Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

An Adsorbate Biased Dynamic 3D Porous Framework for Inverse CO_2 Sieving over C_2H_2

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Experimental section

Materials

All the reagents employed are commercially available and used as provided without further purification. $Ni(NO_3)_2 \cdot 6H_2O$ has been obtained from Spectrochem. 1,4-naphthalele dicarboxylicacid (1,4-H_2ndc), KOH were obtained from Alfa Aeser.

Synthesis

A mixture containing $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 mmol, 0.145 g), 1,4-H_2ndc (0.5 mmol, 0.108 g) and KOH (1.0 mmol, 0.056 g) is suspended in teflon bomb containing 10 mL water and stirred for 30 mins. The solution was then heated at 180 °C for a period of 10 days. The dark green colored block-shaped crystals of **1** were then collected and further washed in water for several times. Yield: 80 % (with respect to metal). Anal. Calc. for $C_{36}O_{19}Ni_4H_{18}$ C: 43.711; H: 1.83; Found C: 44.98; H: 2.01. FT-IR (KBr pellet, 4000–400 cm^{-1}): 3444 (br), 1610 (s), 1590 (w), 1412 (s).

Physical measurements

Elemental analyses are carried out using a Thermo Fischer Flash 2000 Elemental Analyzer. FT-IR spectra are recorded on a Bruker IFS 66v/S spectrophotometer using KBr pellets in the region 4000-400 cm^{-1}. The in-situ DRIFTs measurements were carried out using an FT-IR spectrophotometer (BRUKER, Vertex 70B) within a removable sample compartment using an MCT detector. The 10 mg of activated sample or **1′** was evenly coated on the glass disc of 1 cm diameter and placed inside the evacuable/purgeable sample compartment for monitoring reaction progress of by increasing CO_2 (99.995 %) pressure inside the sample chamber in a regular manner. Similar procedure has been followed by only allowing CO_2 gas inside the chamber in absence of the sample as a control study. All the signals were collected through MCT detector with 4 cm^{-1} resolution and 64 scans at a regular time interval. At first, the molecular CO_2 peaks are identified by dosing CO_2 in the chamber with increasing flow through MFC (mass flow controller). Next, the MOF peak has been identified by keeping the sample coted disc after releasing CO_2 from the chamber. Finally, the exclusive spectra appeared and increased from CO_2-interacted MOF by dosing CO_2 in higher flow in the chamber. These peaks are recorded with regular intervals and analysed over the solo MOF and molecular CO_2 peaks appeared after infrared radiation. Thermogravimetric analyses (TGA) are carried out (Metler Toledo) in nitrogen atmosphere in the temperature range of 30–700 °C (heating rate 5 °C min^{-1}). The powder XRD pattern of the compounds has been recorded by using Cu-Kα radiation

(Bruker D8 Discover; 40 kV, 30 mA). The patterns have been agreed with those calculated from single crystal structure determination.

X-ray crystallography

X-ray single-crystal structure data of **1** has been collected on a Bruker Smart-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source with graphite monochromated Mo-Kα radiation (λ= 0.71073 Å) operating at 50 kV and 30 mA. The program SAINT[1] is used for the integration of diffraction profiles and absorption correction was made with SADABS[2] program. All the structures are solved by SIR92[3] and refined by full-matrix least-squares method using SHELXL-97.[4] All the hydrogen atoms are fixed by HFIX and placed in ideal positions. Potential solvent accessible area or void space is calculated using the PLATON multipurpose crystallographic software. All the crystallographic and structure refinement data of **1** are summarized in **Table S1**. Selected bond lengths and angles for **1** are given in **Table S2-3**, respectively. All calculations were carried out using SHELXS 97,[5] PLATON,[6] and WinGX system, Ver 1.80.05.

Table S1 Crystal data and structure refinement parameters of **1.**

Parameters	
Empirical Formula	$C_{36}O_{19}Ni_4H_{18}$
Formula weight	989.26
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	7.0744(1)
b, Å	13.6038(3)
c, Å	20.6602(4)
α, deg	98.903(1)
β, deg	96.002(1)
γ, deg	101.590(1)
V, Å^3	1905.31(6)
Z	2
T, K	298
μ, mm^{-1}	2.028
D_{calcd}, g/cm^3	1.724
F (000)	996

Total reflections	114743
Unique reflections	14547
λ(Mo-Kα)	0.71073
R_{int}	0.079
GOF on F^2	1.06
$R_1[I>2\sigma(I)]^a$	0.0410
R_w[all data]^b	0.1236

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

Table S2 Selected bond lengths (Å) for **1**.

Ni1-O13	1.9853(14)	Ni1-O5	2.0073(15)
Ni1-O11	2.0966(15)	Ni1-O8	2.1047(15)
Ni1-O14	2.1639(16)	Ni2-O15	2.0222(14)
Ni2-O13	2.0376(15)	Ni2-O6	2.0377(15)
Ni2-O12	2.0422(15)	Ni2-O2	2.0661(15)
Ni2-O14	2.1914(17)	Ni3-O15	2.0125(15)
Ni3-O13	2.0189(14)	Ni3-O3	2.0360(16)
Ni3-O7	2.0552(15)	Ni3-O9	2.0675(15)
Ni3-O16	2.2103(16)	Ni4-O15	1.9740(14)
Ni4-O10	1.9888(15)	Ni4- O4	2.0345(16)
Ni4-O8	2.0694(15)	Ni4-O11	2.1409(15)
Ni4-O16	2.1852(16)	Ni1-O1	2.0319(16)

Table S3 Selected bond angles (°) for **1**.

O13-Ni1-O5	101.87(6)	O13-Ni1- O1	90.06(6)	O5-Ni1-O1	93.97(7)
O13-Ni1-O11	85.72(6)	O5-Ni1-O11	168.19(7)	O1-Ni1-O11	95.07(6)
O13-Ni1-O8	94.13(6)	O5-Ni1-O8	86.85(6)	O1-Ni1-O8	175.48(6)
O11-Ni1-O8	83.55(6)	O13-Ni1-O14	173.75(6)	O5-Ni1-O14	83.78(6)
O1-Ni1-O14	86.84(6)	O11-Ni1-O14	89.14(6)	O8-Ni1-O14	88.83(6)
O15-Ni2-O13	81.38(6)	O15-Ni2-O6	86.72(6)	O13-Ni2-O6	100.06(6)
O15-Ni2-O12	92.30(6)	O13-Ni2-O12	89.85(6)	O6-Ni2-O12	169.76(7)
O15-Ni2-O2	174.46(6)	O13-Ni2-O2	93.34(6)	O6-Ni2-O2	95.89(7)
O12-Ni2-O2	85.99(6)	O15-Ni2-O14	93.23(6)	O13-Ni2-O14	173.82(6)
O6-Ni2-O14	82.55(6)	O12-Ni2-O14	87.34(7)	O2-Ni2-O14	91.95(6)
O15-Ni3-O13	82.08(6)	O15-Ni3-O3	94.45(6)	O13-Ni3-O3	176.45(6)

O15-Ni3-O7	91.13(6)	O13-Ni3-O7	92.83(6)	O3-Ni3-O7	86.46(7)
O15-Ni3-O9	102.05(6)	O13-Ni3-O9	89.83(6)	O3-Ni3-O9	91.64(7)
O7-Ni3 -O9	166.79(7)	O15-Ni3-O16	175.34(6)	O13-Ni3-O16	93.57(6)
O3-Ni3-O16	89.88(6)	O7-Ni3-O16	87.42(6)	O9-Ni3-O16	79.50(6)
O15-Ni4-O10	102.92(6)	O15-Ni4-O4	91.23(6)	O10-Ni4-O4	92.82(7)
O15-Ni4-O8	85.65(6)	O10-Ni4-O8	167.28(6)	O4-Ni4-O8	96.41(6)
O15-Ni4-O11	93.76(6)	O10-Ni4 -O11	86.72(6)	O4-Ni4-O11	174.96(6)
O8-Ni4-O11	83.32(6)	O15-Ni4-O16	172.65(6)	O10-Ni4-O16	84.15(6)
O4-Ni4-O16	86.38(6)	O8-Ni4-O16	87.72(6)	O11-Ni4-O16	88.59(6)

Table S4 Comparison of cell parameters at different states: (**1′** is indexed using TOPAS Programme and rehydrated **1** by Fullprof software). Change in respective crystal structures transforming from as-synthesized to desolvated to rehydrated MOFs.

	a **(Å)**	***b*** **(Å)**	***c*** **(Å)**	**α (°)**	**β (°)**	**γ (°)**	***V*** **(Å^3)**	lattice
	Cell parameters							
As-synthesized (**1**)/ Open-pore phase	7.07440	13.6038	20.6602	98.9030	96.0020	101.5900	1905.31	Triclinic
Desolvated **1′**	20.4495	9.7947	8.9130	90	90	90	1785.23	Orthorhombic
Rehydrated **1**	7.081	13.802	20.864	98.486	96.655	101.691	1952.52	Triclinic

Table S5 List of atomic coordinates for the MOF **1** (Extracted from CIF file).

Atoms	**X**	**Y**	**Z**
Ni1	-0.03780(4)	0.64442(2)	0.78876(2)
Ni2	0.43189(4)	0.65325(2)	0.78674(2)
Ni3	0.17855(4)	0.43885(2)	0.73715(2)
Ni4	0.64199(4)	0.44476(2)	0.73276(2)
O1	0.0628(2)	0.78054(12)	0.76152(8)
O2	0.3871(2)	0.79880(12)	0.78712(8)
O3	0.2172(2)	1.29433(12)	0.73612(8)
O4	0.5413(2)	1.30797(12)	0.75940(8)
O5	0.1034(2)	0.68897(13)	0.88144(7)
O6	0.3970(2)	0.65037(13)	0.88314(7)
O7	-0.0895(2)	0.56852(13)	1.17183(7)

O8	0.1627(2)	0.49291(11)	1.18208(7)
O9	0.2028(2)	0.42838(13)	0.63758(7)
O10	0.5027(2)	0.39820(13)	0.64097(7)
O11	0.2320(2)	0.41685(11)	0.29860(7)
O12	0.4812(2)	0.33819(13)	0.30381(7)
O13	0.1560(2)	0.58533(11)	0.74194(7)
O14	-0.2617(2)	0.71193(12)	0.82946(8)
O15	0.4527(2)	0.50597(11)	0.77968(7)
O16	0.8707(2)	0.37691(12)	0.69338(8)
C1	0.2379(3)	0.83041(16)	0.77015(10)
C2	0.2698(3)	0.93974(16)	0.76065(11)
C3	0.3910(4)	1.01310(18)	0.80854(12)
H3	0.453681	0.993704	0.844767
C4	0.4223(4)	1.11678(17)	0.80390(12)
H4	0.504599	1.165234	0.837035
C5	0.3325(3)	1.14689(16)	0.75101(11)
C6	0.2101(3)	1.07333(16)	0.69865(11)
C7	0.1773(3)	0.96775(16)	0.70386(11)
C8	0.0593(4)	0.89545(18)	0.65041(12)
H8	0.034986	0.826505	0.653003
C9	-0.0189(5)	0.9253(2)	0.59540(13)
H9	-0.09493	0.876529	0.560995
C10	0.0143(5)	1.0285(2)	0.59038(13)
H10	-0.039805	1.048011	0.552711
C11	0.1262(4)	1.10103(19)	0.64060(12)
H11	0.147444	1.169418	0.636622
C12	0.3662(3)	1.25973(15)	0.74885(10)
C13	0.2517(3)	0.66670(16)	0.90957(10)
C14	0.2433(3)	0.65200(17)	0.98012(10)
C15	0.2784(4)	0.56354(19)	0.99644(11)
H15	0.334478	0.521761	0.967842
C16	0.2305(4)	0.53485(18)	1.05638(11)
H16	0.259051	0.475297	1.067609
C17	0.1420(3)	0.59394(16)	1.09852(10)
C18	0.1190(3)	0.69135(17)	1.08567(10)
C19	0.1749(4)	0.72168(17)	1.02603(10)
C20	0.1651(5)	0.8208(2)	1.01542(13)
H20	0.200536	0.841174	0.976615
C21	0.1051(6)	0.8868(2)	1.06064(14)
H21	0.104327	0.952461	1.053298
C22	0.0439(5)	0.8567(2)	1.11865(14)
H22	-0.000403	0.901873	1.148867
C23	0.0494(4)	0.76174(19)	1.13057(12)
H23	0.00687	0.742348	1.168768
C24	0.0653(3)	0.55046(15)	1.15500(9)
C25	0.3415(3)	0.40257(16)	0.61105(10)
C26	0.3201(3)	0.37851(17)	0.53658(10)
C27	0.2330(4)	0.43875(19)	0.50201(10)

