Supplementary Methods and Discussion

1- Ligand and MOM Synthesis:

All chemicals with the exception of 1,2-bis(4-pyridyl)acetylene (dpa) were obtained commercially and used as received without further purification. Synthesis of dpa was accomplished by minor modification of a previously reported procedure.\(^1\)

1,2-bis(4-pyridyl)acetylene, dpa

Br\(_2\) (3.5 mL, 10.8 g, 68 mmol) was added dropwise to a stirred solution of trans-1,2-bis(4-pyridyl)ethylene (3.52 g, 19.3 mmol) in HBr (48%, 46.5 mL) at 0°C. The mixture was stirred at 120°C for 2 hours and subsequently cooled to room temperature yielding an orange precipitate. After chilling in ice for 30 min. the solid was filtered, washed with water, and then stirred in aqueous NaOH (2 M, 120 mL) for 30 min. The resulting white solid, 1,2-dibromo-1,2-bis(4-pyridyl)ethane, was filtered, washed with 250 mL of water, and dried under vacuum for 24 hours (yield 5.1 g, 77%). Finely cut Na (2.2 g, 96 mmol) was stirred in t-BuOH (120 mL, dried over 4 Å molecular sieves) at 80°C under nitrogen until dissolution (20 hrs.). 1,2-dibromo-1,2-bis(4-pyridyl)ethane (4.0 g, 11.7 mmol) was added in portions and the mixture was stirred under
nitrogen at 80°C for 4 hrs. The mixture was next cooled to room temperature and EtOH was added (20 mL), followed by water (20 mL, CAUTION!). The brown solution was extracted with CHCl₃ until the extracts became colorless (ca. 4 × 70 mL) and then the CHCl₃ was evaporated to give a brown solid, which was recrystallized from toluene (overall yield 43%).

SIFSIX-2-Cu, {[Cu(dpa)₂(SiF₆)]ₙ}

**Synthesis:** Room temperature diffusion of an ethanol solution of dpa (2 mL, 0.115 mmol) into an ethylene glycol solution of CuSiF₆ (2 mL, 0.149 mmol) produced purple rod-shaped crystals of SIFSIX-2-Cu after 2 weeks in 87.4% yield (based on dpa).

SIFSIX-2-Cu-i, {[Cu(dpa)₂(SiF₆)₂•2.5CH₃OH]

**Synthesis:** Blue plate single crystals of SIFSIX-2-Cu-i were synthesized in 99.8% yield (based on dpa) by room temperature diffusion of a methanol solution of CuSiF₆ (2 mL, 0.149 mmol) into a DMSO solution of dpa (2 mL, 0.115 mmol) for 1 week. An alternative direct mixing method was used to produce powdered samples of SIFSIX-2-Cu-i. A methanol solution of dpa (4 mL, 0.270 mmol) was stirred with an aqueous solution of CuSiF₆ (4 mL, 0.258 mmol) resulting in a purple precipitate, which was then heated at 85°C for 12 hrs (83.3% yield based on dpa).

SIFSIX-3-Zn, {[Zn(pyr)₂(SiF₆)]ₙ},

SIFSIX-3-Zn was synthesized using a previously known procedure at room temperature by diffusion of a methanol solution of pyrazine (2 mL, 1.3 mmol) into a methanol solution of ZnSiF₆ (2 mL, 0.6 mmol). Crystals were harvested after 3 days.
2- Low Pressure Gas Sorption Measurements:

Crystalline samples of SIFSIX-2-Cu-i and SIFSIX-3-Zn were activated for low pressure gas sorption analysis by washing the as-synthesized material with DMF followed by solvent exchange in methanol (MeOH) for 3 days. Each of the activated samples (80 – 160 mg) were transferred to a pre-weighted 6-mm large bulb glass sample cell and evacuated at room temperature for 92 hours (SIFSIX-2-Cu-i) and 25 hours (SIFSIX-3-Zn) on an Autosorb-1C (Quantachrome Instruments) low-pressure adsorption instrument, equipped with a turbo molecular vacuum pump. The low pressure gas sorption isotherms in Figure S5 were collected on an ASAP 2020 Surface Area and Porosity Analyzer (Micromeritics) after activation of SIFSIX-2-Cu and SIFSIX-2-Cu-i as follows. As-synthesized SIFSIX-2-Cu was exchanged with 1:1 ethylene glycol/ethanol for 3 days and then ethanol for 5 days. The sample was degassed at room temperature under high vacuum (<5µm Hg) for 16 hours prior to sorption analysis. During evacuation a color change from dark purple to aqua blue was observed. SIFSIX-2-Cu-i (synthesized by direct mixing) was activated by solvent exchange in MeOH for 3 days followed by evacuation at room temperature for 16 hours, during which time a color change from light purple to light blue occurred.

