Benchmark Acetylene Binding Affinity and Separation through Induced Fit in a Flexible Hybrid Ultramicroporous Material

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## Supplementary Information

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1. Methods and Instrumentation

Synthesis of coordination networks

Synthesis of [Zn(SiF$_6$)(bpe)$_2$]$_n$-CHCl$_3$ (pcu-SIFSI-X-bpe-Zn): Commercially available reagents were purchased in high purity grade and used as received. In a typical reaction, a solution of methanol containing ZnSiF$_6$.xH$_2$O (10 mg, 0.05 mmol) in 2 mL was carefully layered on top of 1,2-bis(4-pyridyl) ethane (37 mg, 0.2 mmol) in 2 mL of chloroform. Middle of the tube 2 mL of 1:1 mixture of chloroform and methanol solution was used as buffer. Then test tube was sealed with parafilm and the contents allowed to diffuse slowly at room temperature. Colourless crystals were obtained after couple of days in buffer layer solution. pcu-SIFSIX-bpe-Zn is a “1st generation” sorbent, i.e. after being removed from the mother liquor the isolated crystals lost solvent and converted to an amorphous solid as determined by PXRD.

Synthesis of [Zn(SiF$_6$)(bpe)$_2$]$_n$-5MeOH (sql-SIFSI-X-bpe-Zn-α): In a typical reaction, a solution of methanol containing 1,2-bis(4-pyridyl) ethane (37 mg, 0.2 mmol) in 3 mL was carefully layered on top of ZnSiF$_6$.xH$_2$O (20 mg, 0.1 mmol) in 3 mL of MeOH. After complete addition of reagents, the test tube was sealed with parafilm and kept aside at room temperature. Colourless cubic crystals were obtained after a few hours suitable for further analysis. The calculated yield for the sql-SIFSIX-bpe-Zn-α was found to be 60% based on ZnSiF$_6$.xH$_2$O as the limiting reagent.

Preparation of [Zn(SiF$_6$)(1,2-Bis(4-pyridyl)ethane)$_2$] (sql-SIFSI-X-bpe-Zn-β): Crystals of the sql-SIFSIX-bpe-Zn-β were prepared by heating sql-SIFSIX-bpe-Zn-α at 60 °C under vacuum for 12h. The phase conversion from α to β occurs completely based upon PXRD comparisons so the estimated yield of sql-SIFSIX-bpe-Zn-β is quantitative.

Preparation of [Zn(SiF$_6$)(1,2-Bis(4-pyridyl)ethane)$_2$].C$_2$H$_2$ (sql-SIFSI-X-bpe-Zn-β⊃C$_2$H$_2$): sql-SIFSIX-bpe-Zn-β⊃C$_2$H$_2$ were obtained when sql-SIFSIX-bpe-Zn-β exposed to C$_2$H$_2$ gas at 298 K less than 1 bar.

Preparation of [Zn(SiF$_6$)(1,2-Bis(4-pyridyl)ethane)$_2$].C$_2$H$_2$ (sql-SIFSI-X-bpe-Zn-β⊃C$_2$H$_2$): sql-SIFSIX-bpe-Zn-β⊃C$_2$H$_2$ were obtained when sql-SIFSIX-bpe-Zn-β exposed to C$_2$H$_2$ gas at 298K 1 bar.
Preparation of $[\text{Zn(SiF}_6\text{)}(1,2\text{-Bis(4-pyridyl)ethane})_2\text{]}\text{2C}_2\text{H}_2$ (sql-SIFSIX-bpe-Zn-$\gamma\supset\text{2C}_2\text{H}_2$): sql-SIFSIX-bpe-Zn-$\gamma\supset\text{2C}_2\text{H}_2$ were obtained when sql-SIFSIX-bpe-Zn-$\beta$ exposed to C$_2$H$_2$ gas at 195K 1 bar.

In-situ variable temperature PXRD, PXRD and SCXRD experiments: PXRD experiments were conducted using a PANalytical Empyrean™ diffractometer equipped with a PIXcel3D detector operating in scanning line detector mode with an active length of 4 utilising 255 channels. The diffractometer is outfitted with an Empyrean Cu LFF (long fine-focus) HR tube (9430 033 7310x) operated at 40 kV and 40 mA and Cu K-alpha radiation ($\lambda_{\alpha} = 1.540598 \text{ Å}$). Incident beam optics included the Fixed Divergence slit with anti-scatter slit PreFIX module, with a 1/8° divergence slit and a 1/4° anti-scatter slit, as well as a 10 mm fixed incident beam mask and a Soller slit (0.04 rad). Divergent beam optics included a P7.5 anti-scatter slit, a Soller slit (0.04 rad), and a Ni $\beta$ filter. In a typical experiment, data was collected via a continuous scan in the range of 5°-45° (2θ) with a step-size of 0.02° at a scan rate of 0.1° min$^{-1}$. Raw data was then evaluated using the X'Pert HighScore Plus™ software v4.1 (PANalytical, The Netherlands). In situ variable temperature PXRD was collected under N$_2$ atmosphere by increasing the temperature 10 °C/10 min; water cooling system was adopted to control the temperature. SCXRD data were collected on a Bruker Quest diffractometer equipped with a CMOS detector and IμS microfocus X-ray source (Cu Kα, $\lambda = 1.5418 \text{ Å}$). Absorption corrections were applied by using the multi-scan program SADABS. Structural solution and refinement against Fobs data were carried out using the SHELXL programs.

