briefly dried at suction, then under high vacuum at 50°C overnight to yield 1.2 g of brown solid. Elemental Analysis for calculated formula $C_{54}H_{42}O_3Si_3$: C = 70.02 % (calc.: 78.79 %), H = 5.50 % (5.14 %), N = 0.68 % (0.0 %).

- *Preparation* $\{[(C_2)_3\text{-}C_6H_3]_2[(CH_3)_3Si\text{-}C_6H_2\text{-}CHNC_2H_4NH_2]_3\}_n$ *(**2**):* A resealable flask was charged with 50 mg of **1** and 10 mL of EDA and heated at 85 ^{o}C for 72 h. The resulting dark brown solid was collected by filtration and exchanged for 3 days in MeOH, refreshing MeOH at least once every 24 hours. Elemental Analysis for calculated formula $C_{60}H_{60}N_6Si_3$: C = 65.72 % (calc.: 75.90 %), H = 6.11 % (6.37 %), N = 7.91 % (8.85 %).

The observed differences/discrepancies between calculated and experimental values for **1** and **2** are typical for that kind of materials due to the presence of unreacted halogen functionalities and other residual impurities, as previously demonstrated by Cooper and coworkers.[6]

Thermogravimetric analysis

Materials **1** and **2** have been dried at 50 °C for one hour prior to perform TGA measurements. **1** and **2** show similar thermal behavior. They are stable up to *ca.* 300 °C and 250°C respectively, and the structures slowly start decomposing at higher temperature. The weight loss occurring at 30 °C observed for **2** is attributed to solvent/water coordinated to the free amines through hydrogen bonding. Slower degradation of **2**, occurring at lower temperature is attributed to the progressive departure of grafted amine. Residual weight is attributed to SiO_2 formed from the degradation of TMS moieties under air.

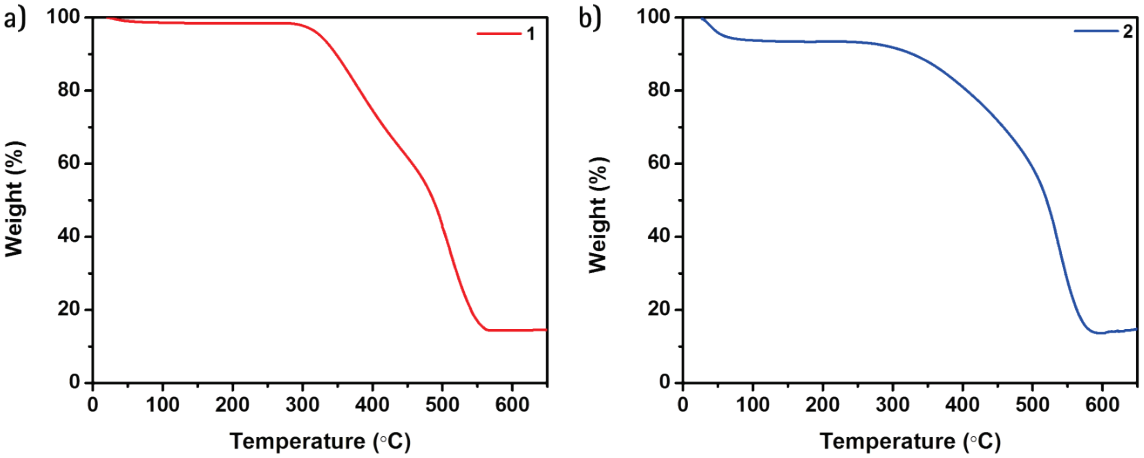


Fig. S3 *TGA of a)* ***1*** *and b)* ***2****.*

Infrared spectroscopy

IR measurements performed on **1** show the presence of both building blocks in the material, with the characteristic $\nu_{C=O}$ band (1700 cm^{-1}) attributed to the aldehyde group for TMSBA moieties and signal corresponding to $\nu_{C\equiv C}$ bond (2160 cm^{-1}) for TEB moieties. Absence of the $\nu_{C=O}$ band from aldehydes in **2** indicates efficiency of the substitution of the aldehyde, also confirmed by the presence of the $\nu_{C=N}$ band (1628 cm^{-1}). Despite the presence of a broad band (3500-3000 cm^{-1}) due to hydrogen bonding in **2**, it is possible to assign two bands from ν_{N-H} (3354 and 3287 cm^{-1}).

