

Supporting Information

Tetracarboxylate Linker Based Flexible Cu^{II} Frameworks: Efficient Separation of CO₂ from CO₂/N₂ and C₂H₂ from C₂H₂/C₂H₄ Mixtures

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Synthesis of L1-ester: A mixture of dimethyl 5-hydroxy isophthalate (10.0 mmol), 1,4-dibromobutene (5mmol) , dibenzo 18 crown-6 (0.277 mmol) , and K₂CO₃ (16 mmol) were stirred in dry THF (40 ml) under dry atmosphere using a well fitted guard tube at 70°C for 24 hours. After this time 20ml 10 % aqueous Na₂CO₃ solution was added at 0°C under an ice bath. The resulting white solid was filtered and washed with water for several times and finally with diethyl ether and dried under vacuum.

Synthesis of 5,5'-(1,4-(2-butene))bis(oxy)diisophthalic acid (L1): A mixture of L1 ester(2mmol), KOH (20mmol), 40 ml MeOH and 40 ml distilled water were stirred at 80° C in oil bath for 48 hours. The reaction mixture was filtered to remove any unreacted starting materials. 30 ml 6(M) HCl was added dropwise to filtrate at 0°C under stirring. The white precipitate was filtered and washed with distilled water for several times and dried under vacuum. ¹H NMR (400 MHz, DMSO-d₆): δ = 13.13 (br, 4H), 8.01 (s, 2H), 7.43 (s, 4H), 5.21 (s, 2H), 4.32 (s, 4H). HRMS-EI (*m/z*) for [C₂₀H₁₆O₁₀ + H₂O] Calcd. 434.0849, found 434.1084.

Synthesis of 5,5'-(1,4-phenylenebis(methylene))bis(oxy)diisophthalic acid (L2): The synthetic procedure of L2 is similar to that of L1, where 1,4- Bis-

bromomethyl-benzene is used instead of 1,4-dibromobutene. ¹H NMR (400 MHz, DMSO-d6): δ = 13.29 (br, 4H), 8.05 (s, 2H), 7.69 (s, 4H), 7.47 (s, 4H), 5.21 (s, 4H). HRMS-EI (m/z) for [C₂₄H₁₈O₁₀ + H₂O] Calcd. 484.1006, found 484.1234.

IAST Selectivity:

The ideal adsorbed solution theory (IAST) was used to predict the selectivity in binary mixture adsorption of CO₂/N₂ and C₂H₂/C₂H₄ from the experimental pure-gas isotherms. The single-component isotherms were fit to a single-site Langmuir-Freundlich equation (equation 3). IAST assumes the adsorbed phase to be in a two-dimensional solution in equilibrium with the bulk phase. The binary adsorption of A and B, according to IAST these two equations are to be followed:

$$yP_t = xP_a \text{ -----(1)}$$

$$(1 - y)P_t = (1 - x)P_b \text{ -----(2)}$$

where *x* and *y* denote the molar fraction of A in the adsorbed phase and the molar fraction of A in the bulk phase, respectively. *P_t* is the total gas pressure; *P_a* and *P_b* are the pressure of component A and B at the same spreading pressure as that of the mixture, respectively. The equation used to fit the single component gas mixture is as follows.

$$Y = Y_0 \left(\ln \frac{BP^n}{(1+BP^n)} \right) \text{-----(3)}$$

The molar fraction of A in the adsorbed phase can be obtained from the following equation:

$$Y_{0,a} \ln \left(1 + \frac{B_a P_t^{n1} y}{x} \right) - Y_{0,b} \ln \left(1 + \frac{B_b P_t^{n2} (1-y)}{(1-x)} \right) = 0 \text{-----(4)}$$

Where *Y_{0,a}*, *B_a* and *n1* are the Langmuir-Freundlich fitting parameters of adsorption equilibrium of pure A, *Y_{0,b}*, *B_b* and *n2* are Langmuir-Freundlich parameters of adsorption equilibrium of pure B. The unknown *x* in Eq. (4) has been solved by Matlab (Version 7.8

(R2009a), The MathWorks, Inc.) for fixed Pt and y values. Then calculated the predicted adsorption selectivity, which is defined as

$$S = \frac{x_1/y_1}{x_2/y_2}$$

Where x_i and y_i are the mole fractions of component i ($i = 1, 2; A, B$) in the adsorbed and bulk phases, respectively. The IAST calculations were carried out for equimolar gas-phase mixtures.