Coincidence PXRD sorption measurements: Coincident PXRD measurements were measured on a Rigaku Smartlab with CuKα radiation (Rigaku, Japan) connected to a BELSORP-18PLUS volumetric adsorption equipment (MicrotracBEL Japan, Corp.) and synchronized with each other. To control the temperature, the adsorption equipment was connected to a cryostat. The sample was placed on a copper plate and activated under high vacuum (at a pressure around 200 Pa) at 353 K for 12 h. The weight of the evacuated sample (~100 mg) was determined under inert atmosphere and set on a cryostat system for in-situ evacuation under high vacuum (< 10$^{-2}$ Pa) at 353 K for 2 h prior to the experiments. C$_2$H$_2$ and CO$_2$ adsorption was carried out by setting the temperature of the cryostat at the measurement temperature (298 K and 195 K), followed by controlled introduction of gas to the sample cell. The in-situ PXRD pattern of the sample containing adsorbate was simultaneously measured at each equilibrium point of the adsorption isotherms.

Coincidence FTIR measurement: The in-situ infra-red (IR) spectroscopy/adsorption measurements were carried out using a JASCO FT/IR-4700 connected to BELSORP-18PLUS (MicrotracBEL, Japan, Corp) volumetric adsorption analyser equipped
with cryostatic temperature controllers. Those apparatuses were synchronized with each other and each IR spectra was obtained at each point of the sorption isotherms. The activated sample of known weight (~100 mg) was placed on a copper plate and before measurement start the sample has been activated again under dynamic vacuum (< 10–2 Pa) at 60 °C for 2 h. C2H2 adsorption was carried out by setting the temperature of the cryostat at the measurement temperature (298 K), followed by controlled introduction of C2H2 gas to the sample cell. The FTIR pattern of the sample containing adsorbate was simultaneously measured at each equilibrium point of the adsorption isotherms.

**Isobar measurements:** Isobar measurements were carried out using a BELSORP-18PLUS (MicrotracBEL, Japan, Corp) volumetric adsorption analyzer equipped with cryostatic temperature controllers. An activated sample of ~100 mg was placed in the sorption analyzer before measurement and the sample was activated again at 80 °C for two hours in order to remove adsorbed moisture. The sorption analyzer was programmed to measure uptake at 1 bar at 10 °C intervals. Sorption uptake was measured individually for each gas (C2H2, C2H4 and CO2) while increasing the temperature from 195 K to 298 K. After each gas measurement, the sample was activated at 80 °C for two hours.

**Dynamic gas breakthrough measurements:** In a typical breakthrough experiment, ~ 0.50 g of finely grinded sample was placed in quartz tube (8 mm diameter) to form a fixed bed. Then the adsorbent bed was purged under a 20 cm³ min⁻¹ flow of He gas at 65°C for 6 hours to activate the sample prior to breakthrough experiment. Upon cooling to room temperature, a binary gas mixture (C2H2/CO2 or C2H2/C2H4) containing equal volume of gas species (0.2 ml min⁻¹/0.2 ml min⁻¹) was introduced to mix with the He flow to perform breakthrough experiments at 25 °C and 1 bar (the total gas flow here is 20.4 ml min⁻¹). The outlet composition was continuously monitored by a gas chromatography (Shimadzu GC2030 with a FID detector, C2H2/C2H4) or mass spectrum (C2H2/CO2) until complete breakthrough was achieved. After each breakthrough experiment, the packed column bed was regenerated at 65 °C with constant He flow (20 cm³ min⁻¹) overnight to ensure complete sample regeneration.

**In-situ PG-DSC measurements:** Samples were activated *in-situ* in the PG-DSC for two hours at 353 K under dynamic vacuum to ensure that all moisture was removed during sample loading. A further activation for one hour at 353 K was run between each set of cycles at the various temperatures. Experimental runs for C2H2 were completed isothermally at 298 K and 308 K. PG-DSC measurements were carried out using a Setaram µDSC7 Evo module equipped with a high-pressure sample holder. The required gas was introduced to the system from Proportion Air QPV1M pressure regulator, which is able to control a pressure gradient from vacuum to 10 bar. The pressure gradient was set to increase from 0
(vacuum) to 1 bar over 1500 seconds, which is at a rate of 0.04 bar/min. The pressure was then held at 1 bar for 2000 seconds to ensure that the heat flow stabilized and equilibrium was reached, after which the pressure was decreased back to 0 (vacuum) at the same rate (0.04 bar/min). This was repeated for at least 3 cycles to a maximum of 10, to ensure reproducibility in the results. Data were recorded and analyzed using the Calisto software package from Setaram. The pressure reading for vacuum was $2.3 \times 10^{-1}$ mbar.

The pressure gradient profile used for the experiments, the flat areas indicate where the experiment was held at a specific pressure to ensure equilibrium was reached.