H27	0.17095	0.485418	0.523897
C28	0.2361(4)	0.43094(19)	0.43311(10)
H28	0.176656	0.473011	0.410314
C29	0.3254(3)	0.36229(16)	0.39920(10)
C30	0.4060(3)	0.29224(17)	0.43287(10)
C31	0.4016(3)	0.30073(17)	0.50271(10)
C32	0.4720(4)	0.2280(2)	0.53564(12)
H32	0.471297	0.232978	0.581011
C33	0.5402(5)	0.1514(2)	0.50215(13)
H33	0.584189	0.104291	0.524619
C34	0.5446(5)	0.1431(2)	0.43410(13)
H34	0.591671	0.090479	0.411593
C35	0.4803(4)	0.21162(19)	0.40024(12)
H35	0.485355	0.205219	0.355019
C36	0.3482(3)	0.37120(16)	0.32883(9)
Ni1	0.96220(4)	0.64442(2)	0.78876(2)
Ni1	0.03780(4)	0.35558(2)	0.21124(2)
Ni1	0.03780(4)	0.35558(2)	1.21124(2)
Ni2	-0.56811(4)	0.65325(2)	0.78674(2)
Ni2	0.56811(4)	0.34675(2)	0.21326(2)
Ni3	0.17855(4)	1.43885(2)	0.73715(2)
Ni3	1.17855(4)	0.43885(2)	0.73715(2)
Ni3	-0.17855(4)	0.56115(2)	1.26285(2)
Ni4	-0.35801(4)	0.44476(2)	0.73276(2)
Ni4	0.64199(4)	1.44476(2)	0.73276(2)
Ni4	0.35801(4)	0.55524(2)	0.26724(2)
Ni4	0.35801(4)	0.55524(2)	1.26724(2)
O3	0.2172(2)	0.29433(12)	0.73612(8)
O4	0.5413(2)	0.30797(12)	0.75940(8)
O7	0.0895(2)	0.43148(13)	0.82817(7)
O8	-0.1627(2)	0.50709(11)	0.81792(7)
O8	0.8373(2)	0.50709(11)	0.81792(7)
O11	-0.2320(2)	0.58315(11)	0.70140(7)
O11	0.7680(2)	0.58315(11)	0.70140(7)
O12	0.5188(2)	0.66181(13)	0.69619(7)
O14	0.7383(2)	0.71193(12)	0.82946(8)
O16	-0.1293(2)	0.37691(12)	0.69338(8)
O17	-0.2161(4)	0.89750(18)	0.80080(15)
O18	-0.2585(13)	0.7371(10)	0.9656(6)
O19	0.7591(4)	0.17817(19)	0.68974(14)

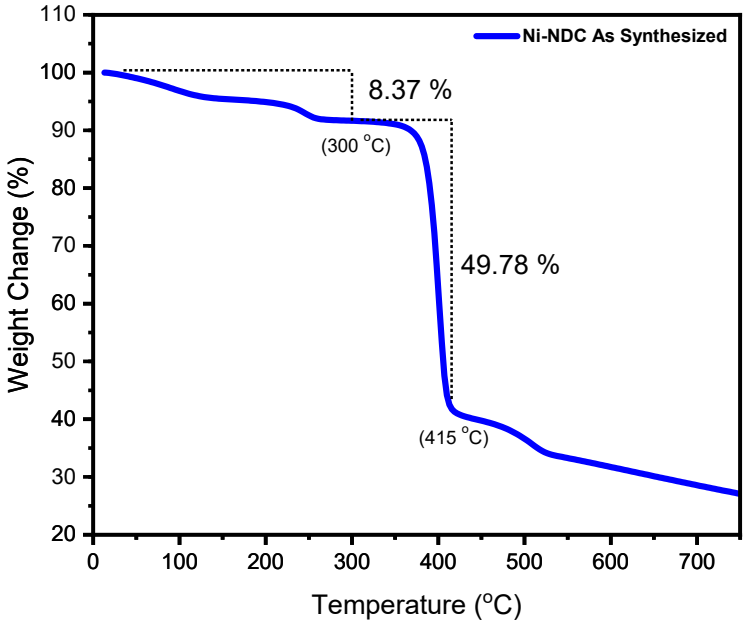

Figure S1 Thermogravimetric analysis of Ni-NDC MOF.

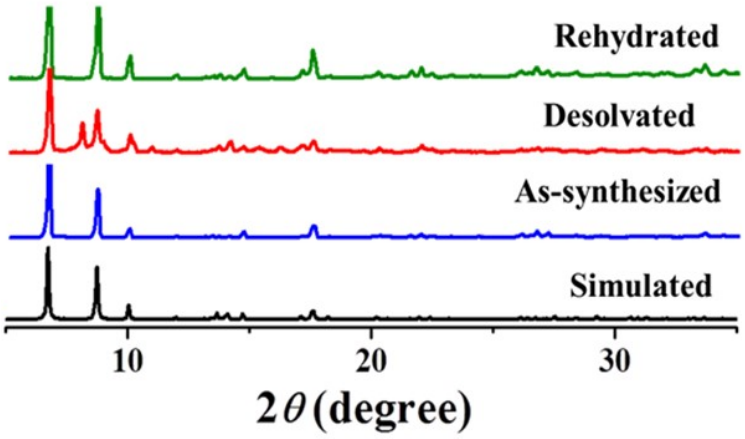

Figure S2 PXRD pattern of **1** recorded at different states: (I) simulated (II) as-synthesized (III) desolvated **1′** (activated phase) (IV) rehydrated phase of **1′**.

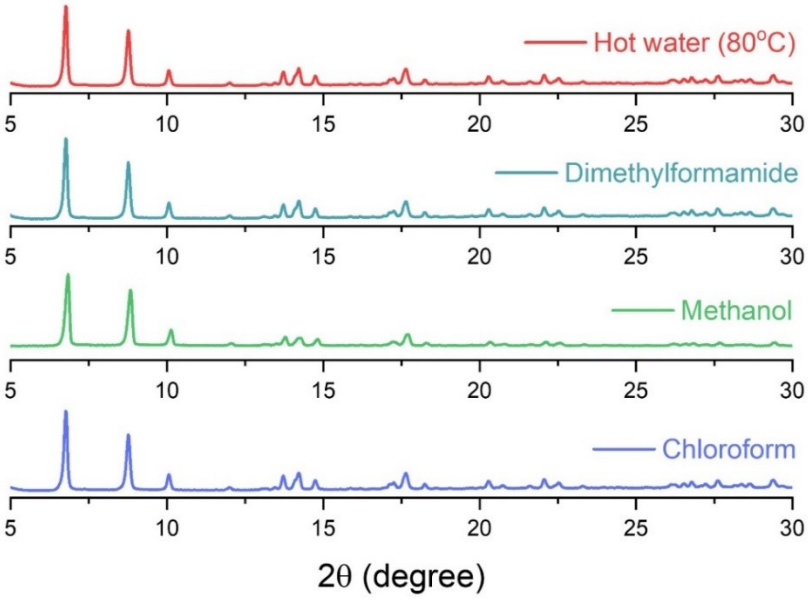

Figure S3 PXRD patterns for Ni-NDC MOF showing stability after treatment with different solvents.

Adsorption details

The adsorption isotherms of CO_2 (at 195, 273 and 298 K), N_2 (at 77 and 298 K), CH_4, C_2H_2, C_2H_4 and C_2H_6 (at 298 and 273 K) of **1′** have been measured using AUTOSORB IQ2 instrument. The compound **1** has been activated at 195 °C under 1×10^{-1} Pa vacuum for about 16 h prior to measurement of the isotherms. All the gases used for adsorption measurement are of scientific/research grade with 99.999% purity. Dead volume is measured with helium gas. The adsorbates are passed into the sample cells, and then the change of the pressure is monitored and the degree of adsorption is determined by the decrease in pressure at the equilibrium state. All operations are software defined and automatic. For diffusion, the relation of particle-vapor speed can be expressed by film thickness and diffusion coefficient. The graph represents $(C - C_{e1}/C_{01} - C_{e1})$ vs time (sec), where C is the density of the adsorbate. Additionally, C_{e1}, C_{01} are the gas phase density at equilibrium point and saturated vapor pressure by considering n-th (here we choose the 1st point where n=1) point at P/P_0. For measuring the adsorption rate from CO_2 adsorption, we choose the 2nd point and corresponding kinetic plot with LDF (linear driving force) fitting are as given Figure S6.[7,8]

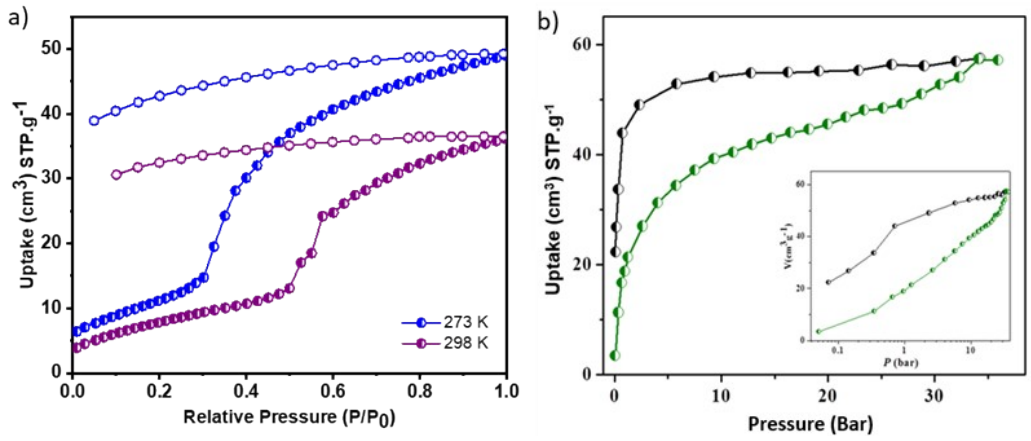

Figure S4 (a) CO_2 adsorption isotherm of **1′** at 273 and 298 K, respectively, reports shifting in gate opening pressure upon changing measurement temperature. (b) High-pressure CO_2 adsorption isotherm at 273 (black) and 298 K (green, inset).