Heat of Adsorption Calculation:

The Virial type expression of the following type has been used to fit the combined isotherms data collected at 273 and 293 K.

$$\ln(P) = \ln(A) + \frac{1}{T} \sum_{i=0}^m a_i A_i + \sum_{i=0}^n b_i B_i$$

Here, P is the pressure expressed in torr, A is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m, n represent the number of coefficients required to describe the isotherms. The values of m and n are gradually increased until the contribution of extra added a and b coefficients were negligible for the overall final fit. The values of the virial coefficient a_i were taken to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^m a_i A_i$$

Q_{st} is the coverage dependent isosteric heat of adsorption and R is the universal gas constant.

Solvent Adsorption in 2'

The solvent adsorption profiles of **2** are quite interesting. **2'** adsorbs 188 mL.g⁻¹ H₂O, and the adsorption isotherm shows a gated behaviour. In this case, the adsorption increases slowly till the gate opening pressure $P/P_0 = 0.12$. Beyond this pressure, the hydrophilic nature of the framework is reflected through the steep uptake till $P/P_0 = 0.15$. It shows 3 more steps at $P/P_0 = 0.15$ and $P/P_0 = 0.70$ and $P/P_0 = 0.78$ (**Figure 5(b)**). As discussed in case of **1**, the adsorption amount decreases with the increasing kinetic diameter of the solvent. Hence, **2'** takes up 66 mL.g⁻¹ MeOH and 81 mL.g⁻¹ EtOH. In both cases, the adsorption profile is type-I in nature, which further confirms the microporous nature of **2**. **2'** adsorbs almost no benzene which further proves its hydrophilicity (**Figure S7(b)**).

Table S1. Selected bond distances (Å) for **1**.

Cu1 -O1	1.931(8)	Cu1-N1	2.319(10)
Cu1-N3	2.030(10)	Cu1-N6	2.042(14)
Cu2-O5	1.973(10)	Cu2-N5	2.043(12)
Cu2-N4	2.035(12)	Cu2-O7	1.936(9)
Cu1-O4	1.968(8)	Cu1 -N2	2.355(17)

Table S2. Selected bond angles (°) for **1**.

O1 -Cu1-N1	90.1(4)	O1 -Cu1-N3	90.2(4)
O1-Cu1 -N6	89.9(5)	O1-Cu1-O4	179.7(2)
N1-Cu1-N6	90.5(4)	N4-Cu2-N5	90.6(5)
O5-Cu2-N4	90.6(4)	O7-Cu2-N4	95.6(5)
O5-Cu2-N5	90.6(5)	N2-Cu2-N5	95.7(5)

Table S3. Hydrogen bond parameters (Å) for **1**.

O1wA – O3	2.820	O3w – N8	3.024
O1wB – O3	2.671	O2wA – O6	2.894
O1wC – N7	3.048	O1wC-O1wA	2.506

Table S4. Selected bond distances (Å) for **2**.

Cu1-O1	1.939(4)	Cu2-O5	1.910(4)
Cu1-O3	1.944(4)	Cu2-O5w	2.347(6)
Cu1-O7	2.250(4)	Cu2-N7	1.99(3)
Cu1-N2	2.038(5)	Cu2-O12	1.925(4)
Cu1-N1	2.028(5)	Cu2-N6	2.07(3)

Table S5. Selected bond angles (°) for **2**.

O1-Cu1-O3	176.46(18)	O1-Cu1-O7W	88.22(16)
O1-Cu1 – N1	87.31(17)	O1-Cu1-N2	88.9(2)
O3-Cu1-O7w	93.84(16)	O5-Cu2-O5W	91.21(19)
O5-Cu2-N7	94.0(5)	O5-Cu2-O12	177.94(19)
O12-Cu2-N6	91.7(5)	N3-Cu2-N6	174.6(7)

Table S6. Hydrogen bond parameters (Å) for **2**.