The apparent surface areas of SIFSIX-2-Cu-i and SIFSIX-3-Zn were determined from the nitrogen adsorption isotherm collected at 77 K and the CO₂ adsorption isotherm collected at 298 K, respectively by applying the Brunauer-Emmett-Teller (BET) and Langmuir models. The determination of the isosteric heat of adsorption ($Q_{st}$) for CO₂ in Figure 2c (main article) was estimated by applying the Clausius-Clapeyron expression using the CO₂ sorption isotherms measured at 258, 273, 288 and 298 K for SIFSIX-2-Cu-i and 298, 308, 318, 328 and 338 K for SIFSIX-3-Zn. The bath temperature was precisely controlled using a Julabo recirculating control system containing a mixture of ethylene glycol and water. Data points below 0.76 Torr were not used for this calculation, in order to avoid possible artifacts at very low coverage. The $Q_{st}$ curves in Figure S5c were estimated by applying the virial equation to the CO₂ isotherms at 273 and 298 K (Figures S12 and S13).
3- High Pressure Single Gas and Binary Gas Sorption Procedure and Measurements:

Single Gas Sorption (gravimetric technique)

Adsorption equilibrium measurements of pure gases were performed using a Rubotherm gravimetric-densimetric apparatus (Bochum, Germany) (Scheme S1), composed mainly of a magnetic suspension balance (MSB) and a network of valves, mass flowmeters and temperature and pressure sensors. The MSB overcomes the disadvantages of other commercially available gravimetric instruments by separating the sensitive microbalance from the sample and the measuring atmosphere and is able to perform adsorption measurements across a wide pressure range, i.e. from 0 to 20 MPa. The adsorption temperature may also be controlled within the range of 77 K to 423 K. In a typical adsorption experiment, the adsorbent is precisely weighed and placed in a basket suspended by a permanent magnet through an electromagnet. The cell in which the basket is housed is then closed and vacuum or high pressure is applied.

Scheme S1. Representation of the Rubotherm gravimetric-densimetric apparatus.
The evacuated adsorbent is then exposed to a continuous gas flow (typically 50 mL/min) or static mode at a constant temperature. The gravimetric method allows the direct measurement of the reduced gas adsorbed amount $\Omega$. Correction for the buoyancy effect is required to determine the excess adsorbed amount using equation 1, where $V_{\text{adsorbent}}$ and $V_{\text{ss}}$ refer to the volume of the adsorbent and the volume of the suspension system, respectively. These volumes are determined using the helium isotherm method by assuming that helium penetrates in all open pores of the materials without being adsorbed. The density of the gas is determined experimentally using a volume-calibrated titanium cylinder. By weighing this calibrated volume in the gas atmosphere, the local density of the gas is also determined. Simultaneous measurement of adsorption capacity and gas phase density as a function of pressure and temperature is therefore possible. The excess uptake is the only experimentally accessible quantity and there is no reliable experimental method to determine the absolute uptake. For this reason, only the excess amounts are considered in this work.

$$\Omega = m_{\text{excess}} - \rho_{\text{gas}} (V_{\text{adsorbent}} + V_{\text{ss}})$$  \hspace{1cm} (1)

The pressure is measured using two Drucks high pressure transmitters ranging from 0.5 to 34 bar and 1 to 200 bar, respectively, and one low pressure transmitter ranging from 0 to 1 bar. Prior to each adsorption experiment, about 100 mg to 300 mg sample is outgassed at 433 K at a residual pressure $10^{-4}$ mbar. The temperature during adsorption measurements is held constant by using a thermostated circulating fluid.