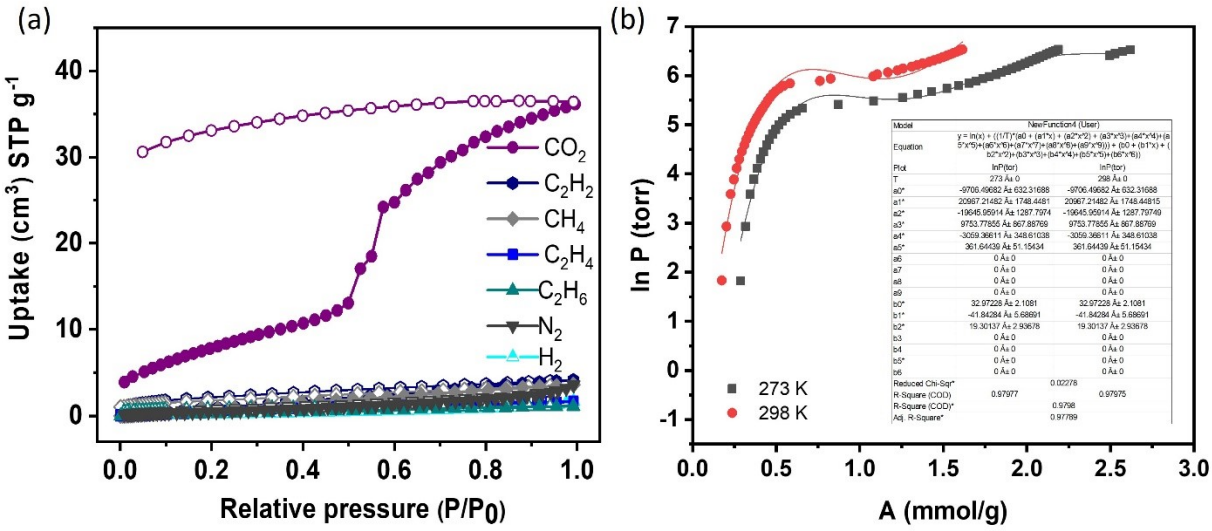

Figure S5 (a) N_2, H_2, CO_2 and different hydrocarbon (CH_4, C_2H_2, C_2H_4, C_2H_6) adsorption isotherms at 298 K for **1′**. (b) Virial fitting corresponding to figure 2c.

Table S6 Physical parameters of selected gas and vapor adsorbate.[9-11]

	Molecular dimension (Å)			Boiling point (K)	Polarizability×10^{25} cm^3	Dipole moment× 10^{18} esu cm	Quadruple moment×10^{26} esu cm^2
	x	y	z				
CO_2	3.18	3.33	5.36	216.55	29.11	0.109	4.3
CH_4	3.63	3.98	3.98	111.66	25.93	--	--
C_2H_2	3.32	3.34	5.76	188.40	33.3-39.3	--	4.71
C_2H_4	3.28	4.18	4.84	169.42	42.52	--	1.5
C_2H_6	3.81	4.08	4.82	184.55	44.3-44.7	0.366	0.65

The adsorption isotherms of different solvents (MeOH at 293 K and H_2O at 298 K) for **1′** are measured in the vapor state by using a BELSORP-aqua3 volumetric adsorption instrument from BEL, Japan. All the samples of about ~100 mg is prepared by adopting a similar procedure mentioned earlier prior to measurement of the isotherms. The solvent molecules used to generate the vapor are degassed fully by repeated evacuation. Dead volume is measured with Helium gas. The adsorbate was placed into the sample cell, then the change of the pressure is monitored, and the degree of adsorption is determined by the decrease in pressure at the equilibrium state.

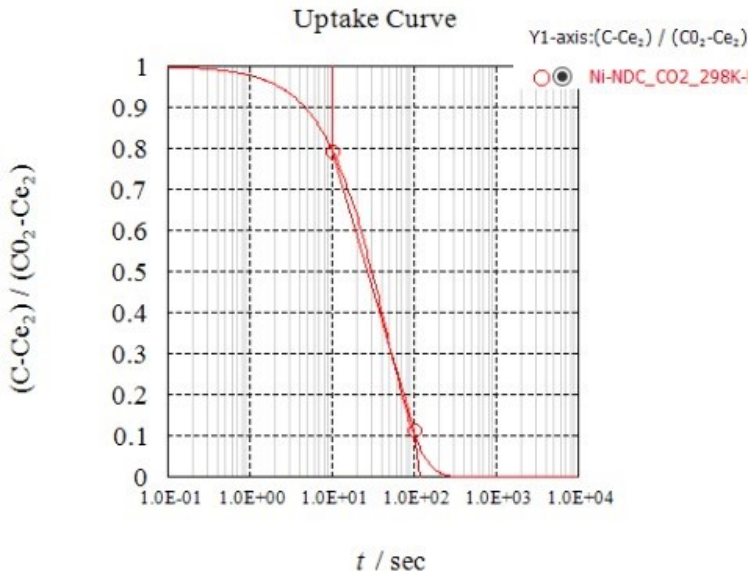

Figure S6 CO_2 kinetics measurement graph, showing LDF fitting and the corresponding rate contact value is $k = 2.21 \times 10^{-2}\ s^{-1}$.

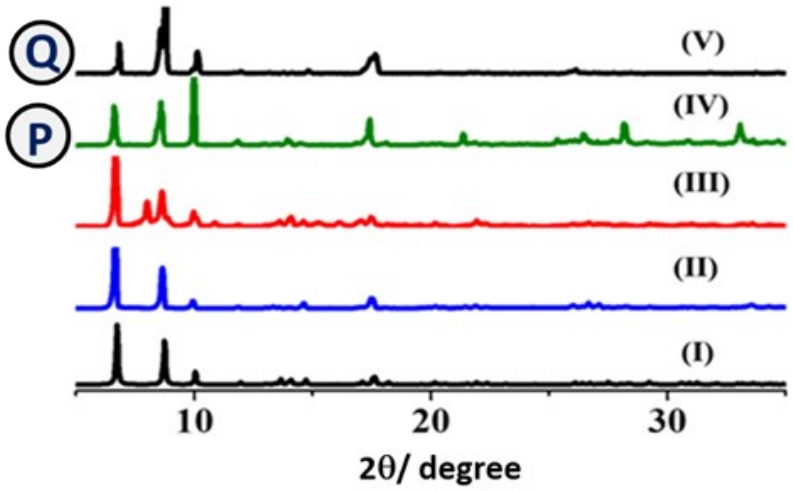

Figure S7 The blue circle P, Q represents the point in Figure 2 (main text) where the PXRD has been recorded. PXRD patterns of **1** recorded at different states: (I) simulated (II) **1** (III) desolvated **1′** (IV) **1′** at P and (V) **1′** at Q.

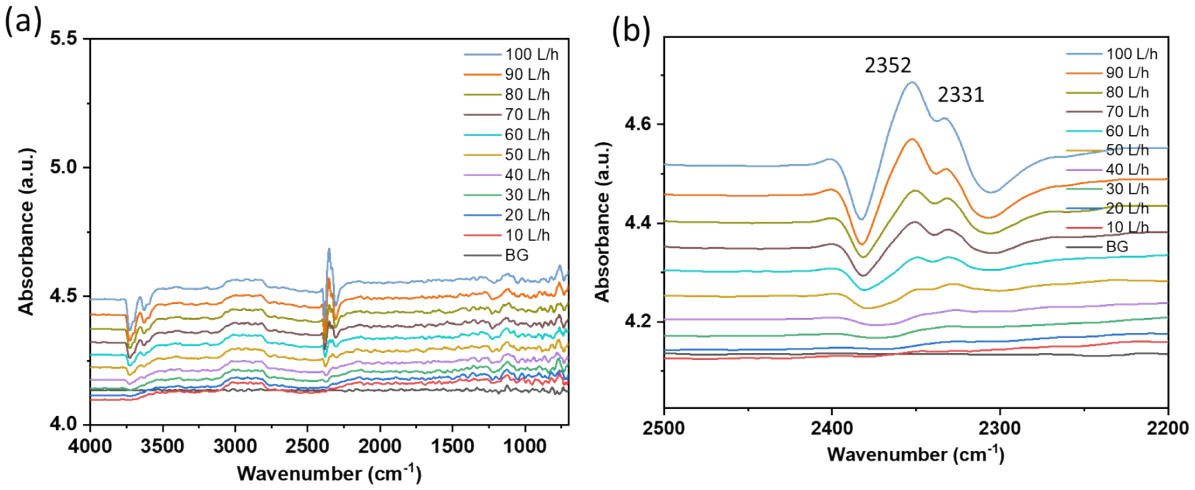

Figure S8 *In-situ* DRIFTS of regulated increase of CO_2 flow rate inside the IR chamber in absence of the sample. The lagend represents the flow in L/h of CO_2 dosed in regular interval.

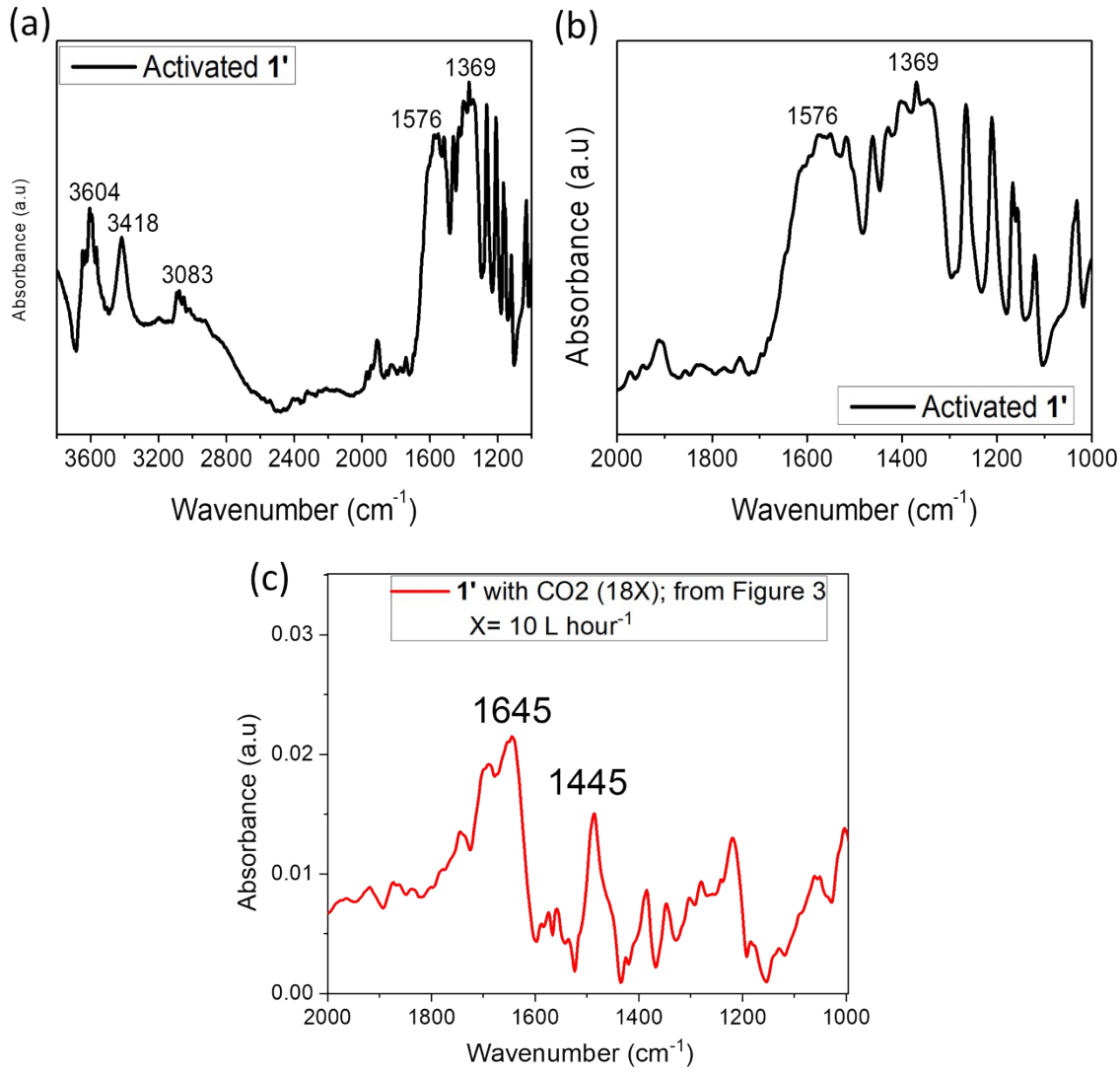

Figure S9 (a) *In situ* DRIFT of activated **1** (**1′**) without CO_2 presence. (b) Same spectra as shown in (a), with X-axis wavenumber ranging from 2000 to 1000 cm^{-1}. (c) One of the representative spectra of activated **1′** dozed with CO_2 pressure, as shown in **Figure 3**. Here the spectra of 18x is showing where, x= 10 L $hour^{-1}$.