O1w – O4	2.668(7)	O5w – O6w	2.949(11)
O1w – O2	2.808(7)	O7w – O2	2.767(6)

07w -02w	2.758(9)	03w -06	2.787(8)
05w -013	2.897(8)	03w -013	2.781(7)

Figures

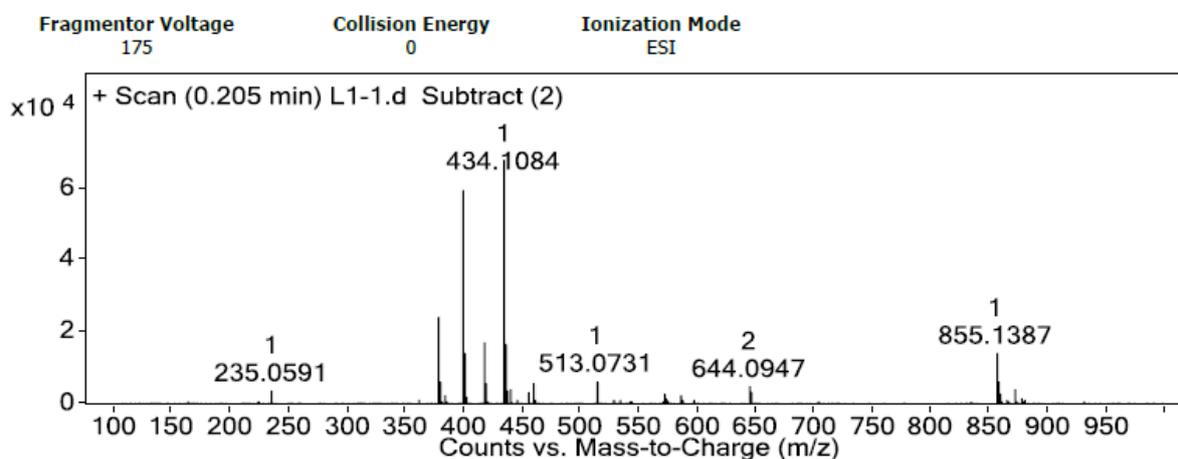


Figure S1 HRMS spectrum of **L1** showing the peak at 434, owing to the addition of a water adduct (Calcd. 18.0153) to the ligand **L1** (Calcd. 416.0743).

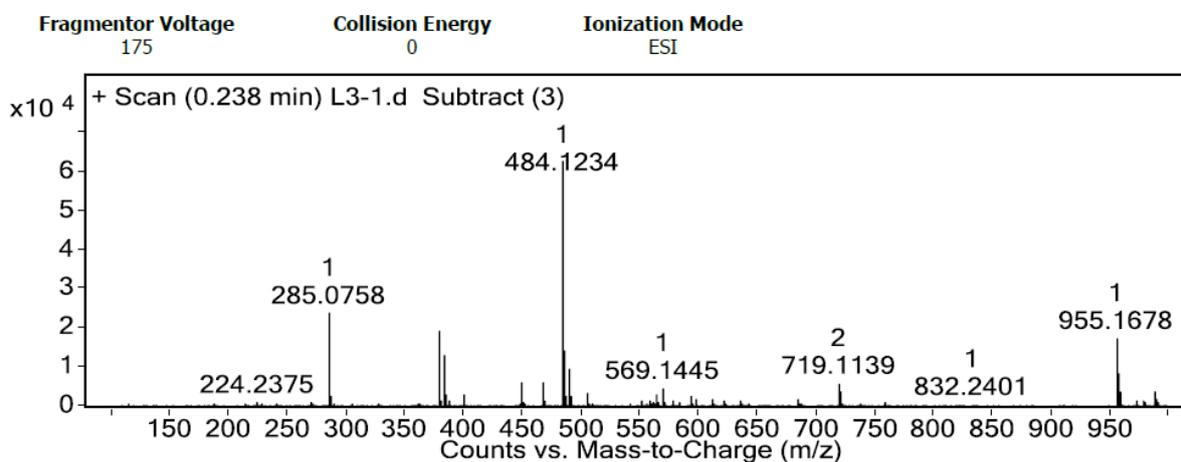


Figure S2 HRMS spectrum of **L2** showing the peak at 484.1084, owing to the addition of a water adduct (Calcd. 18.0153) to the ligand **L2** (Calcd. 466.3937).