Heatflow is gained from the pressure DSC analysis, which is converted to Qint by integrating the area under the curve against time. Qint is coupled to the loading from volumetric sorption analysis and this is differentiated to give Qdiff and the RT term is added to finally give Qst.
In-situ single crystal measurements:

Activation Procedure
Single crystals of the as-synthesised material of appropriate size, possessing suitable morphology and ability to extinguish plane polarized light were glued onto a glass fibre with cyanoacrylate glue (to minimize exposure to ambient atmosphere). The glass fibre was then inserted into an environmental gas cell (EGC) consisting of a 0.3 mm glass Lindemann Capillary attached to a steel nut with epoxy, which is then screwed into a valve body. The EGC allows for pressurisation/evacuation of the immediate crystal environment while the valve allows for this environment to be isolated and transported to the diffractometer. The EGC was then connected to a turbo-vacuum pump (pressure: \(~3 \times 10^{-3}\) millibar) while also immersed in oil, which was heated to 65 °C for approximately 18 hours. After this treatment the crystals transform from clear to opaque. The valve was then closed and the EGC removed from the apparatus.

Aphost Structure Determination
For the apohost data collection the crystal (in an EGC) was placed on the diffractometer while under vacuum. X-ray intensity data were recorded on a Bruker SMART APEX II diffractometer. The instrument is equipped with an Incoatec \(\mu\)S molybdenum (\(\lambda = 0.71073\) Å) microfocus X-ray source and a CCD area detector. The diffractometer is fitted with a 700 Series Cryostream Plus cryostat from Oxford Cryosystems, which is used to control the sample temperature. It was quickly noted (from both the diffraction frames and subsequent investigation of the reciprocal lattice) that the as-synthesised crystals become non-merohedrally twinned once the guest is removed. The crystals were generally composed of two major twin domains with at least two more minor twin domains (all crystals investigated displayed this behaviour once activated). Owing to the nature of the twinning, where many reflections overlap, attaining ideal data completeness and quality proved problematic. In an attempt to maximise the data completeness multiple omega and phi scans were carried out in a high redundancy strategy to increase data overlap.
To determine the structure of the twinned crystal, twinned reflections were deconvoluted using the CELL_NOW\textsuperscript{1} routine. This identified two major domains in the crystal and their respective unit cells. Two problems were encountered during this process. Firstly, as noted previously, many reflections between domains were found to overlap. Secondly, although the two major domains were indexed, there were still multiple minor domains (>2) remaining which accounted for approximately a quarter of the data. It was noted that if these minor domains were included and indexed the data completeness would decrease dramatically (perhaps as a result of the large number of overlapping reflections). Thus the minor domains were not indexed and treated as composites. The data were then reduced, scaled and adsorption corrected (SAINT\textsuperscript{2} and TWINABS\textsuperscript{3}) using the two major domains.

The structures were solved using a dual-space algorithm or direct methods using SHELXT\textsuperscript{4} or SHELXS-2016/1\textsuperscript{5}, respectively. Structure refinement was carried out with SHELXL-2018/3\textsuperscript{5} using the X-Seed\textsuperscript{6} graphical user interface. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Initial structural refinement was carried out using the HKLF4 file, followed by subsequent refinement with the HKLF5 file (inserting a BASF instruction). Thermal parameters were restrained using the RIGU and SIMU cards because, for the data at hand, they were not always coherent in their direction and relatively large at room temperature. Furthermore, residual electron density is present around the Zn, Si and F atoms. However, this may be explained by their proximity to one another (shielding effects) as well as a contribution due to twinning. Although parameter restraints were applied, they constitute less than 25% of the overall data.

**Gas Loading**
An activated crystal in an EGC was attached to a C\textsubscript{2}H\textsubscript{2} cylinder via a regulator. The system was pressurised to 1 bar and left to equilibrate under static pressure for approximately 6-8 hours. After the valve to the ECG was closed it could be transported to the diffractometer.

**C\textsubscript{2}H\textsubscript{2} Loaded Structure Determination**
The data collection, structure solution and refinement for the C\textsubscript{2}H\textsubscript{2} loaded structure were carried out similarly to the apohost material.

**Procedure for Determining 195 K Structure**

**Activation Procedure**
The activation procedure employed was the same as for the room temperature structures.

**Variable Pressure Structure Determination at Low Temperature**
To avoid fluctuations in gas pressure as a result of differences in measurement temperature
and loading temperature a vertical EGC setup with a portable gas reservoir was used. The setup consists of a glass capillary epoxied into a steel nut and into which a crystal glued to a glass fibre may be inserted and attached. The steel nut is then screwed into an assembly consisting of a stainless steel housing. The housing is attached to a large gas reservoir by means of flexible tubing such that changing the temperature of the gas cell does not affect the pressure of the gas at the sample. The assembly is attached to the omega stage of the diffractometer.

For the measurement the system was evacuated and subsequently pressurised to 1 bar from a C\textsubscript{2}H\textsubscript{2} cylinder. The system was then placed on the diffractometer at 195 K and left to equilibrate overnight. Measurements consisted of a 180° omega scan, after which the gas cell assembly was manually rotated by 90° and another 180° omega scan was carried out. This procedure was repeated until the amount of data gathered was deemed sufficient (in this case 5 to 6 iterations to ensure appropriate overlap and high redundancy because of the non-merohedral twinning).