**Mixture Gas Adsorption (gravimetric-densimetric-gas analysis technique)**

Adsorption measurements of binary gas mixtures were carried out using a Rubotherm gravimetric-densimetric technique coupled to a gas analyzer (gas chromatography (GC) or mass spectrometry (MS)) (Scheme S2) enabling accurate measurements of mixture gas adsorption in the pressure range of 0-10 bar. The gas dosing system comprise three mass flow controllers (MFC) for gas premixing. Premixed gases can be also supplied. The adsorbent sample (up to 2 g) is placed in a sample a closed holder to prevent blowing the fine powder samples during gas expansion from the dosing cell to adsorption cell, and outgassed at a maximum temperature of 298 K before the actual adsorbent mass is measured.
Scheme S2. Representation of the Rubotherm gravimetric-densimetric-gas analysis (GDGA) apparatus for mixture gas adsorption at low and high pressure.

At the beginning of an experiment, the whole installation is under vacuum, and then the premixed gas is supplied to the first dosing volume (V1) while the adsorption cell is kept isolated (V4 and V6 closed). Knowing the dosing volume, the pressure and the temperature and using an appropriate \((p-v-T)\) equation of state (EOS) the amount of gas introduced can be determined and controlled to match the amount of adsorbent available for analysis which is a critical factor influencing the accuracy of the set-up. The circulation pump is switched on to homogenize the gas mixture. The system allows checking the initial gas composition by sampling the premixed gas to the gas analysers. Once the mixture is completely homogeneous it is directed in the adsorption cell by opening valves V4 and V6 then the circulation pump is switched on. Once the adsorption equilibrium is reached, the circulation pump is switched off and the mass is monitored with the magnetic balance, the mass being recorded every 10 min. If the standard deviation is under 50 μg, the value is recorded; otherwise, the circulation pump is switched on for additional time and the control of equilibrium state is repeated. When the mass is stable, the mass, temperature and pressure are then recorded. Valve V11 is then opened and the gas phase after adsorption analyzed by GC or MS. Using an appropriate \((p-v-T)\) EOS for the studied...
mixture, in addition to the pressure, temperature and gas mixture composition after adsorption, the number of mole adsorbed of compound 1 can be calculated using equation (2):

\[
n_{1\text{ads}} = \frac{P \cdot V \cdot y'_1}{R \cdot T} + y_1 \cdot \left(\frac{m_{\text{ads}}}{M_2} - \frac{P \cdot V \cdot y'_1}{R \cdot T} - \frac{P \cdot V \cdot y'_2}{R \cdot T}\right) \cdot \frac{1}{1 + y_1 \cdot \left(\frac{M_1}{M_2} - 1\right)}^{m_{\text{sample}}}
\]

(2)

Where:

- \(n_{1\text{ads}}\): adsorbed amount of compound 1,
- \(P\): pressure in the dosing cell
- \(V\): volume of the dosing cell
- \(y'_1\): gas phase composition before adsorption
- \(y_1\): gas phase composition after adsorption of compound 1
- \(T\): temperature
- \(R\): ideal gas constant
- \(m_{\text{ads}}\): total adsorbed amount in mg
- \(M_1\): Molecular weight of compound 1
- \(M_2\): Molecular weight of compound 2
- \(m_{\text{sample}}\): mass of the evacuated sample

The number of mole adsorbed of compound 2 \(n_{2\text{ads}}\) is calculated using equation 3:

\[
n_{2\text{ads}} = \frac{m_{\text{adstot}}}{M_1 \cdot y_1 + M_2 \cdot y_2} - n_{1\text{ads}}
\]

(3)

The adsorbed phase composition of compound 1 and 2 is then calculated using equations 4 and 5:

\[
x_1 = \frac{n_{1\text{ads}}}{n_{\text{adstot}}} \quad (4); \quad x_2 = \frac{n_{2\text{ads}}}{n_{\text{adstot}}} \quad (5)
\]

The selectivity of compound 2 over 1 is then calculated using equation 6:

\[
S_{2/1} = \frac{x_2}{x_1} \cdot \frac{y'_2}{y'_1}
\]

(6)
4- Column Breakthrough Test Set-up, Procedure and Measurements:

The experimental set-up used for dynamic breakthrough measurements is shown in Scheme S3. The gas manifold consisted of three lines fitted with mass flow controllers. Line “A” is used to feed an inert gas, most commonly helium, to activate the sample before each experiment. The other two lines, “B” and “C” feed a mixture of CO₂ and other gases like N₂, CH₄, H₂. Hence, gas mixtures with concentrations representative of different industrial gases may be prepared. Whenever required, gases flowing through lines “B” and “C” may be mixed before entering a column packed with SIFSIX-2-Cu-i and SIFSIX-3-Zn using a four-way valve. The stainless steel column was 27 mm in length with 4 mm of inner (6.4 mm outer) diameter. The column downstream was monitored using a Hiden mass spectrometer. In a typical experiment, 0.1-0.4 g of adsorbent was treated at 298 K overnight under helium flow of 5 mL/min, then the gas flow was switched to the desired gas mixture at the same flow rate. The complete breakthrough of CO₂ and other species was indicated by the downstream gas composition reaching that of the feed gas. Experiments in the presence of 74% relative humidity were performed by passing the gas mixture through water vapor saturator at 20°C.

Scheme S3. Representation of the column breakthrough experiment.
The adsorption capacity for each compound was estimated from the breakthrough curves using the following equation:

\[ n_{\text{adi}} = FC_t_i \]  

(7)

where \( n_{\text{adi}} \) is the adsorption capacity of the compound \( i \), \( F \) is the total molar flow, \( C_i \) is the concentration of compound \( i \) entering the column and \( t_i \) is the time corresponding to compound \( i \), which is estimated from the breakthrough profile.

The selectivity of \( \text{CO}_2 \) over species \( i \) in the binary mixture of \( \text{CO}_2 \) and species \( i \) is determined using the following equation:

\[ S_{\text{CO}_2/i} = \frac{x_{\text{CO}_2}}{x_i} \cdot \frac{y_{\text{CO}_2}}{y_i} \]  

(8)

where \( x \) and \( y \) refer to the molar composition of the adsorbed phase and the gas phase, respectively.
5- Kinetics of Gas Adsorption:

Kinetic studies of CO\textsubscript{2}, N\textsubscript{2}, O\textsubscript{2}, H\textsubscript{2} and CH\textsubscript{4} adsorption on SIFSIX-3-Zn were carried out using the Rubotherm gravimetric apparatus operating in dynamic regime (Scheme S1). Initially, SIFSIX-3-Zn was properly evacuated at 298 K. In order to achieve an immediate constancy of pressure (0.5 bar) during the kinetics tests and avoid the often noisy uptake during the rapid introduction of the studied gas, an initial baseline was set-up using helium gas at 0.5 bar for single gases and 1 bar for mixture, then the studied single gas or mixture is flushed with a flow of 300 ml/min to avoid any dependence of the kinetics on the mass flow controller. The fractional uptake was calculated by dividing the non-equilibrium uptake at time t\textsubscript{i} by the equilibrium uptake at equilibrium. Adsorption kinetics analysis involving CO\textsubscript{2}/N\textsubscript{2}:10/90 was carried out at 5 bar to compensate for the combination of the low CO\textsubscript{2} partial pressure and the large amount of material studied (1 g).
6- X-Ray Diffraction Studies:

Powder X-Ray Diffraction (PXRD):

PXRD patterns were recorded at room temperature on a Bruker D8 ADVANCE diffractometer at 20 kV, 5 mA for Cu-Kα (λ = 1.54056 Å), with a scan speed of 1 s/step and a step size of 0.02° in 2θ (total scan duration = 30 min.).

Single-Crystal X-Ray Diffraction:

Single crystal x-ray diffraction data for SIFSIX-2-Cu were collected using a Bruker-AXS SMART-APEXII CCD diffractometer equipped with CuKα radiation (λ = 1.54178 Å). Diffraction data for SIFSIX-2-Cu-i were collected using synchrotron radiation (λ = 0.49594 Å) at the Advanced Photon Source, Chicago, IL.