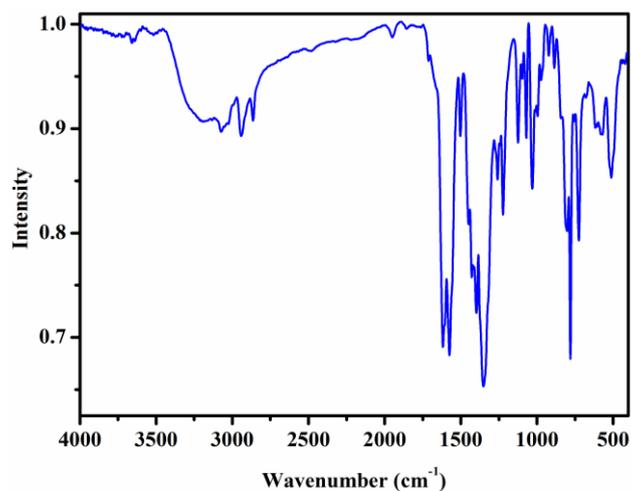


Figure S3 IR spectrum of **1**.

Table S7 Principal Peaks in IR (**Figure 2**).

Peak Position	Nature	Vibration
1568, 1618 cm^{-1}	strong	C=O stretch
778 cm^{-1}	strong	Aromatic C-H stretch
1358 cm^{-1}	strong	C-N stretch

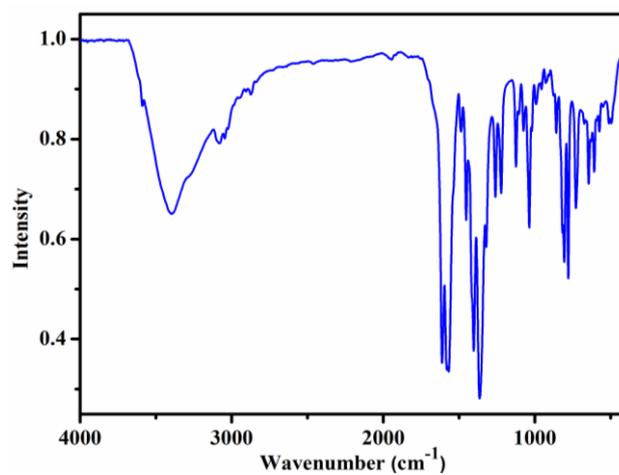


Figure S4 IR spectrum of **2**.

Table S8 Principal peaks in the IR spectrum of **2** (**Figure 4**)

Peak Position	Nature	Vibration
1570, 1616 cm^{-1}	strong	C=O stretch
782 cm^{-1}	strong	Aromatic C-H stretch
1265, 1354 cm^{-1}	strong	C-N stretch
3900 cm^{-1}	medium, broad	water