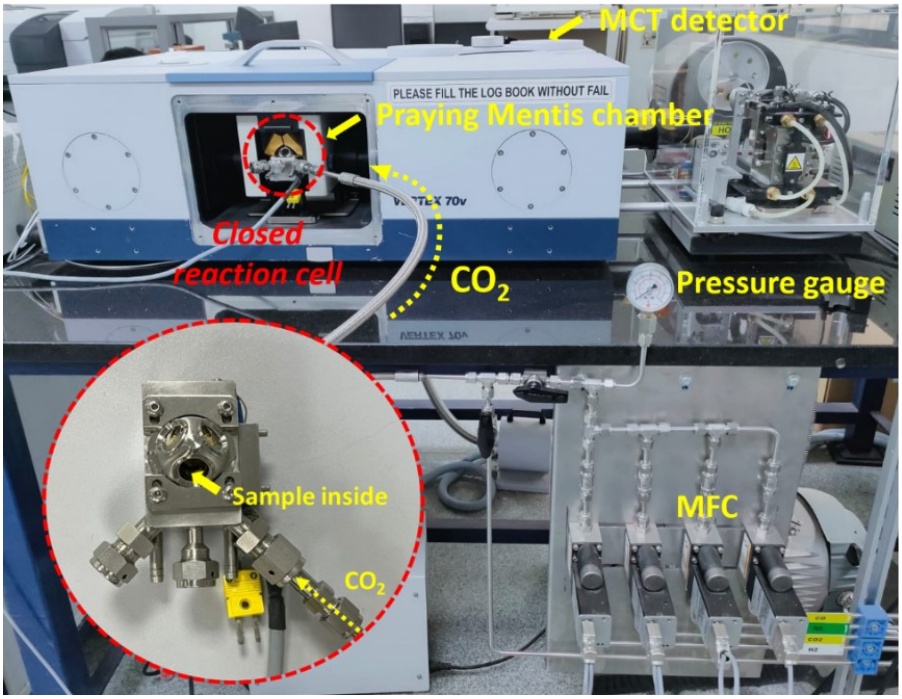

Figure S10 Pictorial representation of in-situ DRIFT assembly during data collections.

Table S7 Selected FTIR wavenumber ranges of CO_2-MOF interaction.

Wavenumbers (cm^{-1})	**Assignments**
3734 to 3695	Complex pattern; due to -OH vibrational frequencies and CO_2 overtones
3662 to 3562	Bridging hydroxyl groups of the framework
2383, 2362, 2340 and 2312	$Ni^{\delta+}$-$O^{\delta-}$CO type interaction; $\nu_3(CO_2)$ mode in interaction with open metal sites
2264	Ni···O interaction with CO_2
1645 and 1487	O-C-O stretch signals of carboxylaye

Computation details:

All the theoretical calculations were performed using density functional theory (DFT) in Gaussian16 program package.[12] The calculations were performed using B3LYP exchange-correlation functional along with 6-31+G** basis set for all atoms except for Ni atoms, for which LANL2DZ, which utilized a widely used effective core potential (ECP)- type basis set, was used.[13-21] The calculations were performed in the absence of any solvent. Grimme's d3 dispersion was also used to tackle weak interactions.[22-24]

Cartesian coordinates of the computed structures

Coordinates are given in standard XYZ format

Table S8 DFT-optimized geometry of **CO_2-bound model** (singlet), computed at the B3LYP-D3/ 6-31+G** (HCO)/ LANL2DZ (Ni) level in the absence of any solvent.

Atom		x	y	z
O	-1	-7.18650200	-2.13265000	3.91321900
O	-1	-7.10206500	-2.57626100	1.71899000
O	-1	-1.28153400	0.90761300	4.44417700
O	-1	-0.64820700	0.28772200	2.39019600
C	-1	-6.69467000	-2.01066600	2.75952900
C	-1	-5.44624800	-1.16651000	2.67805800
C	-1	-4.35264600	-1.70912100	2.07609400
C	-1	-3.08476100	-1.10401700	2.22861200
C	-1	-2.92611000	0.01239100	3.01554400
C	-1	-4.06759900	0.67077300	3.56237400
C	-1	-5.35272900	0.08436300	3.36495000
C	-1	-6.49769000	0.78181100	3.82576800
C	-1	-6.38486800	1.98221900	4.43856400
C	-1	-5.12217200	2.54689600	4.67741600
C	-1	-3.99531800	1.90812400	4.25893600
C	-1	-1.53140000	0.45205600	3.32052000
O	-1	-8.30318500	-2.61201600	-3.05608300
O	-1	-8.21879900	-3.05570900	-5.25020900
O	-1	-2.39826800	0.42816300	-2.52502200
O	-1	-1.76489400	-0.19170500	-4.57893400
C	-1	-7.81133000	-2.49004900	-4.20967600
C	-1	-6.56293000	-1.64587600	-4.29124300
C	-1	-5.46940300	-2.18855300	-4.89320200
C	-1	-4.20151700	-1.58345000	-4.74068200
C	-1	-4.04279100	-0.46697500	-3.95375500
C	-1	-5.18428200	0.19140800	-3.40692700
C	-1	-6.46941200	-0.39500300	-3.60435000
C	-1	-7.61437300	0.30244500	-3.14353400
C	-1	-7.50160300	1.50277000	-2.53063400
C	-1	-6.23876900	2.06744000	-2.29181700
C	-1	-5.11197700	1.42874100	-2.71026800
C	-1	-2.64808600	-0.02731900	-3.64878200
O	-1	6.99604300	5.93901800	1.30750600
O	-1	7.01103900	5.58633800	-0.90034200
O	-1	1.83424800	1.19989500	1.47611300
O	-1	2.41960200	0.48799000	-0.56698000
C	-1	6.68728100	5.29355000	0.27301000
C	-1	5.79672600	4.07876000	0.42389500
C	-1	4.75571200	4.15999100	1.30424200
C	-1	3.76617400	3.15564300	1.33401500
C	-1	3.82882000	2.06924300	0.49215300
C	-1	4.95809000	1.89963100	-0.37684500
C	-1	5.95446100	2.92494200	-0.39883100
C	-1	7.11452500	2.72941200	-1.19817600
C	-1	7.29034000	1.58168400	-1.91189400
C	-1	6.30799500	0.58148700	-1.90025500
C	-1	5.17302700	0.73745600	-1.15581400

C	-1	2.62671200	1.17218300	0.45426800
Ni	-1	1.31068800	-0.41613900	2.70376900
O	-1	3.20077500	-1.14646700	2.85547600
O	-1	3.35014600	-1.49404300	5.07960900
O	-1	8.88626800	-5.06413900	1.95400100
O	-1	9.02532900	-5.34335500	4.19042200
O	-1	0.48030400	-1.98948000	3.63258100
O	-1	0.39596100	-1.54589700	5.82684700
O	-1	-5.42450700	-5.02984300	3.10163300
O	-1	-6.05786900	-4.40983600	5.15556500
O	-1	1.66256600	0.81596400	4.22273000
C	-1	3.75953900	-1.59972100	3.89622100
C	-1	5.03392900	-2.37706300	3.69148600
C	-1	5.15673000	-3.59799600	4.32137800
C	-1	6.29618100	-4.39734100	4.13860800
C	-1	7.31692000	-3.96808500	3.32976700
C	-1	7.25648100	-2.68989700	2.69303500
C	-1	6.08650600	-1.88328200	2.87001100
C	-1	6.06150000	-0.60175700	2.26070800
C	-1	7.11924200	-0.13904000	1.53624300
C	-1	8.26397200	-0.92687100	1.37132900
C	-1	8.33597000	-2.17166600	1.93391300
C	-1	8.51229800	-4.87616900	3.13567100
C	-1	-0.01143800	-2.11163400	4.78629100
C	-1	-1.25986900	-2.95578700	4.86775600
C	-1	-2.35339600	-2.41310900	5.46971400
C	-1	-3.62132100	-3.01815600	5.31732000
C	-1	-3.77993100	-4.13462200	4.53026400
C	-1	-2.63848200	-4.79294900	3.98355900
C	-1	-1.35331200	-4.20659300	4.18085900
C	-1	-0.20835000	-4.90404100	3.72004200
C	-1	-0.32123500	-6.10437700	3.10727200
C	-1	-1.58393100	-6.66905400	2.86842100
C	-1	-2.71078700	-6.03028200	3.28689900
C	-1	-5.17467800	-4.57422000	4.22541400
Ni	-1	0.83788700	-0.71718900	-1.02802200
Ni	-1	-0.81559300	1.64896700	-2.04138500
Ni	-1	-0.17140900	1.88113300	1.16007200
O	-1	2.08417000	-1.62564200	-4.11387900
O	-1	2.23348700	-1.97342600	-1.88959500
O	-1	7.76960900	-5.54352200	-5.01520400
O	-1	7.90857300	-5.82278700	-2.77887300
O	-1	-0.63633600	-2.46895500	-3.33658100
O	-1	-0.72072100	-2.02526200	-1.14245400
O	-1	-6.54118900	-5.50920900	-3.86766900
O	-1	-7.17455200	-4.88920200	-1.81373500
O	-1	0.64380300	3.10680800	-1.95432900
O	-1	0.62888300	3.45955400	0.25351300
O	-1	5.80578800	7.84598500	-2.12290900
O	-1	5.22038100	8.55782900	-0.07987600
O	-1	0.54592200	0.33610300	-2.74617400
O	-1	-0.49566300	0.63377200	-0.33175300
O	-1	0.01593300	3.09955100	2.96458000
C	-1	2.64285200	-2.07918200	-3.07300300
C	-1	3.91726900	-2.85644500	-3.27772000
C	-1	4.04007100	-4.07737900	-2.64782800
C	-1	5.17956100	-4.87678000	-2.83072000
C	-1	6.20023700	-4.44745000	-3.63953300
C	-1	6.13982000	-3.16928000	-4.27616800
C	-1	4.96984800	-2.36266500	-4.09919400