IR values for **1** (cm^{-1}): 3500-3000(br), 2949(m), 2892(m), 2160(w), 1700(s), 1576(s), 1411(m), 1242(s), 1215(w), 1077(m), 1084(s), 972(w), 870(m), 832(vs), 750(m).

IR values for **2** (cm^{-1}): 3500-3000(br), 3354(w), 3287(w), 3021(w), 2945(m), 2862(m), 2168(w), 1628(m), 1583(s), 1492(m), 1444(w), 1312(w), 1247(s), 1140(w), 829(vs), 750(m), 726(s), 691(s).

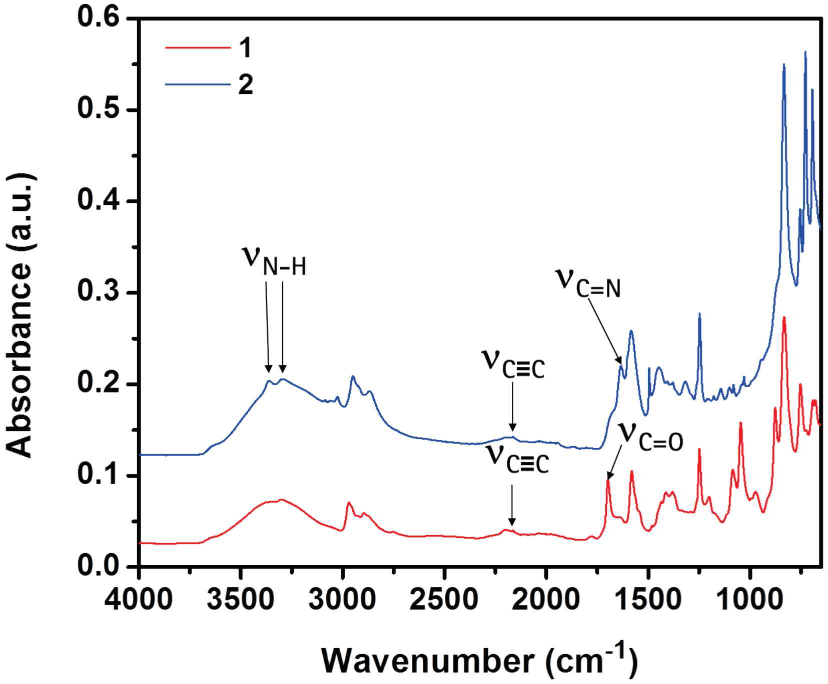


Fig. S4 *FT-IR spectra for **1** and **2**.*