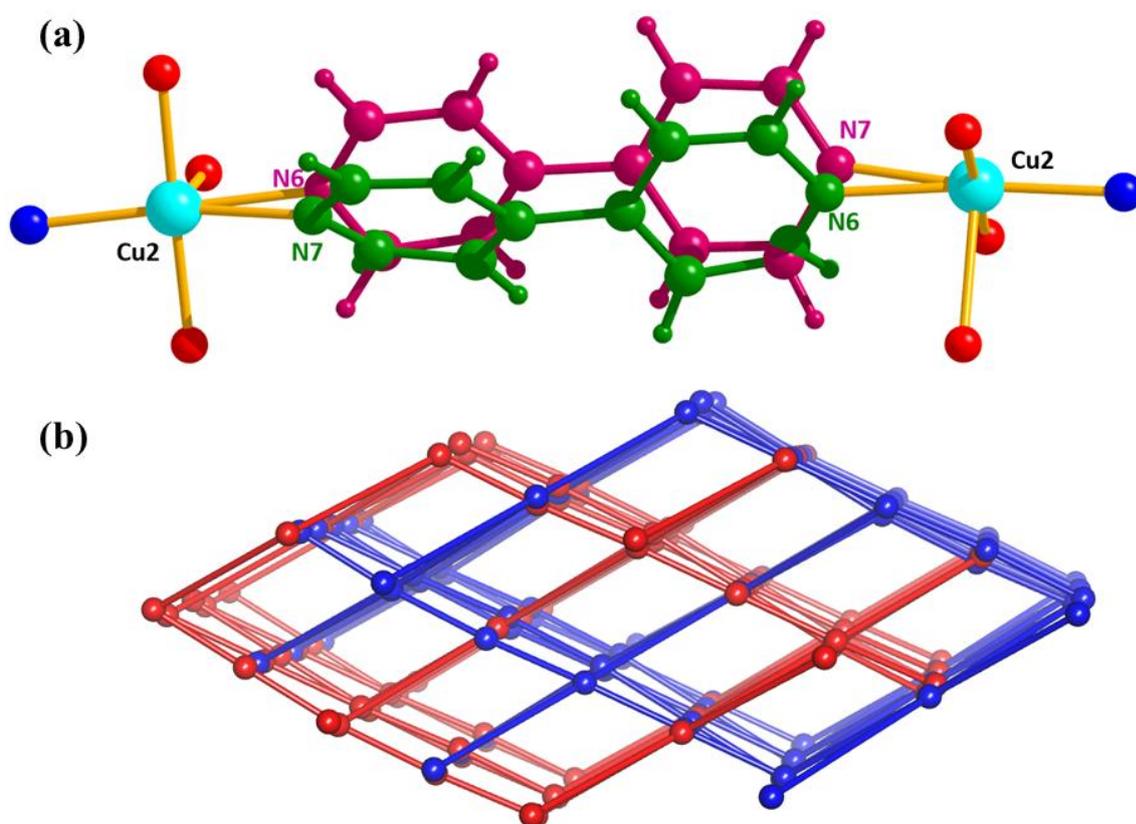


Figure S5 (a) The coordination sphere of Cu2 in **2** showing the positional disorder in the structure **(b)** TOPOS analysis displaying the interpenetrated net in **2**.

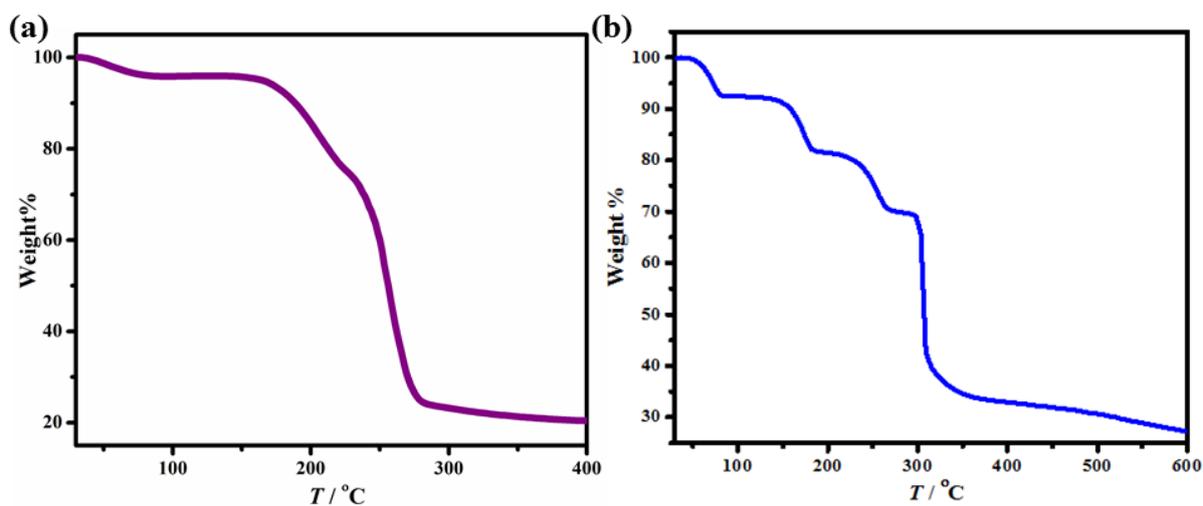


Figure S6 TGA for (a) compound 1 and (b) compound 2.