Data processing was carried out by identifying the major domain for each run (using the CELL\_NOW\textsuperscript{1} routine) and exporting the unit-cell parameters and subsequent orientation matrix as a .p4p file. The use of more than one domain resulted in a dramatic reduction in the quality of data when solution was attempted. The data were reduced using the standalone SAINT\textsubscript{plus}\textsuperscript{2} module, which allows the user to define a specific orientation matrix for each run (using the previously generated .p4p files). The data were scaled and absorption corrected using the SAINT\textsuperscript{2} and SADABS\textsuperscript{7} routines.

The structure was solved with a dual-space algorithm using SHELXT\textsuperscript{4}. Structure refinement was carried out with SHELXL-2018/3\textsuperscript{5} using the X-Seed\textsuperscript{6} graphical user interface. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. Thermal parameters were restrained using the RIGU and SIMU instructions because, for the data at hand, they were not always coherent in their direction and relatively large at room temperature. There are notable areas of residual electron density within the final structure. These can be attributed to “missed” twinning as only one of the twin domains was employed in data reduction. Neither use of the TWIN command nor variations in scaling and absorption correction were successful in treating the spurious electron density. Furthermore, any attempt at refining these residual peaks as part of the model was unsuccessful (implying that they are artefacts of the electron density landscape). Although parameter restraints were applied, they constitute less than 25% of the overall data.
Supplementary crystallographic data for this manuscript has been deposited at the Cambridge Crystallographic Data Centre under deposition numbers CCDC 2048414-2048416, 2048419, 2088146 and 2092588. These data can be obtained free of charge from http://www.ccdc.cam.ac.uk/data_request/cif. Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Readers are welcome to comment on the online version of the paper.

2. Physicochemical properties

**Table S1.** List of physical and electronic parameters for the C$_2$H$_2$, CO$_2$, C$_2$H$_4$ and CH$_4$.

|                  | C$_2$H$_2$ | CO$_2$ | C$_2$H$_4$ | CH$_4$ |
|------------------|------------|--------|------------|--------|
| Kinetic diameter(Å) | 3.3        | 3.3    | 4.16       | 3.8    |
| Boiling point(K)  | 189.3      | 194.7  | 169.45     | 111.65 |
| Size (Å$^3$)      | 3.32 X 3.34 X 5.7 | 3.18 X 3.33 X 5.36 | 3.28 X 4.18 X 4.84 | -      |
| Quadrupole moment $10^{40}$ θ (cm$^2$) | 20.4       | 13.4   | 5          | 0      |
| Dipole moment(D)  | 0          | 0      | 0          | 0      |
| Polarizability(Å$^3$) | 3.59       | 2.65   | 4.25       | 2.60   |
| Reduction Energy (kJ/mol) | 172.0       | 351.4  | -          | -      |
3. Comparison of induced fit sorbents

Table S2. Comparison of selected features of framework sorbents that exhibit induced fit
4. Crystallographic details

**Table S3.** Crystal data and refinement parameters.

|                         | sql-SIFSIX-bpe-Zn-α | sql-SIFSIX-bpe-Zn-β | sql-SIFSIX-bpe-Zn-β’≥2C6H6 at 298K | sql-SIFSIX-bpe-Zn-γ≥4C6H6 at 195K | sql-SIFSIX-bpe-Zn-β≥2C6H6 at 298K |
|-------------------------|----------------------|----------------------|--------------------------------------|-----------------------------------|-------------------------------------|
| **Formula**             | C_{26}H_{32}F_{6}N_{4}O_{2}SiZn | C_{24}H_{24}F_{6}N_{4}SiZn | C_{26}H_{26}F_{6}N_{4}SiZn | C_{28}H_{28}F_{6}N_{4}SiZn | C_{26}H_{26}F_{6}N_{4}SiZn |
| **cF.W.**               | 640.04               | 575.95               | 1203.98                              | 628                               | 597.61                              |
| **T (K)**               | 150(2)               | 298(2)               | 298(2)                               | 195(2)                            | 298(2)                              |
| **Space group**         | C2/c                 | P-1                  | P-1                                 | P-1                               | P-1                                 |
| **a (Å)**               | 20.592(8)            | 10.007(3)            | 10.1538(14)                         | 9.885(13)                         | 10.048(8)                           |
| **b (Å)**               | 7.7951(3)            | 11.493(3)            | 11.4817(15)                         | 11.288(2)                         | 11.480(10)                          |
| **c (Å)**               | 19.7325(11)          | 14.446(4)            | 14.3544(19)                         | 15.495(3)                         | 14.348(12)                          |
| **α (°)**               | 90                   | 97.87(2)             | 96.023(5)                           | 69.80(16)                         | 96.93(7)                            |
| **β (°)**               | 118.21(1)            | 103.37(2)            | 104.261(5)                          | 89.992(13)                        | 103.69(7)                           |
| **γ (°)**               | 90                   | 114.710(19)          | 115.742(5)                          | 65.438(15)                        | 115.13(8)                           |
| **V (Å³)**              | 2971.2(2)            | 1416.2(8)            | 1417.2(3)                           | 1403.5(6)                         | 1409.0(2)                           |
| **Z**                   | 4                    | 2                    | 2                                    | 2                                 | 2                                   |
| **Dx (g cm⁻³)**         | 1.523                | 1.351                | 1.411                                | 1.434                             | 1.404                               |
| **μ (mm⁻¹)**            | 2.280                | 0.967                | 0.970                                | 0.948                             | 0.230                               |
| **Data collected/unique** | 2525/2519           | 5315/3198            | 5851/4321                           | 4160/1451                         | 5673/4508                           |
| **Wavelength (Å)**      | 0.71073              | 0.71073              | 0.71073                              | 0.71073                           | 0.41190                             |
| **R₁ (I>2σ(I))**        | 0.0442               | 0.1208               | 0.0901                               | 0.1611                            | 0.089                               |
| **wR₂ (all data)**      | 0.1174               | 0.3496               | 0.2562                               | 0.450                             | 0.276                               |
| **GOF**                 | 1.063                | 1.065                | 1.037                                | 1.027                             | 1.07                                |
| **CCDC no.**            | 2048419              | 2048415              | 2088146                              | 2092588                           | 2048416                             |
|                                   | pcu-SIFSIX-bpe-Zn |
|-----------------------------------|-------------------|
| **Formula**                       | C24H24F6N4SiZn    |
| cF.W.                             | 575.95            |
| **T (K)**                         | 140(2)            |
| **Space group**                   | Ima2              |
| **a (Å)**                         | 15.2206(6)        |
| **b (Å)**                         | 16.7157(9)        |
| **c (Å)**                         | 15.0888(10)       |
| **α (°)**                         | 90                |
| **β (°)**                         | 90                |
| **γ (°)**                         | 90                |
| **V (Å³)**                         | 5365.5(4)         |
| **Z**                             | 4                 |
| **D_x (g cm⁻³)**                  | 0.713             |
| **μ (mm⁻¹)**                      | 1.127             |
| **Data collected/unique**         | 2009/1563         |
| **Wavelength (Å)**                | 0.71073           |
| **R₁ (I>2σ(I))**                  | 0.1027            |
| **wR₂ (all data)**                | 0.2796            |
| **GOF**                           | 1.068             |
| **CCDC no.**                      | 2048414           |
5. Structure of pcu 3D net