C	-1	4.94490400	-1.08121200	-4.70852400
C	-1	6.00258200	-0.61842300	-5.43296200
C	-1	7.14737600	-1.40632700	-5.59790400
C	-1	7.21930900	-2.65104900	-5.03529300
C	-1	7.39561600	-5.35553400	-3.83363000
C	-1	-1.12810600	-2.59101400	-2.18291900
C	-1	-2.37652700	-3.43516900	-2.10144800
C	-1	-3.47005500	-2.89249200	-1.49949000
C	-1	-4.73800300	-3.49752200	-1.65198100
C	-1	-4.89666600	-4.61407000	-2.43893500
C	-1	-3.75510200	-5.27238700	-2.98577000
C	-1	-2.46997200	-4.68597600	-2.78834600
C	-1	-1.32501000	-5.38342400	-3.24916400
C	-1	-1.43791700	-6.58374200	-3.86202900
C	-1	-2.70061400	-7.14841900	-4.10088000
C	-1	-3.82744600	-6.50966300	-3.68230500
C	-1	-6.29136000	-5.05358700	-2.74388700
C	-1	0.95264100	3.75234200	-0.91983900
C	-1	1.84319500	4.96713100	-1.07072300
C	-1	2.88421000	4.88590200	-1.95107200
C	-1	3.87381000	5.89017600	-1.98087100
C	-1	3.81116400	6.97657600	-1.13900900
C	-1	2.68183000	7.14626000	-0.26998400
C	-1	1.68538500	6.12088400	-0.24799100
C	-1	0.52537400	6.31649600	0.55125200
C	-1	0.34958000	7.46420800	1.26506500
C	-1	1.33192500	8.46440500	1.25342700
C	-1	2.46689400	8.30843600	0.50898600
C	-1	5.01325300	7.87363200	-1.10113700
O	-1	-1.10080200	2.62010100	-4.00462000
O	-1	-7.88365700	6.82055600	-0.32339400
O	-1	-7.73426600	6.47283700	1.90088500
O	-1	-2.19814400	2.90274100	-1.22472400
O	-1	-2.05911800	2.62340400	1.01157900
C	-1	-7.32497700	6.36701500	0.71748400
C	-1	-6.05055900	5.58975200	0.51276700
C	-1	-5.92775700	4.36881900	1.14265700
C	-1	-4.78826700	3.56941700	0.95976500
C	-1	-3.76751600	3.99881200	0.15094700
C	-1	-3.82800600	5.27691700	-0.48568300
C	-1	-4.99798100	6.08353200	-0.30870700
C	-1	-5.02285000	7.36505100	-0.91804400
C	-1	-3.96524600	7.82777500	-1.64247500
C	-1	-2.82045300	7.03987000	-1.80741700
C	-1	-2.74844300	5.79521500	-1.24481300
C	-1	-2.57221200	3.09066200	-0.04314300
H	-1	-8.69385100	7.27428600	-0.07985200
H	-1	-8.97558300	-3.60736900	-5.03914000
H	-1	-8.03372000	-5.17301400	-2.13448700
H	-1	-7.85883200	-3.12796500	1.93000100
H	-1	-6.91703600	-4.69364800	4.83481500
H	-1	6.55501800	8.42436100	-1.96249000
H	-1	7.52503100	6.70182200	1.06275800
H	-1	8.66327700	-6.37101600	-3.00573700
H	-1	9.78007400	-5.89152300	3.96354500
H	-1	0.76129900	-4.47361000	3.85936000
H	-1	0.56015700	-6.62846900	2.80170200
H	-1	-0.55653100	-7.10780500	-4.16766800
H	-1	-0.35535300	-4.95303200	-3.10978000
H	-1	-3.66727700	-6.46678300	3.08818000

H	-1	-1.66097500	-7.60497000	2.35555900
H	-1	-2.77767300	-8.08429900	-4.61380500
H	-1	-4.78394600	-6.94620600	-3.88089400
H	-1	-3.36939600	-2.00561900	-0.90938500
H	-1	-5.58560000	-3.08147900	-1.14860500
H	-1	-3.35392500	-1.99945600	-5.24409600
H	-1	-5.57002300	-3.07543800	-5.48329400
H	-1	-8.58400700	-0.12798500	-3.28295100
H	-1	-8.38300300	2.02679900	-2.22497500
H	-1	-6.16170700	3.00335700	-1.77895800
H	-1	-4.15549200	1.86525900	-2.51155300
H	-1	-2.23715400	-1.51999100	1.72519300
H	-1	-4.45323600	-2.59599300	1.48597600
H	-1	-7.46732700	0.35135300	3.68644800
H	-1	-7.26627700	2.50629500	4.74411700
H	-1	-5.04513000	3.48281200	5.19027700
H	-1	-3.03883200	2.34466600	4.45759700
H	-1	-2.25273600	-1.52619900	6.05976000
H	-1	-4.46889700	-2.60221800	5.82081900
H	-1	4.07719500	-0.46517400	-4.59682400
H	-1	5.95736100	0.35341100	-5.87837600
H	-1	7.97205200	-1.03248500	-6.16803500
H	-1	8.10163300	-3.24122200	-5.16983400
H	-1	5.25178200	-5.82364500	-2.33763800
H	-1	3.25352800	-4.42106000	-2.00897400
H	-1	7.07403100	0.83277200	1.09078300
H	-1	9.08864900	-0.55298300	0.80122700
H	-1	9.21829600	-2.76182600	1.79933700
H	-1	5.19381000	0.01430200	2.37244100
H	-1	6.36839700	-5.34415400	4.63179000
H	-1	4.37014300	-3.94169600	4.96016400
H	-1	4.68769800	5.80576900	-2.67033800
H	-1	2.94933700	4.05516700	-2.62229400
H	-1	3.20804100	9.08016400	0.51492500
H	-1	1.19207700	9.35450800	1.83053800
H	-1	-0.54356200	7.60269900	1.83779100
H	-1	-0.22088700	5.55081600	0.59282400
H	-1	7.86071100	3.49516100	-1.23984900
H	-1	8.18351300	1.44315500	-2.48456500
H	-1	6.44784300	-0.30861600	-2.47736700
H	-1	4.43188000	-0.03427300	-1.16175300
H	-1	4.69053600	4.99073200	1.97545000
H	-1	2.95229500	3.24000100	2.02349600
H	-1	-6.71430000	4.02513700	1.78151100
H	-1	-4.71605800	2.62253100	1.45280900
H	-1	-1.86607600	5.20509700	-1.37930500
H	-1	-1.99580400	7.41371700	-2.37758700
H	-1	-4.01047600	8.79959200	-2.08792600
H	-1	-5.89051500	7.98114300	-0.80629600
H	-1	-1.92537900	3.10671600	-3.93475500
H	-1	-0.32109500	3.16362600	-4.13966500
H	-1	-0.80860600	3.58622900	3.03443500
H	-1	0.79566900	3.64303000	2.82952800
H	-1	1.27434700	1.67346400	4.03605700
H	-1	-1.23434700	0.13234600	0.02112100
H	-1	1.34304100	0.75186200	-3.08284200
O	0	1.50226600	-2.57521800	0.86155600
C	0	2.56061500	-3.07922400	0.83813900
O	0	3.59388200	-3.61919400	0.80154500
H	-1	0.11123000	-1.86756500	-3.30379400

H	-1	0.22335100	-0.19865000	-3.47527400
H	-1	1.27341800	0.45589100	5.02351000
H	-1	-0.34566700	1.11251900	4.50554700

Total Electronic Energy = -8111.142086 (Hartree/Particle).

Table S9 DFT-optimized geometry of **C_2H_2-bound model** (singlet), computed at the B3LYP-D3/ 6-31+G** (HCO)/ LANL2DZ (Ni) level in the absence of any solvent.

Atom		x	y	z
O	-1	-7.19356300	-2.04058000	3.91027500
O	-1	-7.11158900	-2.48999900	1.71713600
O	-1	-1.24723500	0.91724800	4.44525100
O	-1	-0.61929500	0.28381400	2.39383800
C	-1	-6.69806200	-1.92799300	2.75720000
C	-1	-5.43771900	-1.10170000	2.67615600
C	-1	-4.35083700	-1.66095300	2.07726200
C	-1	-3.07481100	-1.07346400	2.23074300
C	-1	-2.90179500	0.04226800	3.01560700
C	-1	-4.03483300	0.71784100	3.55903900
C	-1	-5.32775900	0.14918900	3.36058300
C	-1	-6.46356800	0.86368800	3.81791600
C	-1	-6.33488900	2.06368600	4.42838800
C	-1	-5.06477100	2.61101000	4.66827600
C	-1	-3.94631400	1.95552600	4.25312700
C	-1	-1.50147600	0.46309300	3.32214600
O	-1	-8.30482000	-2.51896600	-3.05996000
O	-1	-8.22289800	-2.96846700	-5.25299700
O	-1	-2.35854400	0.43878000	-2.52488300
O	-1	-1.73041800	-0.19432300	-4.57637000
C	-1	-7.80929500	-2.40639600	-4.21293900
C	-1	-6.54897600	-1.58008500	-4.29407800
C	-1	-5.46217000	-2.13940400	-4.89296700
C	-1	-4.18614200	-1.55191400	-4.73948700
C	-1	-4.01305100	-0.43612000	-3.95462900
C	-1	-5.14608700	0.23945400	-3.41119600
C	-1	-6.43901600	-0.32919800	-3.60965300
C	-1	-7.57482400	0.38530300	-3.15231900
C	-1	-7.44619900	1.58521800	-2.54174600
C	-1	-6.17594400	2.13253300	-2.30188900
C	-1	-5.05754800	1.47712200	-2.71701200
C	-1	-2.61281400	-0.01552300	-3.64812200
O	-1	7.10589700	5.82476900	1.31260700
O	-1	7.11974200	5.46722100	-0.89446500
O	-1	1.87730400	1.15924500	1.48196600
O	-1	2.45629100	0.43483400	-0.55848400
C	-1	6.78985500	5.18152000	0.27892800
C	-1	5.88199700	3.97973200	0.43079400
C	-1	4.84070800	4.07750300	1.30913300
C	-1	3.83705500	3.08727100	1.33927300
C	-1	3.88583000	1.99831000	0.49980600
C	-1	5.01410200	1.81094700	-0.36684200
C	-1	6.02487000	2.82205900	-0.38922700
C	-1	7.18344300	2.60849300	-1.18611300

C	-1	7.34429200	1.45688600	-1.89710700
C	-1	6.34792100	0.47066600	-1.88509800
C	-1	5.21397700	0.64420300	-1.14298800
C	-1	2.67132100	1.11822400	0.46173400
Ni	-1	1.32925000	-0.44586400	2.71168800
O	-1	3.20826200	-1.20356600	2.86869200
O	-1	3.34900700	-1.54811500	5.09388800
O	-1	8.83963700	-5.20254600	1.98554700
O	-1	8.97087300	-5.47893900	4.22279100
O	-1	0.47525300	-2.00616100	3.64302600
O	-1	0.39309300	-1.55672400	5.83602500
O	-1	-5.47119900	-4.96404500	3.10788400
O	-1	-6.09931100	-4.33080500	5.15939100
O	-1	1.69548400	0.78299400	4.22980200
C	-1	3.75901200	-1.66182500	3.91150500
C	-1	5.02257000	-2.45773400	3.71059100
C	-1	5.12705100	-3.67893600	4.34326200
C	-1	6.25543000	-4.49465300	4.16418100
C	-1	7.28352100	-4.08155200	3.35624000
C	-1	7.24221700	-2.80399600	2.71671900
C	-1	6.08343000	-1.98059300	2.88993800
C	-1	6.07755500	-0.70013900	2.27790100
C	-1	7.14296900	-0.25392300	1.55433100
C	-1	8.27675900	-1.05816300	1.39308900
C	-1	8.33022000	-2.30265000	1.95841200
C	-1	8.46630700	-5.00680900	3.16615900
C	-1	-0.02055700	-2.11883500	4.79589700
C	-1	-1.28079000	-2.94516400	4.87698300
C	-1	-2.36759600	-2.38584500	5.47587300
C	-1	-3.64366200	-2.97327700	5.32251500
C	-1	-3.81663900	-4.08906500	4.53752700
C	-1	-2.68364200	-4.76458100	3.99421900
C	-1	-1.39067400	-4.19598700	4.19255100
C	-1	-0.25486600	-4.91048500	3.73521900
C	-1	-0.38360600	-6.11040800	3.12477300
C	-1	-1.65372400	-6.65773400	2.88488500
C	-1	-2.77218100	-6.00224900	3.30003500
C	-1	-5.21691600	-4.50960300	4.23114400
Ni	-1	0.85853800	-0.74890200	-1.01977900
Ni	-1	-0.75965100	1.63817300	-2.04102300
Ni	-1	-0.11781500	1.86796500	1.16097200
O	-1	2.09723000	-1.68139100	-4.10152100
O	-1	2.23777300	-2.02651700	-1.87625100
O	-1	7.72840200	-5.68094800	-4.98459300
O	-1	7.85954000	-5.95739200	-2.74743900
O	-1	-0.63624300	-2.48461300	-3.32724800
O	-1	-0.71816200	-2.03511100	-1.13421000
O	-1	-6.58245500	-5.44243200	-3.86235100
O	-1	-7.21056800	-4.80919100	-1.81084500
O	-1	0.72000700	3.07547500	-1.95445900
O	-1	0.70623800	3.43308800	0.25260700
O	-1	5.94859700	7.74103300	-2.12389800
O	-1	5.36975000	8.46540000	-0.08340000
O	-1	0.58443300	0.30474900	-2.74065300
O	-1	-0.45703300	0.62220500	-0.32870100
O	-1	0.08357500	3.08752600	2.96333900
C	-1	2.64765400	-2.14055100	-3.05871000
C	-1	3.91133700	-2.93613800	-3.25954800
C	-1	4.01581700	-4.15734000	-2.62687700
C	-1	5.14423400	-4.97311400	-2.80608100