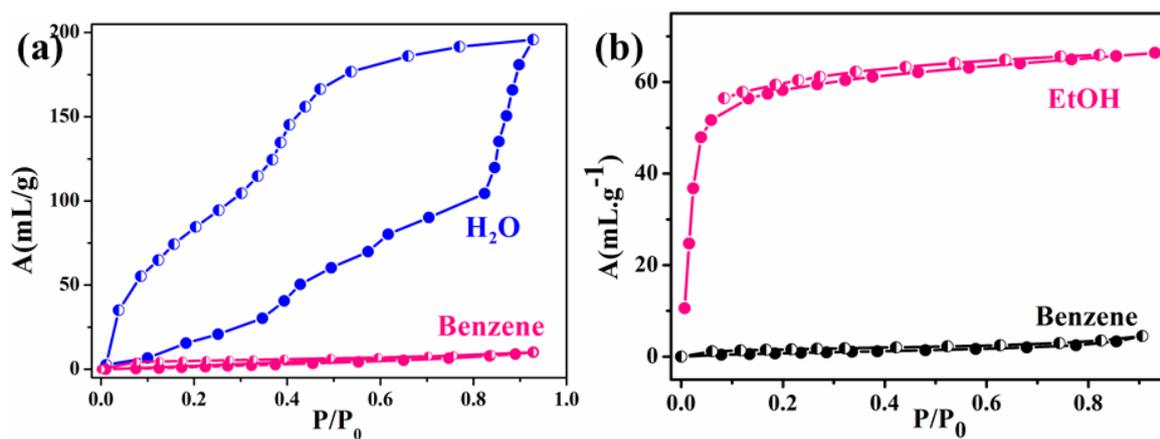


Figure S7 Solvent adsorption isotherms for (a) compound 1' and (b) compound 2'.