Figure S1. Structural representation of pcu-SIFSIIX-bpe-Zn, a 3D network.
6. *In-situ* variable temperature PXRD

**Figure S2.** *In-situ* variable temperature PXRD measured from RT to 60 °C (right). The PXRD pattern undergoes new phase transformation at 60 °C that corresponds to beta phase. In the alpha phase only two planes exists (2,0,0) and (2,0,-2), when temperature reaches to 60 °C three new planes appear (0,1,-1), (1,-1,0) and (1,0,-1). Structural transformation as shown from alpha to beta (left side). In the case of alpha the SIFSIX ions are aligned regularly but, in the beta, the SIFSIX ions very distorted.
7. DSC, TGA measurements and SEM images

**Figure S3.** DSC measurements for alpha phase (a) and beta phase (b). a) A small peak at 60 °C was identified as phase transformation from alpha to beta, while the peak at 100 °C may be due to the loss of water adsorbed during preparation for measurement. The two peaks at 160 °C and 220 °C correspond to framework decomposition. b) First peak just above 100 °C is belongs to water loss and 125 °C peak assign as phase change. Followed peaks at higher temperatures is due to phase change and decomposition of the framework. More studies into phase change behaviors of this compound are under way.
Figure S4. Thermogravimetric analysis for alpha (blue) and beta (red). Alpha shows weight loss ~13% that corresponds to ~5 MeOH molecules per unit cell. Both alpha and beta were stable up to ~190 °C.
Figure S5. SEM images for alpha phase.
Figure S6. SEM images for beta phase.
**Figure S7.** Thermogravimetric analysis for beta phase after soaked in different solvents.
8. Gas sorption studies

![Graph showing gas sorption isotherm](image)

**Figure S8.** Gas sorption isotherm measured at 195 K for C₂H₂, adsorption (filled) and desorption (empty).
Figure S9. Gas sorption isotherm measured at 195 K for CO$_2$, adsorption (filled) and desorption (empty).
Figure S10. Gas sorption isotherm measured at 77 K for N₂, adsorption (filled) and desorption (empty).
9. PXRD comparison

Figure S11. PXRD patterns comparison of alpha experimental compared with alpha calculated. Similarly, beta experimental with beta calculated, and PXRD pattern after sorption experiments compared. Small shift observed for beta PXRD patterns was due to vacuum condition (orange and above).
Figure S12. PXRD patterns measured for the beta phase after soaked in different solvents, such as methanol, ethanol, isopropanol, dichloromethane, acetonitrile and acetone.
10. Schematic representation of structural transformation

Figure S13. Schematic representation of switching and capture of C₂H₂. In beta and gamma phases the C₂H₂ found within 2D layer with occupancy 2 and 4 respectively.
Figure S14. PXRD pattern comparison of gamma phase from *in-situ* PXRD vs. calculated PXRD from *in-situ* SCXRD.
11. *In-situ* single crystal structure of gamma at 195 K

**Figure S15.** C$_2$H$_2$ binds in the gamma phase within and in between the 2D layers. There are four distinct sites with occupancy 0.5 for each C2H2 site. Full occupancy was not completely reached due to slow kinetics of loading.
12. Gas sorption