Indexing was performed using APEX2² (difference vectors method). Data integration and reduction were performed using SaintPlus 6.01³. Absorption correction was performed by the multi-scan method implemented in SADABS⁴. Space groups were determined using XPREP implemented in APEX2. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F2) contained in APEX2 and WinGX v1.70.01⁵-⁸ programs packages. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using a riding model with isotropic thermal parameters: U_{iso}(H) = 1.2U_{eq}(-CH). For SIFSIX-2-Cu the contribution of heavily disordered solvent molecules was treated as diffuse using the Squeeze procedure implemented in Platon⁹,¹⁰. In the structure of SIFSIX-2-Cu-i a methanol molecule is disordered over two positions. The amount of methanol in the crystal was established through occupancy refinement of the oxygen atom. The hydrogen atom of the hydroxyl group was placed in a geometrically calculated position and refined using an H···F distance restraint. This distance was chosen based on a search of the Cambridge Structural Database¹¹. For both structures the disordered SiF₆ was refined using the SADI geometry restraint. Crystal data and refinement conditions are shown in Tables S1 and S2.
7 - Effect of moisture upon gas adsorption:

The impact of water vapor on CO₂ capacity and selectivity was evaluated in both SIFSIX-2-Cu-i and SIFSIX-3-Zn. CO₂ cyclic adsorption studies were performed at humidity levels similar to those in real applications, i.e. 74%RH. Results are summarized below:

- Water vapor adsorption isotherms for SIFSIX-2-Cu-i and SIFSIX-3-Zn collected under pure N₂ atmosphere reveal type I behavior with water uptakes of 20 wt% and 11 wt%, respectively at 74%RH.

- Water sorption affinity/capacity was reduced in the presence of CO₂ gas mixtures as revealed by breakthrough experiments at 74%RH for both CO₂/H₂:30/70 and CO₂/N₂:10/90 mixtures (1.2-1.5 wt% for SIFSIX-2-Cu-i and SIFSIX-3-Zn). Each material, particularly SIFSIX-3-Zn, exhibits remarkably selective CO₂ adsorption in the presence of water. (Figures S15a, b and S16a,b).

- Interestingly, the presence of water in the mixture (e.g. CO₂/H₂:30/70) has a negligible effect at elevated CO₂ concentrations. Breakthrough time for CO₂ in the presence of 74%RH is only marginally shorter than under dry conditions, thus CO₂ uptake and selectivity in the humid mixture are only slightly reduced (1.61 mmol/g and 191 at 74%RH vs. 1.99 mmol/g and 237 at 0%RH for SIFSIX-2-Cu-i; Figure S15b).

Analysis of the effect of adsorption/breakthrough cycling on SIFSIX-3-Zn shows very little alteration of CO₂ uptake and selectivity in CO₂/H₂:30/70 and CO₂/N₂:10/90 mixtures after multiple adsorption cycles. Additionally, the CO₂ breakthrough time was not reduced at 74%RH as compared to the breakthrough time at 0%RH (Figures S16a and S16b). This finding is extremely significant; H₂O vapor has a negligible effect on the CO₂ capture properties, in contrast to the benchmark zeolite 13X, where extensive drying of the gas stream is required to achieve optimal separations12-14.

In addition, the PXRD pattern of SIFSIX-2-Cu-i at variable degrees of relative humidity (5-95%; Figure S17) showed that the crystallinity was retained when the compound was in contact with H₂O in the presence of relevant gas mixtures. Variable temperature powder x-ray diffraction (VT-PXRD) experiments reveal thermal stability up to at least 573 K (Figure S18).
Notably, **SIFSIX-3-Zn** exhibits a phase change when exposed to relative humidity higher than 35%, as indicated by PXRD peak shifts and the appearance of additional peaks (Figure S19). Regeneration of the original material, as verified by the reappearance of the major diffraction peaks, is accomplished by heating **SIFSIX-3-Zn** under vacuum for several hours at 323-373 K. Reducing the %RH alone did not reverse the phase change (Figure S20). PXRD analyses of regenerated **SIFSIX-3-Zn** after cyclic breakthrough tests at 74%RH as well as after high pressure sorption experiments confirm the presence of the original material (Figure S21). VT-PXRD experiments demonstrate that **SIFSIX-3-Zn** maintains crystallinity up to 523 K (Figure S22).
8- SIFSIX-3-Zn Modeling Details:

Force field parameters required for modeling sorbate-MOF interactions were established, including repulsion and dispersion parameters, atomic partial point charges, and interacting atomic point polarizabilities according to considerations presented previously\textsuperscript{15-17}. Grand Canonical Monte Carlo (GCMC) simulations were performed to model CO\textsubscript{2} sorption in SIFSIX-3-Zn at experimentally-considered state points.