C	-1	6.17226400	-4.55993800	-3.61399500
C	-1	6.13098300	-3.28239900	-4.25342100
C	-1	4.97219600	-2.45899500	-4.08020100
C	-1	4.96638100	-1.17861500	-4.69226600
C	-1	6.03173600	-0.73232400	-5.41580900
C	-1	7.16558700	-1.53664000	-5.57707700
C	-1	7.21898500	-2.78105400	-5.01172700
C	-1	7.35505200	-5.48519600	-3.80407700
C	-1	-1.13168200	-2.59727100	-2.17420000
C	-1	-2.39202400	-3.42356700	-2.09315600
C	-1	-3.47883000	-2.86424800	-1.49426700
C	-1	-4.75491800	-3.45166200	-1.64772100
C	-1	-4.92794900	-4.56753200	-2.43260500
C	-1	-3.79483500	-5.24304100	-2.97604400
C	-1	-2.50190800	-4.67438900	-2.77758800
C	-1	-1.36610000	-5.38888900	-3.23492100
C	-1	-1.49486200	-6.58879600	-3.84546100
C	-1	-2.76498100	-7.13612000	-4.08535100
C	-1	-3.88341500	-6.48065100	-3.67010500
C	-1	-6.32817200	-4.98798900	-2.73909100
C	-1	1.03612500	3.71878700	-0.92078500
C	-1	1.94398300	4.92057600	-1.07265200
C	-1	2.98527200	4.82280700	-1.95099100
C	-1	3.98898700	5.81296300	-1.98115700
C	-1	3.94021000	6.90192600	-1.14169000
C	-1	2.81187900	7.08936200	-0.27501500
C	-1	1.80103500	6.07818600	-0.25262400
C	-1	0.64251500	6.29183100	0.54416000
C	-1	0.48168700	7.44342200	1.25525000
C	-1	1.47805900	8.42964400	1.24324100
C	-1	2.61200300	8.25610600	0.50113100
C	-1	5.15476300	7.78202200	-1.10358600
O	-1	-1.02773400	2.60905700	-4.00679500
O	-1	-7.75704400	6.91254000	-0.34635900
O	-1	-7.61642500	6.56747900	1.87890600
O	-1	-2.12579600	2.91304800	-1.22943700
O	-1	-1.99459600	2.63653200	1.00769000
C	-1	-7.20661900	6.45338200	0.69645200
C	-1	-5.94293800	5.65779400	0.49561400
C	-1	-5.83845700	4.43659200	1.12828500
C	-1	-4.71003900	3.62081800	0.94908000
C	-1	-3.68193300	4.03405800	0.14116100
C	-1	-3.72329100	5.31153300	-0.49825800
C	-1	-4.88207800	6.13493700	-0.32503900
C	-1	-4.88781500	7.41538200	-0.93710900
C	-1	-3.82253800	7.86160800	-1.66064700
C	-1	-2.68868700	7.05729200	-1.82191500
C	-1	-2.63521200	5.81294400	-1.25657100
C	-1	-2.49922300	3.10873600	-0.04891500
H	-1	-8.56118100	7.37816500	-0.10520000
H	-1	-8.98775200	-3.50895300	-5.04210300
H	-1	-8.07309500	-5.08154400	-2.13251300
H	-1	-7.87642500	-3.03052800	1.92797300
H	-1	-6.96183900	-4.60315700	4.83772300
H	-1	6.70563100	8.30912800	-1.96337500
H	-1	7.64601200	6.57951700	1.06719100
H	-1	8.60682800	-6.51668900	-2.97181900
H	-1	9.71820300	-6.03817600	3.99839800
H	-1	0.72051500	-4.49347200	3.87534000
H	-1	0.49083700	-6.64752400	2.82186000

H	-1	-0.62042500	-7.12588100	-4.14844500
H	-1	-0.39071200	-4.97191500	-3.09473400
H	-1	-3.73438800	-6.42564300	3.10054600
H	-1	-1.74306900	-7.59355800	2.37385600
H	-1	-2.85434300	-8.07190700	-4.59644300
H	-1	-4.84563200	-6.90408600	-3.86946200
H	-1	-3.36669600	-1.97762900	-0.90585100
H	-1	-5.59743400	-3.02264100	-1.14671400
H	-1	-3.34363000	-1.98089900	-5.24053100
H	-1	-5.57426400	-3.02603400	-5.48137300
H	-1	-8.55019000	-0.03171100	-3.29254200
H	-1	-8.32065000	2.12226900	-2.23874100
H	-1	-6.08658000	3.06835800	-1.79086500
H	-1	-4.09534800	1.90053200	-2.51753000
H	-1	-2.23228400	-1.50241400	1.72969200
H	-1	-4.46290300	-2.54757000	1.48883200
H	-1	-7.43893700	0.44665000	3.67779200
H	-1	-7.20934700	2.60078600	4.73128400
H	-1	-4.97542600	3.54683500	5.17930600
H	-1	-2.98411300	2.37896100	4.45255600
H	-1	-2.25546100	-1.49918800	6.06423000
H	-1	-4.48615900	-2.54436200	5.82364500
H	-1	4.10725400	-0.55016800	-4.58338900
H	-1	6.00099600	0.23910000	-5.86334400
H	-1	7.99644000	-1.17567600	-6.14654000
H	-1	8.09313000	-3.38389300	-5.14347300
H	-1	5.20224100	-5.91985400	-2.31088600
H	-1	3.22339900	-4.48853800	-1.98869000
H	-1	7.11224100	0.71748400	1.10675000
H	-1	9.10761300	-0.69715200	0.82365600
H	-1	9.20436800	-2.90547500	1.82663200
H	-1	5.21844700	-0.07167000	2.38680900
H	-1	6.31343200	-5.44134200	4.65947800
H	-1	4.33458900	-4.01015400	4.98138200
H	-1	4.80279600	5.71562400	-2.66900800
H	-1	3.03984000	3.98981200	-2.62035100
H	-1	3.36394900	9.01732000	0.50675400
H	-1	1.34977800	9.32285400	1.81823500
H	-1	-0.41040400	7.59571000	1.82611000
H	-1	-0.11454200	5.53684100	0.58602600
H	-1	7.94042600	3.36355500	-1.22808000
H	-1	8.23641400	1.30456200	-2.46791100
H	-1	6.47620200	-0.42254600	-2.46009200
H	-1	4.46203000	-0.11701100	-1.14861200
H	-1	4.78609100	4.91050600	1.97847800
H	-1	3.02325200	3.18456300	2.02714000
H	-1	-6.63087400	4.10539400	1.76647200
H	-1	-4.65204600	2.67405700	1.44423900
H	-1	-1.76102400	5.21015800	-1.38826800
H	-1	-1.85786000	7.41826200	-2.39141500
H	-1	-3.85328700	8.83301600	-2.10821800
H	-1	-5.74689900	8.04388300	-0.82818500
H	-1	-1.84548500	3.10739700	-3.93940400
H	-1	-0.24020700	3.14124700	-4.14160700
H	-1	-0.73413800	3.58592800	3.03072000
H	-1	0.87113400	3.61966900	2.82852100
H	-1	1.32022700	1.64623200	4.03988300
H	-1	-1.20332400	0.13199500	0.02392300
H	-1	1.38791800	0.70851000	-3.07678900
C	0	2.08881600	-3.22005800	0.87826400

H	0	3.06634300	-2.79332900	0.89637200
C	0	0.96404100	-3.66022400	0.89467300
H	0	-0.02786800	-4.04441900	0.94566300
H	-1	1.29984100	0.43085800	5.02994500
H	-1	0.25561700	-0.22695300	-3.46919400
H	-1	-0.30867900	1.10906900	4.50783900
H	-1	0.11967300	-1.89375300	-3.29440600

Total Electronic Energy = -7999.875089 (Hartree/Particle).

Table S10 Freezed geometry of **desolvated MOF (1')** (singlet), computed at the B3LYP-D3/ 6-31+G** (HCO)/ LANL2DZ (Ni) level in the absence of any solvent.

Atom		x	y	z
O	-1	-7.19787800	-1.99685900	3.92368000
O	-1	-7.11711300	-2.45959100	1.73326600
O	-1	-1.22668000	0.91214300	4.44929200
O	-1	-0.60163500	0.26173800	2.40229200
C	-1	-6.69999100	-1.89522800	2.77061400
C	-1	-5.43240200	-1.08041200	2.68644400
C	-1	-4.34969300	-1.65254000	2.09216900
C	-1	-3.06878800	-1.07530300	2.24391100
C	-1	-2.88703100	0.04337900	3.02257400
C	-1	-4.01481200	0.73190200	3.56066000
C	-1	-5.31239700	0.17339000	3.36381400
C	-1	-6.44250300	0.90036700	3.81557500
C	-1	-6.30413200	2.10269300	4.41930700
C	-1	-5.02959300	2.64031600	4.65767900
C	-1	-3.91637500	1.97274500	4.24773900
C	-1	-1.48356300	0.45353100	3.32845800
O	-1	-8.30465200	-2.50567000	-3.04511400
O	-1	-8.22394100	-2.96848300	-5.23542600
O	-1	-2.33350800	0.40325100	-2.51940000
O	-1	-1.70838700	-0.24709000	-4.56640500
C	-1	-7.80674300	-2.40405500	-4.19808400
C	-1	-6.53917500	-1.58922300	-4.28235000
C	-1	-5.45654300	-2.16141500	-4.87661800
C	-1	-4.17563800	-1.58417900	-4.72487600
C	-1	-3.99380500	-0.46543200	-3.94622000
C	-1	-5.12158500	0.22309200	-3.40813400
C	-1	-6.41917000	-0.33542100	-3.60498000
C	-1	-7.54927700	0.39155600	-3.15321900
C	-1	-7.41096100	1.59380200	-2.54938500
C	-1	-6.13628400	2.13141400	-2.31104500
C	-1	-5.02312700	1.46391800	-2.72095800
C	-1	-2.59033700	-0.05528000	-3.64033600
O	-1	7.17273700	5.72867700	1.29924100
O	-1	7.18619200	5.35832500	-0.90572100
O	-1	1.90358300	1.10991200	1.48875800
O	-1	2.47868000	0.36872700	-0.54682600
C	-1	6.85238100	5.08226500	0.26886900
C	-1	5.93390400	3.88931600	0.42647000
C	-1	4.89242300	4.00119700	1.30289500
C	-1	3.88014600	3.01992800	1.33743300