Figure S16. Gas sorption isotherm for C$_2$H$_2$ (blue), C$_2$H$_4$ (green), CH$_4$ (purple) C$_2$H$_6$ (dark yellow) and CO$_2$ (red) at 298 K.
Figure S17. 10 consecutive cycles of C₂H₂ sorption measurements at 298 K. After each cycle the sample was evacuated for 30 mins.
Figure S18. $\text{C}_2\text{H}_2$ sorption measured from 273 K to 328 K in the interval of 10 °C as plotted on a log scale.
Figure S19. C$_2$H$_2$ sorption measured from 288 to 318 K in 5 °C intervals.
**Figure S20.** CO$_2$ sorption measured from 273 to 328 K in 10 °C intervals.
**Figure S21.** $\text{C}_2\text{H}_4$ sorption measured from 273 to 328 K in 10 °C intervals.
Figure S22. CH\(_4\) sorption measured from 273 to 328 K in 10 °C intervals.
13. Qst of CH$_4$ sorption

**Figure S23.** Isosteric heat of adsorption upon CH$_4$ sorption calculated by clausius-clapeyron equation.
14. *In-situ* PG-DSC

![Graphs showing Qst vs Uptake for C2H2 and C2H4](image)

**Figure S24.** *In-situ* pressure gradient DSC measurements for C2H2 and C2H4. a) Qst vs. C2H2 loading, the obtained Qst ~67 kJ/mol for C2H2 loading upon 0.93 and 1.04 mmol at 298 and 308 K, respectively. c) Qst vs. C2H4 loading at 298 K (39 kJ/mol at 0.3 mmol). Qst plot was obtained by the considering area under the curve from the heat flow vs. time plot and then divided by the uptake from sorption profile at various loadings.
Figure S25. Breakthrough measurements were performed at 1:99 gas mixtures for both C$_2$H$_2$/C$_2$H$_4$ (a) and C$_2$H$_2$/CO$_2$ (b) at 298 K. The concentration is too low to undergo induced fit and good separation under these conditions.
16. Isobar measurements for $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$ and $\text{CO}_2$.

Figure S26. In isobar experiments, the uptake was measured at every 10 °C intervals for $\text{C}_2\text{H}_2$, $\text{C}_2\text{H}_4$, and $\text{CO}_2$ while increasing temperature from 195 to 328 K.
17. Representation of contortion of organic linker

Figure S27. Crystal structure analysis of β⊂empty, β′⊂2C₂H₂ and β⊂2C₂H₂ revealed that ethane chain of ligand undergoes contraction and expansion from one phase to another.
Figure S28. Crystal structure analysis of β-empty phase revealed that SIFSIX pillar aligns equally with all bond distances and slight distortion in bond angles of about ~2°. The F to F distance was found to be 6.87 and 6.75 Å.
Figure S29. Crystal structure analysis of $\beta'$-$2C_{2}H_{2}$ revealed that distortion of bond distances and bond angles of SIFSIX pillar, distorted by 2 to 6 ° of bond angles. The F to F distance was slightly increased (7.02 and 7.24 Å) compared to beta empty.
Figure S30. The bond angles and bond distances were aligned similar to each other in $\beta \supset 2\text{C}_2\text{H}_2$ and $\beta \supset \text{empty}$ phases.
18. DFT calculations for binding positions

Figure S31. DFT calculations for C₂H₂ binding sites in the beta prime structure at 298 K.
**Figure S32.** DFT calculations for C\textsubscript{2}H\textsubscript{4} and CO\textsubscript{2} binding sites in beta phase at 298 K reveals that both were held in a perpendicular fashion with the SIFSix pillars.
Figure S33. DFT calculations for C$_2$H$_2$ binding sites in beta phase at 298 K reveals that C$_2$H$_2$ was held more favorably between two neighboring SIFSIX pillar and metal cavity.
19. Selectivity and interaction energies compared with reported MOFs.

**Table S4.** Selectivity comparison at both bulk and trace gas separations.
20. Isosteric Heat of Adsorption ($Q_{st}$)

The experimental isosteric heat of adsorption ($Q_{st}$) values for C$\textsubscript{2}$H$\textsubscript{2}$ in sql-SIFSix-bpe-Zn were determined by first fitting the C$\textsubscript{2}$H$\textsubscript{2}$ adsorption isotherms at 288, 293, 298, 303, 308, and 313 K to the dual–site Langmuir–Freundlich (DSLF) equation$^{17}$ and subsequently applying the Clausius–Clapeyron method.$^{18}$ The DSLF equation is given by:

$$n = \frac{n_{m1} b_1 P^{(\frac{1}{t_1})} + n_{m2} b_2 P^{(\frac{1}{t_2})}}{1 + b_1 P^{(\frac{1}{t_1})} + b_2 P^{(\frac{1}{t_2})}}$$

where $n$ is the uptake (in mmol g$^{-1}$), $P$ is the pressure (in kPa), $n_{m1}$ and $n_{m2}$ are the saturation uptakes (in mmol g$^{-1}$) for sites 1 and 2, $b_1$ and $b_2$ are the affinity coefficients (in kPa$^{-1}$) for sites 1 and 2, and $t_1$ and $t_2$ represent the deviations from the ideal homogeneous surface (unitless) for sites 1 and 2. The parameters that were obtained from the fitting of the C$\textsubscript{2}$H$\textsubscript{2}$ adsorption isotherms are found in Table S5. All isotherms were fitted with $R^2 > 0.9999$.