Gas sorption experiments

Low pressure sorption data

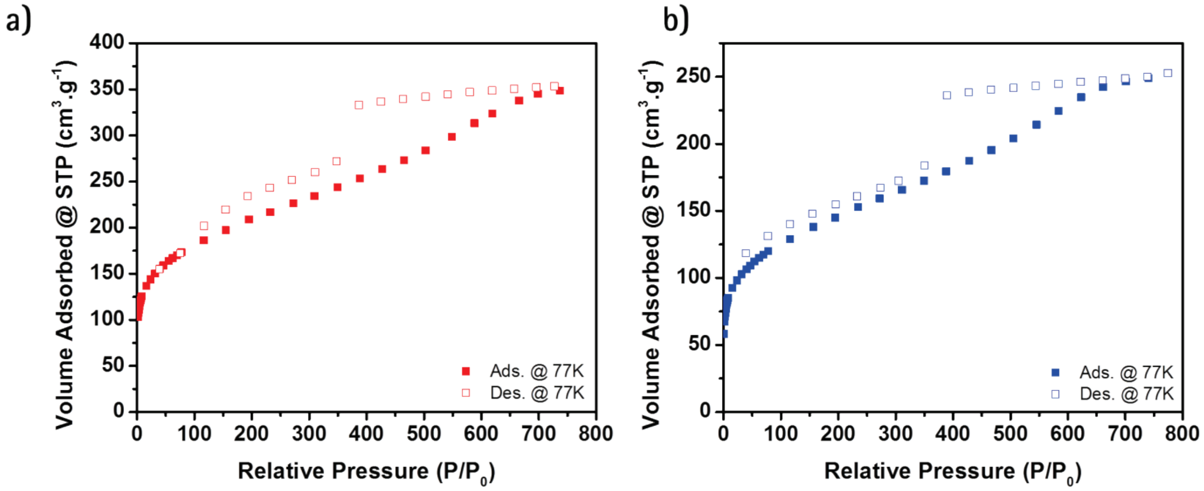


Fig. S5 *Nitrogen sorption isotherms at 77 K for a)* ***1*** *and b)* ***2****.*

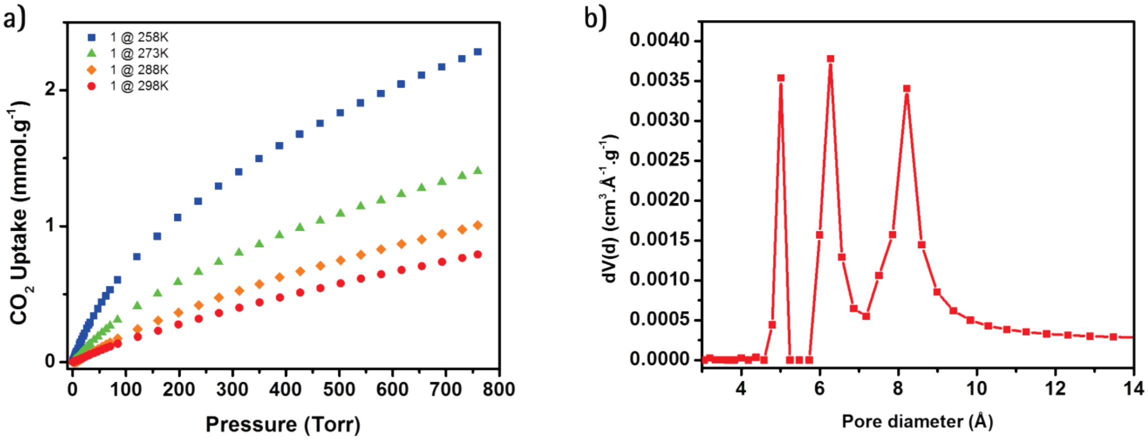


Fig. S6 *a) Variable temperature CO_2 adsorption isotherms for **1** and b) pore size distribution for **1** calculated from the CO_2 sorption isotherm at 273K (NLDFT method, carbon adsorbent).*