C	-1	3.92047400	1.92576800	0.50430000
C	-1	5.04813900	1.72360900	-0.35980700
C	-1	6.06770100	2.72574100	-0.38670200
C	-1	7.22535400	2.49752000	-1.18086000
C	-1	7.37704500	1.34048300	-1.88501800
C	-1	6.37210900	0.36305500	-1.86862400
C	-1	5.23880300	0.55072200	-1.12898000
C	-1	2.69835000	1.05606900	0.46969100
Ni	-1	1.33974900	-0.48404500	2.72738100
O	-1	3.21235000	-1.25584300	2.89068900
O	-1	3.34711200	-1.58934800	5.11798700
O	-1	8.80954100	-5.30925000	2.03774800
O	-1	8.93560100	-5.57389400	4.27671000
O	-1	0.47108700	-2.03069500	3.66594900
O	-1	0.39032200	-1.56796300	5.85636300
O	-1	-5.50005000	-4.93977200	3.14031000
O	-1	-6.12515600	-4.28929200	5.18733700
O	-1	1.71522200	0.75134200	4.23810400
C	-1	3.75744500	-1.71374800	3.93673000
C	-1	5.01439700	-2.52144400	3.74209000
C	-1	5.10745600	-3.73984600	4.38190000
C	-1	6.22890800	-4.56636900	4.20895800
C	-1	7.26155500	-4.16688700	3.39997900
C	-1	7.23216900	-2.89272200	2.75307600
C	-1	6.08038400	-2.05828200	2.92007300
C	-1	6.08641700	-0.78137000	2.30068200
C	-1	7.15657000	-0.34861400	1.57593000
C	-1	8.28351100	-1.16360600	1.42076800
C	-1	8.32543200	-2.40523600	1.99330000
C	-1	8.43647300	-5.10348100	3.21673600
C	-1	-0.02681500	-2.13246500	4.81899400
C	-1	-1.29440500	-2.94728200	4.90316400
C	-1	-2.37703700	-2.37508900	5.49743300
C	-1	-3.65798100	-2.95226700	5.34581400
C	-1	-3.83969900	-4.07100800	4.56702800
C	-1	-2.71195800	-4.75947300	4.02906500
C	-1	-1.41433300	-4.20101900	4.22578800
C	-1	-0.28422700	-4.92799600	3.77402800
C	-1	-0.42265800	-6.13024800	3.17032200
C	-1	-1.69719800	-6.66787100	2.93195000
C	-1	-2.81041600	-6.00029900	3.34189000
C	-1	-5.24320600	-4.48110200	4.26126700
Ni	-1	0.87124800	-0.80369700	-1.00336600
Ni	-1	-0.72482800	1.59145000	-2.04038400
Ni	-1	-0.08495800	1.83414500	1.16115100
O	-1	2.10557600	-1.76465400	-4.07810500
O	-1	2.24036000	-2.09817500	-1.85071000
O	-1	7.70278900	-5.81807700	-4.93095000
O	-1	7.82875100	-6.08276900	-2.69207800
O	-1	-0.63574100	-2.53958700	-3.30274200
O	-1	-0.71645100	-2.07677400	-1.11243100
O	-1	-6.60682400	-5.44858300	-3.82848400
O	-1	-7.23193000	-4.79810300	-1.78145700
O	-1	0.76718400	3.01629700	-1.96017800
O	-1	0.75380400	3.38671400	0.24477800
O	-1	6.03641400	7.63512700	-2.14970100
O	-1	5.46137700	8.37623700	-0.11414400
O	-1	0.60845400	0.24237600	-2.73061400
O	-1	-0.43318400	0.58276100	-0.32186700
O	-1	0.12481000	3.06219200	2.95664800

C	-1	2.65069300	-2.22257500	-3.03196800
C	-1	3.90764500	-3.03027100	-3.22660800
C	-1	4.00070400	-4.24867400	-2.58679800
C	-1	5.12219600	-5.07525500	-2.75986200
C	-1	6.15478100	-4.67569800	-3.56881500
C	-1	6.12541700	-3.40154900	-4.21562200
C	-1	4.97363200	-2.56710900	-4.04862500
C	-1	4.97972500	-1.29027200	-4.66804200
C	-1	6.04981800	-0.85744100	-5.39276800
C	-1	7.17682000	-1.67250800	-5.54795700
C	-1	7.21868000	-2.91406400	-4.97539800
C	-1	7.32969900	-5.61229200	-3.75205800
C	-1	-1.13356700	-2.64129300	-2.14970300
C	-1	-2.40115700	-3.45610900	-2.06553400
C	-1	-3.48378900	-2.88391600	-1.47126500
C	-1	-4.76475400	-3.46107800	-1.62298000
C	-1	-4.94652700	-4.57990000	-2.40166300
C	-1	-3.81867000	-5.26835900	-2.93975600
C	-1	-2.52108500	-4.70984600	-2.74290900
C	-1	-1.39097900	-5.43682300	-3.19467000
C	-1	-1.52943200	-6.63905800	-3.79847200
C	-1	-2.80397200	-7.17668200	-4.03684400
C	-1	-3.91716800	-6.50912600	-3.62680800
C	-1	-6.34998000	-4.98991300	-2.70752700
C	-1	1.08761600	3.66277400	-0.92981200
C	-1	2.00609200	4.85572300	-1.08741300
C	-1	3.04757400	4.74384100	-1.96383800
C	-1	4.05991100	5.72503600	-1.99840300
C	-1	4.01958300	6.81919600	-1.16526900
C	-1	2.89185800	7.02142900	-0.30113600
C	-1	1.87221900	6.01923300	-0.27423500
C	-1	0.71462100	6.24753500	0.51982000
C	-1	0.56295200	7.40455600	1.22407500
C	-1	1.56788800	8.38198300	1.20768100
C	-1	2.70119400	8.19431600	0.46803700
C	-1	5.24170800	7.68889500	-1.13066100
O	-1	-0.98201800	2.55330000	-4.01204400
O	-1	-7.67810700	6.93617600	-0.38504000
O	-1	-7.54324700	6.60271800	1.84234800
O	-1	-2.08081800	2.88281600	-1.23789100
O	-1	-1.95479500	2.61805000	1.00095400
C	-1	-7.13299000	6.47825500	0.66109700
C	-1	-5.87603800	5.67055800	0.46645700
C	-1	-5.78297900	4.45215600	1.10626700
C	-1	-4.66148800	3.62557500	0.93320200
C	-1	-3.62882600	4.02519600	0.12424300
C	-1	-3.65826700	5.29928000	-0.52255700
C	-1	-4.81005200	6.13372000	-0.35556000
C	-1	-4.80388200	7.41062200	-0.97498400
C	-1	-3.73386600	7.84338800	-1.69970400
C	-1	-2.60686400	7.02832200	-1.85489200
C	-1	-2.56492700	5.78683000	-1.28233900
C	-1	-2.45398400	3.08853800	-0.05899400
H	-1	-8.47845500	7.41016200	-0.14759300
H	-1	-8.99373200	-3.50106800	-5.02241300
H	-1	-8.09639900	-5.06478600	-2.10266300
H	-1	-7.88688800	-2.99222200	1.94622100
H	-1	-6.98962500	-4.55597500	4.86613100
H	-1	6.79816800	8.19752700	-1.99147200
H	-1	7.71970700	6.47727200	1.05018600

H	-1	8.57141700	-6.64983000	-2.91228100
H	-1	9.67830900	-6.14089400	4.05649300
H	-1	0.69457400	-4.51868700	3.91300400
H	-1	0.44744700	-6.67668600	2.87162200
H	-1	-0.65933300	-7.18546800	-4.09724100
H	-1	-0.41217100	-5.02755300	-3.05562800
H	-1	-3.77602600	-6.41644600	3.14360100
H	-1	-1.79405900	-7.60580800	2.42619100
H	-1	-2.90085000	-8.11458300	-4.54266600
H	-1	-4.88278800	-6.92531300	-3.82496500
H	-1	-3.36466500	-1.99493500	-0.88780800
H	-1	-5.60412000	-3.02186600	-1.12552900
H	-1	-3.33627600	-2.02335500	-5.22236400
H	-1	-5.57562900	-3.05040900	-5.46006400
H	-1	-8.52806300	-0.01775400	-3.29229700
H	-1	-8.28107400	2.14017800	-2.25059400
H	-1	-6.03940400	3.06935100	-1.80529000
H	-1	-4.05752200	1.88008000	-2.52267600
H	-1	-2.22941200	-1.51444600	1.74641600
H	-1	-4.46874900	-2.54152100	1.50869900
H	-1	-7.42129300	0.49103100	3.67659600
H	-1	-7.17425300	2.64911600	4.71798900
H	-1	-4.93273100	3.57825400	5.16343800
H	-1	-2.95076900	2.38893200	4.44596800
H	-1	-2.25791100	-1.48606900	6.08083100
H	-1	-4.49732800	-2.51316000	5.84338900
H	-1	4.12597000	-0.65375700	-4.56388200
H	-1	6.02809200	0.11162300	-5.84591500
H	-1	8.01148800	-1.32207000	-6.11841500
H	-1	8.08770300	-3.52523500	-5.10255500
H	-1	5.17134300	-6.01959800	-2.25916100
H	-1	3.20464600	-4.56928600	-1.94773700
H	-1	7.13485400	0.62042900	1.12273600
H	-1	9.11817900	-0.81312200	0.85033800
H	-1	9.19445900	-3.01639500	1.86610800
H	-1	5.23268000	-0.14483400	2.40487500
H	-1	6.27805200	-5.51065900	4.70976000
H	-1	4.31135200	-4.06047800	5.02089400
H	-1	4.87369000	5.61666200	-2.68463800
H	-1	3.09571200	3.90656400	-2.62833100
H	-1	3.45973300	8.94897700	0.47025300
H	-1	1.44668200	9.27957200	1.77736800
H	-1	-0.32848400	7.56788400	1.79290400
H	-1	-0.04903300	5.49941300	0.56505000
H	-1	7.98893500	3.24571100	-1.22619000
H	-1	8.26851000	1.17711800	-2.45379000
H	-1	6.49331500	-0.53453300	-2.43831100
H	-1	4.48026400	-0.20393900	-1.13119700
H	-1	4.84423700	4.83848300	1.96737300
H	-1	3.06637400	3.12825400	2.02368400
H	-1	-6.57903700	4.13154400	1.74532800
H	-1	-4.61235300	2.68121100	1.43386500
H	-1	-1.69585900	5.17571300	-1.40944900
H	-1	-1.77222400	7.37876500	-2.42538800
H	-1	-3.75560000	8.81243600	-2.15288700
H	-1	-5.65759200	8.04719100	-0.87077500
H	-1	-1.79548100	3.05911600	-3.94856800
H	-1	-0.18971900	3.07783100	-4.14890000
H	-1	-0.68861400	3.56807000	3.02011400
H	-1	0.91713800	3.58667800	2.81978700

H	-1	1.34760300	1.61643500	4.04301100
H	-1	-1.18415000	0.10110100	0.03260900
H	-1	1.41584000	0.63718900	-3.06803200
H	-1	0.12525000	-1.95515000	-3.27232500
H	-1	0.27592000	-0.29062900	-3.45651200
H	-1	1.31519200	0.40706900	5.04000800
H	-1	-0.28656700	1.09614600	4.51198300

Total Electronic Energy = -7922.535425 (Hartree/Particle).