The fitted parameters were used to calculate the $Q_{st}$ values for a range of uptakes through the Clausius–Clapeyron equation, which is the following:

$$Q_{st} = -R \frac{\partial \ln P}{\partial (1/T)}$$

where $T$ is the temperature (in K) and $R$ is the ideal gas constant. The partial derivative term actually represents the slope of the plot of $\ln P$ vs. $1/T$ for a number of isotherms at different temperatures at various loadings. Therefore, the above $Q_{st}$ equation can be simplified to:

$$Q_{st} = -mR$$
where $m$ is the slope, which can be calculated by the following for six different temperatures and their corresponding pressures:

$$m = \frac{\sum \frac{1}{T_i} \ln P_i - \frac{1}{6} \left( \sum \frac{1}{T_i} \right) \left( \sum \ln P_i \right)}{\sum \left( \frac{1}{T_i} \right)^2 - \frac{1}{6} \left( \sum \frac{1}{T_i} \right)^2}$$

The $P_i$ values were back-calculated for a range of uptakes using the DSLF equation via an iterative technique (e.g., the Newton–Raphson method).\(^\text{19}\)

| Parameter | 288 K       | 293 K       | 298 K       | 303 K       | 308 K       | 313 K       |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|
| $n_m1$ (mmol g\(^{-1}\)) | 1.600752    | 1.886782    | 2.537936    | 1.591395    | 0.268632    | 1.338113    |
| $b_1$ (kPa\(^{-1}\)) | 4.746388    | 0.023751    | 0.022787    | 1.431032    | 0.128949    | 0.884182    |
| $t_1$     | 0.721597    | 3.301869    | 3.603137    | 0.715466    | 1.261404    | 0.692667    |
| $n_m2$ (mmol g\(^{-1}\)) | 2.982156    | 1.596264    | 1.566928    | 0.758757    | 1.501361    | 0.361694    |
| $b_2$ (kPa\(^{-1}\)) | 0.015515    | 3.373885    | 2.128017    | 0.024708    | 1.116860    | 0.203808    |
| $t_2$     | 3.344843    | 0.760310    | 0.728258    | 1.823105    | 0.692303    | 0.981279    |
| $R^2$     | 0.999990    | 0.999984    | 0.999981    | 0.999966    | 0.999965    | 0.999995    |
Figure S34. $C_2H_2$ adsorption isotherms of beta phase at 298, 308 and 318 K fitted using the DSLF equation.
Figure S35. C\textsubscript{2}H\textsubscript{4} adsorption isotherms of beta phase at 273 and 288 K fitted using the DSLF equation.
Figure S36. CH₄ adsorption isotherms of beta phase at 298, 288, and 273 K fitted using the DSLF equation.
**Figure S37.** CO$_2$ adsorption isotherms of beta phase at 273 and 298 K fitted using the DSLF equation.
21. Ideal Adsorbed Solution Theory (IAST)

The selectivities of C\textsubscript{2}H\textsubscript{2} over C\textsubscript{2}H\textsubscript{4}, CO\textsubscript{2}, and CH\textsubscript{4} for the adsorbate mixture compositions of interest in sql-SIFSIX-bpe-Zn were calculated using ideal adsorbed solution theory (IAST).\textsuperscript{20} First, the single-component isotherms were fitted to the dual-site Langmuir-Freundlich equation (DSLF):\textsuperscript{21}

\[
n = \frac{n_{m1} b_1 P^{(\frac{1}{t_1})}}{1 + b_1 P^{(\frac{1}{t_1})}} + \frac{n_{m2} b_2 P^{(\frac{1}{t_2})}}{1 + b_2 P^{(\frac{1}{t_2})}}
\]

where \(n\) is the uptake (in mmol g\textsuperscript{-1}), \(P\) is the pressure (in kPa), \(n_{m1}\) and \(n_{m2}\) are the saturation uptakes (in mmol g\textsuperscript{-1}) for sites 1 and 2, \(b_1\) and \(b_2\) are the affinity coefficients (in kPa\textsuperscript{-1}) for sites 1 and 2, and \(t_1\) and \(t_2\) represent the deviations from the ideal homogeneous surface (unitless) for sites 1 and 2. All isotherms were fitted with \(R^2 \geq 0.999\).

According to IAST, the spreading pressure for adsorbates \(i\) and \(j\) can be calculated using the following equations:

\[
\frac{\pi_i^* A}{RT} = \int_0^{P_i^*(\pi)} \frac{n_i(P)}{P} dP
\]

\[
\frac{\pi_j^* A}{RT} = \int_0^{P_j^*(\pi)} \frac{n_j(P)}{P} dP
\]

where \(A\) represents the specific surface area (assumed to be the same for all adsorbates), \(R\) is the ideal gas constant, \(T\) is the temperature, and \(P_i^*(\pi)\) and \(P_j^*(\pi)\) are the equilibrium
gas phase pressures corresponding to the solution temperature and spreading pressure for the adsorption of pure components $i$ and $j$, respectively. Furthermore, the following equations hold true for a two-component mixture:

\[ \pi_i^* = \pi_j^* \]

\[ Py_i = P_i^* x_i \]

\[ Py_j = P_j^* x_j \]

\[ x_i + x_j = 1 \]

\[ y_i + y_j = 1 \]