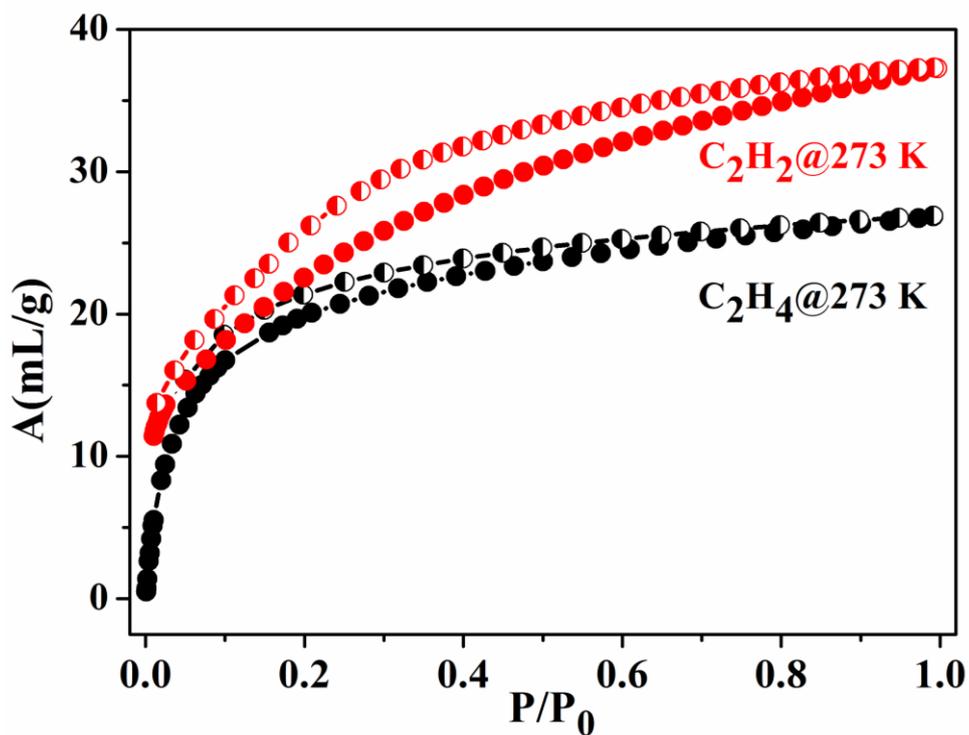


Figure S8 C_2H_2 and C_2H_4 adsorption isotherms at 273 K.

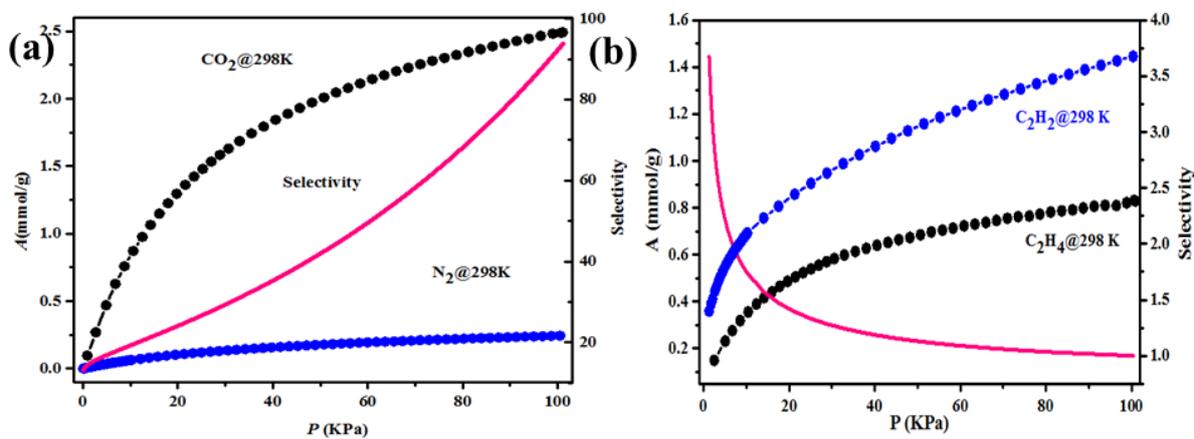


Figure S9 Calculated selectivities for (a) CO_2 and N_2 and (b) C_2H_2 and C_2H_4 at 298 K for 2'.