Table S11 DFT-optimized geometry of **CO_2** (singlet), computed at the B3LYP-D3/ 6-31+G** (CO) level in the absence of any solvent.

Atom	x	y	z
C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16949000
O	0.00000000	0.00000000	-1.16949000

Total Electronic Energy = -188.590582 (Hartree/Particle).

Table S12 DFT-optimized geometry of **C_2H_2** (singlet), computed at the B3LYP-D3/ 6-31+G** (HC) level in the absence of any solvent.

Atom	x	y	z
C	0.00000000	0.00000000	0.60412800
H	0.00000000	0.00000000	1.67085600
C	0.00000000	0.00000000	-0.60412800
H	0.00000000	0.00000000	-1.67085600

Total Electronic Energy = -77.337459 (Hartree/Particle).

Heat of adsorption

The virial expression of the following type has been used to fit the combined single component isotherm at 273 and 298 K.

$$\ln(P) = \ln(A) + \frac{1}{T}\sum_{i=0}^{m} a_i A^i + \sum_{i=0}^{n} b_i A^i \qquad \text{(eq. 6)}$$

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 represents the number of coefficients required to

adequately describe the isotherms (eq. 6). The value of m and n was gradually increased until the contribution of extra added a and b coefficients were negligible towards the final fit. The values of the virial coefficient a_i were taken to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R\sum_{i=0}^{m} a_i A^i + \sum_{i=0}^{n} b_i A^i \qquad \text{(eq. 7)}$$

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

IAST selectivity

The Langmuir fitting is the simplest model to fit isotherms while DSLF or dual-site Langmuir-Freundlich fit the adsorption isotherm more exclusively judged by goodness-of-fit factors. While multiple factors or sites are present between adsorbate-adsorbent integration with wide loading pressure DSLF works for exclusively for data fitting. DSLF can be expressed as follows;

$$n = \frac{a.\,b.p^c}{1 + bp^c} + \frac{a1.\,b1.p^{c1}}{1 + b1p^{c1}} \qquad \text{(Eqn.R1)}$$

where n is the amount adsorbed (the loading) in mmol g^{-1}, p the pressure in torr, a is the maximal loading in mmol g^{-1}, b the affinity constant and c the heterogeneity exponent the product of $b \cdot p^c$ must be dimension-less. We note that in the equation also takes the form with $(b \cdot p)^c$, then b would have simply the unit 1/torr.

The value as obtained from this equation were finally fitted by MATLAB, for the calculation of selectivity.

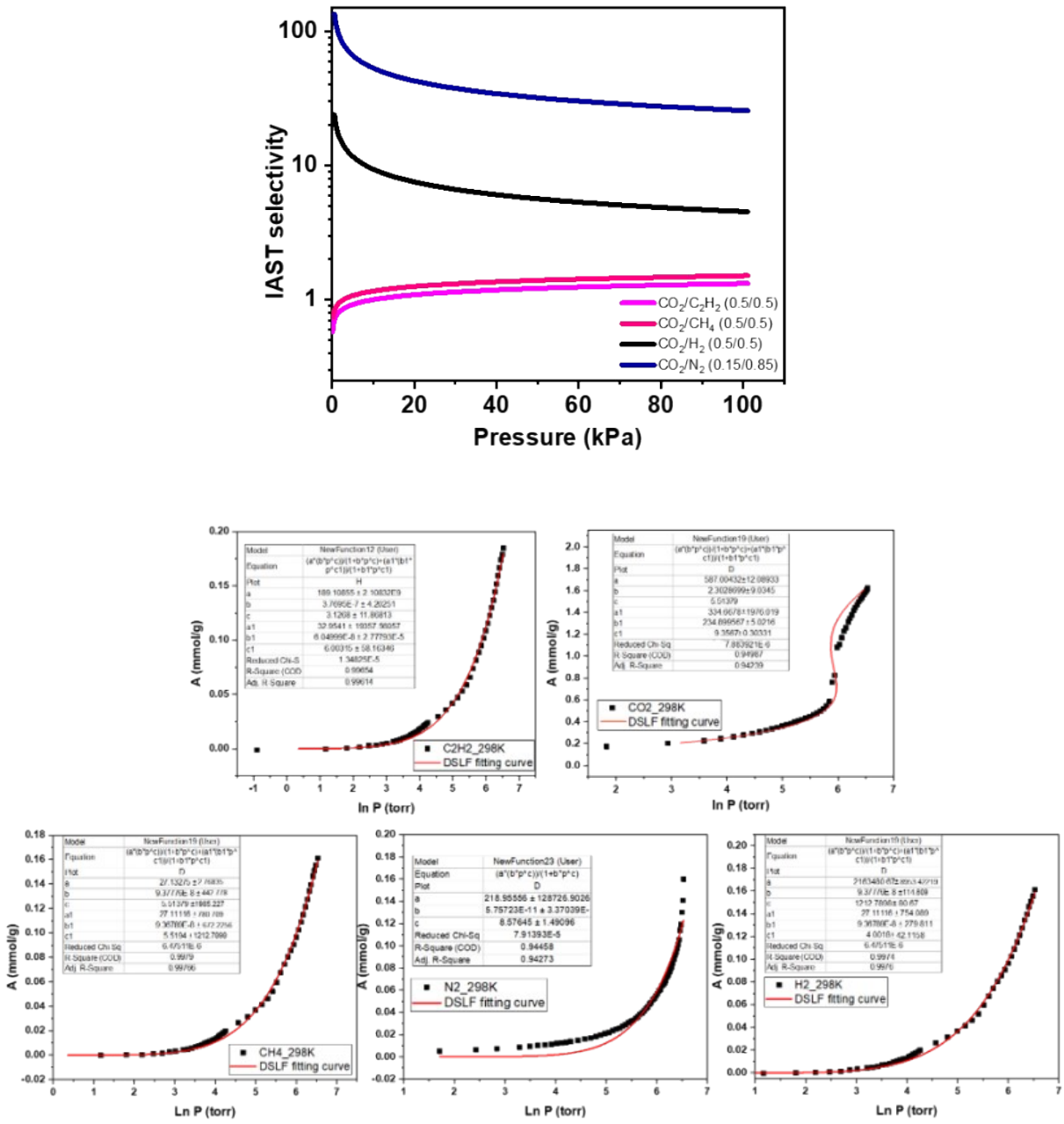

Figure S11 The IAST selectivity curve (top) with DSLF fitting (bottom) for C_2H_2, CO_2, CH_4, N_2 and H_2 adsorption isotherm measured at 298 K.

Dynamic breakthrough separation experiments

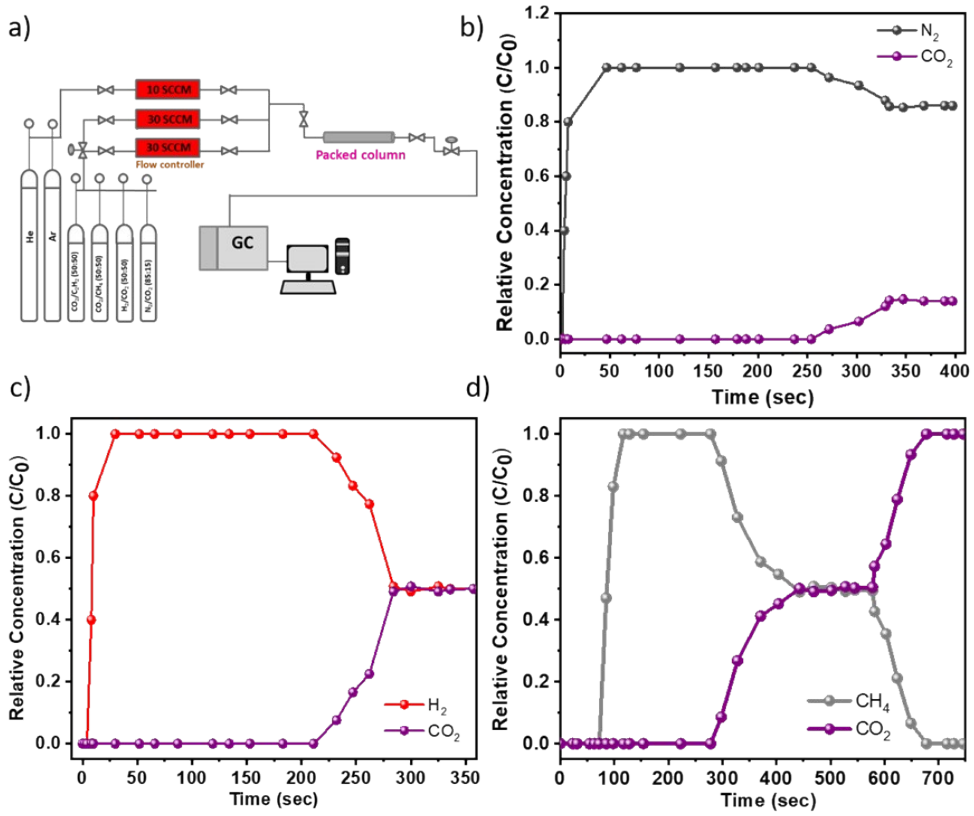

Figure S12 (a) Schematic representation of assembled breakthrough gas separation assembly. (b) Experimental dynamic breakthrough separation under ambient condition.

The real-time adsorption-based separation and purification process of **1′** for CO_2/H_2 (1:1, v/v), CO_2/N_2 (0.85/0.15, v/v), CO_2/CH_4 (1:1, v/v) and CO_2/C_2H_2 (1:1, v/v) gas mixture was analyzed by using packed column of 12.4 cm (~1.65 g of powdered 1) length and 0.3 cm diameter. The sample was first activated at 195 °C for 12 h prior to loading in column and after loading it was further regenerated by the continuous flowing of carrier gas for 1 h. The continuous flow was regulated by mass flow controller by using Helium as a carrier gas for CO_2/N_2, CO_2/CH_4 and CO_2/C_2H_2 and Ar gas for CO_2/H_2, respectively. For CO_2/N_2 and CO_2/H_2 dynamic breakthrough separation was performed and for other hydrocarbon mixtures, stepwise dynamic breakthrough separations were performed to exclusively separate each isomer with polymer grade purity and consecutive sample regeneration (Table S6).

The bi-cyclic C_2H_2/CO_2 breakthrough separation data has been plotted in Figure 6 and this data is given in the main manuscript. The data ensures reproducibility and recyclability of the separation process while in between 1st and 2nd cycle the material is activated by blowing He gas through the column further

initiated the gas mixture flow by keeping other parameters (temp, flow rate, hold time, etc.) same. The C_2H_2 elution and detection quantity through gas chromatography has been analysed by calibrating the outlet gas concentration through the experimentally calibrated (~3000, ~500, ~200 ppm) cylinders.

Table S13 The total flow rate and corresponding breakthrough times are as follows;

Experimental dynamic breakthrough details. Feed gas mixture (A: B)	Conc. (A: B)	Flow rate (total) in $mL.min^{-1}$	Carrier gas	Outlet time (for gas A) in sec	Outlet time for (gas B) in sec
H_2/CO_2	(0.5:0.5)	2.2	Ar	8	232
N_2/CO_2	(0.85:0.15)	2.2	He	4	272
CO_2/CH_4	(0.5:0.5)	2.8	He	85	298
CO_2/C_2H_2	(0.5:0.5)	2.8	He	98	345

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