Here, $x_i$ and $x_j$ are the mole fractions of components $i$ and $j$, respectively, in the adsorbed phase, and $y_i$ and $y_j$ are the mole fractions of components $i$ and $j$, respectively, in the gas phase. The previous seven equations are seven independent equations with nine unknowns. In order to solve for all of the unknowns, two quantities must be specified, particularly $P$ and $y_i$. Utilization of the aforementioned equations yields the following equilibrium expression for adsorbates $i$ and $j$:

\[
\int_0^{py_i \over x_i} \frac{n_i(P)}{P} dP = \int_0^{P(1-y_i) \over (1-x_i)} \frac{n_j(P)}{P} dP
\]

The above equation was solved for $x_i$ using the Newton–Raphson method\textsuperscript{19} for a range of pressures at a specified $y_i$ value. Finally, the selectivity for adsorbate $i$ relative to adsorbate $j$ was calculated using the following:
22. Binding energy calculations

Periodic density functional theory (DFT) calculations were performed to evaluate the relative energies of the $\beta$, $\beta'\supseteq 2\text{C}_2\text{H}_2$, and $\beta\supseteq 2\text{C}_2\text{H}_2$ phases as well as the adsorption energy ($\Delta E$) for the $\text{C}_2\text{H}_2$ molecules in $\beta'\supseteq 2\text{C}_2\text{H}_2$ and $\beta\supseteq 2\text{C}_2\text{H}_2$. These calculations were performed using the Vienna ab initio Simulation Package (VASP)$^{22}$ with the projector augmented wave (PAW) method,$^{23}$ Perdew–Burke–Ernzerhof (PBE) functional,$^{24}$ and the DFT-D2 correction method of Grimme.$^{25}$

The unit cells for the $\beta$, evacuated $\beta'\supseteq 2\text{C}_2\text{H}_2$, and evacuated $\beta\supseteq 2\text{C}_2\text{H}_2$ structures were fully relaxed, i.e., the position of all atoms and lattice parameters were optimized. All optimizations were converged to within $10^{-6}$ eV. The resulting energies of the optimized structures were divided by the number of formula units in the unit cell such that a proper comparison of the energies between the different phases can be made. The calculated energies for all three phases are displayed in Table S6.

For calculating the $\Delta E$ for $\text{C}_2\text{H}_2$, first, the single-crystal structures of $\beta'\supseteq 2\text{C}_2\text{H}_2$ and $\beta\supseteq 2\text{C}_2\text{H}_2$ were completely optimized. Next, single-point energies were computed for the empty unit cell and $\text{C}_2\text{H}_2$ molecules, individually, based on these relaxed structures. The $\Delta E$ for all $\text{C}_2\text{H}_2$ molecules in $\beta'\supseteq 2\text{C}_2\text{H}_2$ and $\beta\supseteq 2\text{C}_2\text{H}_2$ were calculated by the following:

$$\Delta E = E(\text{MOF} + \text{C}_2\text{H}_2) - E(\text{MOF}) - E(\text{C}_2\text{H}_2)$$

where $E(\text{MOF} + \text{C}_2\text{H}_2)$ is the energy of the unit cell of the MOF with the $\text{C}_2\text{H}_2$ molecules, $E(\text{MOF})$ is the energy of the empty unit cell, and $E(\text{C}_2\text{H}_2)$ is the energy of the $\text{C}_2\text{H}_2$ molecules. In order to determine the adsorption energy per $\text{C}_2\text{H}_2$ in each structure, the calculated $\Delta E$ values were divided by the total number of $\text{C}_2\text{H}_2$ molecules in the unit cell. The calculated $\Delta E$ values per $\text{C}_2\text{H}_2$ in $\beta'\supseteq 2\text{C}_2\text{H}_2$ and $\beta\supseteq 2\text{C}_2\text{H}_2$ are listed in Table S7.

$$S_{i,j} = \frac{x_i y_j}{x_j y_i}$$
Table S6. Calculated energies per formula unit (in kJ mol\(^{-1}\)) for the optimized unit cell of the \(\beta\), evacuated \(\beta'\supseteq 2\text{C}_2\text{H}_2\), and evacuated \(\beta'\supseteq 2\text{C}_2\text{H}_2\) phases as determined through periodic DFT calculations using VASP.

| Phase                        | \(E\) (kJ mol\(^{-1}\)) |
|------------------------------|--------------------------|
| \(\beta\)                   | –37028.81                |
| Evacuated \(\beta'\supseteq 2\text{C}_2\text{H}_2\) | –37046.69                |
| Evacuated \(\beta'\supseteq 2\text{C}_2\text{H}_2\) | –37041.40                |

Table S7. Calculated adsorption energies (in kJ mol\(^{-1}\)) per \(\text{C}_2\text{H}_2\) in \(\beta'\supseteq 2\text{C}_2\text{H}_2\) and \(\beta\supseteq 2\text{C}_2\text{H}_2\) as determined from periodic DFT calculations using VASP.

| Structure        | \(\Delta E\) (kJ mol\(^{-1}\)) |
|-----------------|--------------------------------|
| \(\beta'\supseteq 2\text{C}_2\text{H}_2\) | –48.27                          |
| \(\beta\supseteq 2\text{C}_2\text{H}_2\)   | –32.88                          |
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