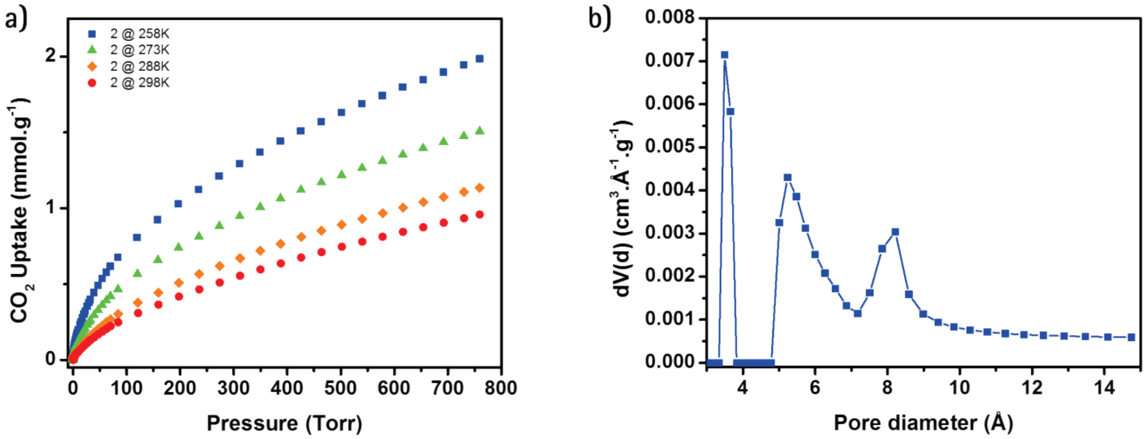


Fig. S7 *Variable temperature CO_2 adsorption isotherms for **2** and b) pore size distribution for **2** calculated from the CO_2 sorption isotherm at 273K (NLDFT method, carbon adsorbent).*

High pressure sorption data

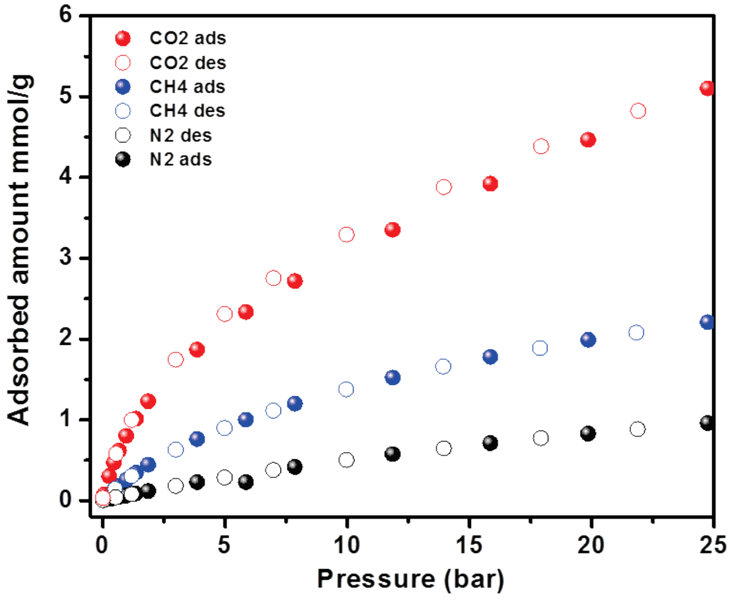


***Fig. S8** Adsorption of CO_2, N_2 and CH_4 on **1** at 298 K.*

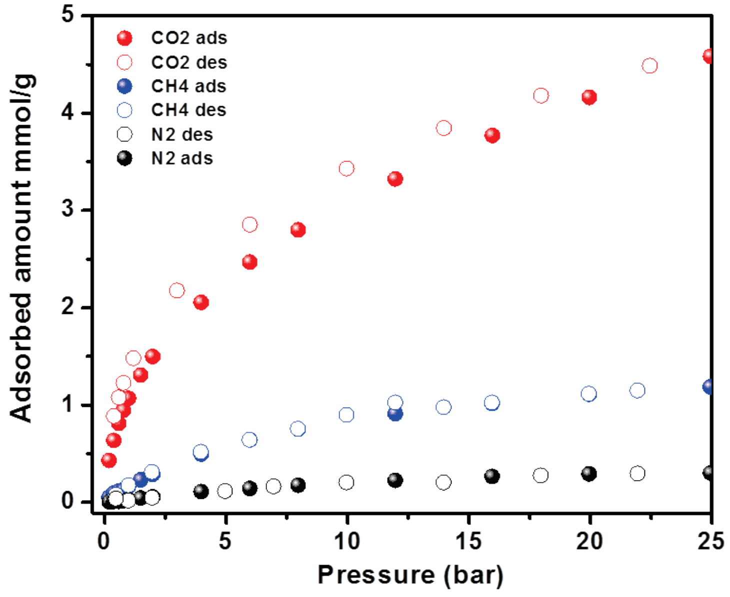


***Fig. S9** Adsorption of CO_2, N_2 and CH_4 on **2** at 298 K.*

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