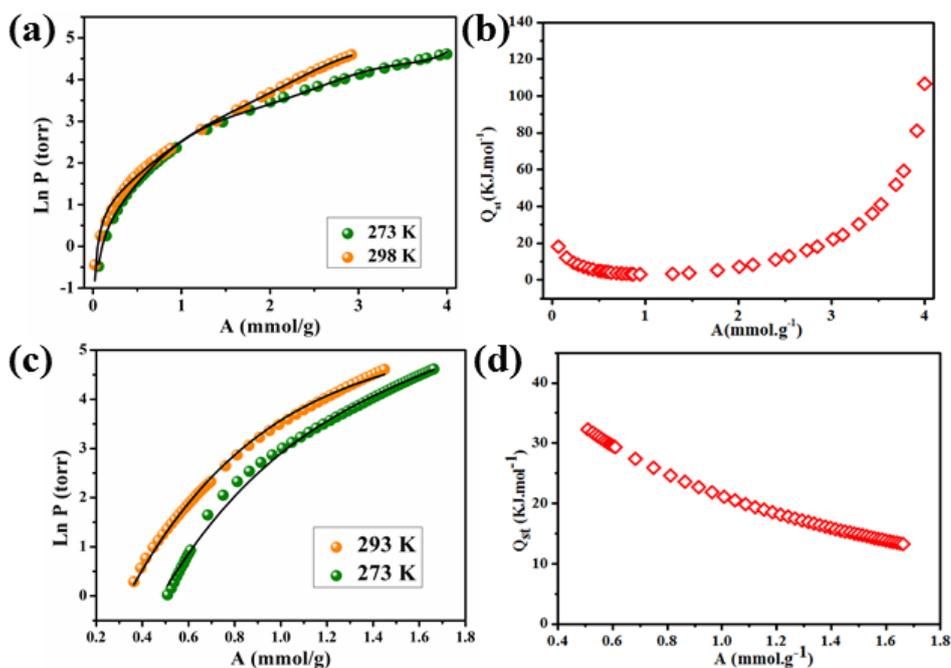


Figure S10 (a) Adsorption isotherms for CO₂ at 273 and 298 K fitted in the Virial Equation for **2'**. (b) Change in the heat of enthalpy with loading of CO₂ in **2'** calculated from the Virial fitting of the adsorption isotherms at 273 and 298 K. (c) Adsorption isotherms for C₂H₂ at 273 and 293 K fitted in the Virial Equation for **2'**. (d) Change in the heat of enthalpy with loading of C₂H₂ in **2'** calculated from the Virial fitting of the adsorption isotherms at 273 and 293 K.

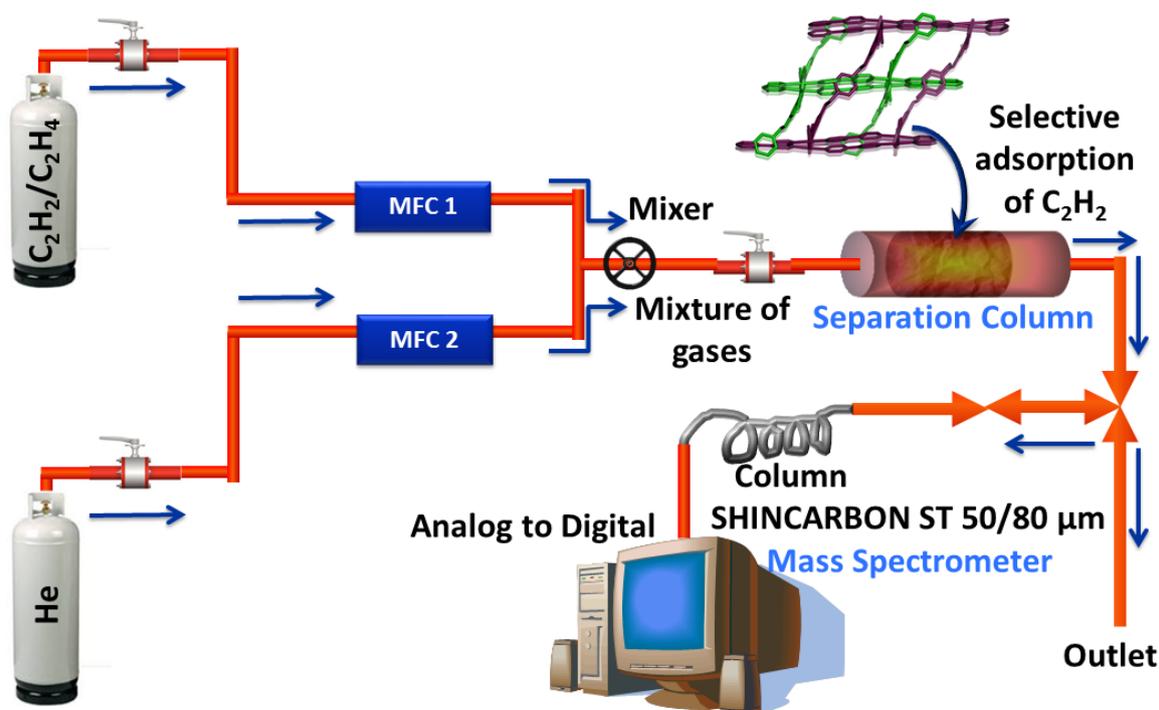


Figure S11 Scheme showing the setup for breakthrough experiment