GCMC-generated CO\textsubscript{2} adsorption isotherms for SIFSIX-3-Zn (Figure S25) are in good agreement with experimental data. The associated molecular configurations reveal that maximum loading at the temperatures considered occurs at one CO\textsubscript{2} molecule per unit cell. Figure S26 shows the electropositive carbon atoms of CO\textsubscript{2} interacting strongly with four negatively charged framework fluorine atoms, directing the carbon atoms along the channels parallel to the SIFSIX-3-Zn pillars, consistent with steric constraints.

The simulated Q\textsubscript{st} values are in excellent agreement with experiment, showing a relatively constant Q\textsubscript{st} of ca. 45 kJ/mol for loadings of up to one CO\textsubscript{2} molecule per unit cell (Figure S27). This is consistent with saturation of the favored sorption sites.

The polarizable CO\textsubscript{2} model used in this work was developed using a previously described procedure\textsuperscript{18,19}. To verify the accuracy of the model in the bulk environment, an isothermal pressure-density plot was produced at 298.15 K using Grand canonical Monte Carlo (GCMC) methods and the results were compared to the corresponding experimental data\textsuperscript{20}. The isotherm for the model was found to be in excellent agreement with experimental data for the considered pressure range to within joint uncertainties (Figure S28).
**Supplementary Data Tables and Figures**

**Table S1. Crystal data and structure refinement for SIFSIX-2-Cu**

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<th>Property</th>
<th>Value</th>
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</thead>
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<td><strong>Identification code</strong></td>
<td>SIFSIX-2-Cu, [Cu(dpa)(_2)(SiF(_6))](_n)</td>
</tr>
<tr>
<td><strong>Empirical formula</strong></td>
<td>C(<em>{24})H(</em>{16})CuF(_6)N(_4)Si</td>
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<td><strong>Formula weight</strong></td>
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<td><strong>Crystal system, space group</strong></td>
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</tr>
<tr>
<td></td>
<td>b = 13.6316(14) Å, β = 90°</td>
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<tr>
<td></td>
<td>c = 7.9680(10) Å, γ = 90°</td>
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<td><strong>Absorption coefficient</strong></td>
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<td><strong>F(000)</strong></td>
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<td><strong>Crystal size</strong></td>
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<td><strong>Limiting indices (h, k, l)</strong></td>
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<td><strong>Reflections collected / unique</strong></td>
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<td><strong>Max. and min. transmission</strong></td>
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<td><strong>Largest diff. peak and hole</strong></td>
<td>0.654 and -0.366 e/Å(^3)</td>
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Table S2. Crystal data and structure refinement for SIFSIX-2-Cu-i

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<td>Unit cell dimensions</td>
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<td></td>
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<td>Crystal size</td>
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<td>Reflections collected / unique</td>
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<td>Largest diff. peak and hole</td>
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**Table S3.** Comparison of experimental and theoretical micropore volumes (cm³/g) of SIFSIX-2-Cu and SIFSIX-2-Cu-i.

<table>
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<th>MOM</th>
<th>( V_{\text{calc}} )^a</th>
<th>( V_{\text{exp}} )^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIFSIX-2-Cu</td>
<td>1.10</td>
<td>1.15</td>
</tr>
<tr>
<td>SIFSIX-2-Cu-i</td>
<td>0.25</td>
<td>0.26</td>
</tr>
</tbody>
</table>

^a calculated by Platon^9,10
^b experimental value determined by t-plot method

**Table S4.** Force field parameters for the polarizable CO₂ model used in the molecular simulations in this work.

<table>
<thead>
<tr>
<th>Atomic Site</th>
<th>Distance (Å)^a</th>
<th>( \sigma ) (Å)</th>
<th>( \varepsilon ) (K)</th>
<th>( q ) (e⁻)</th>
<th>( \alpha^o ) (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
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<td>3.30366</td>
<td>19.61757</td>
<td>0.77134</td>
<td>1.2281</td>
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<tr>
<td>O</td>
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<td>0.00000</td>
<td>0.00000</td>
<td>-0.38567</td>
<td>0.7395</td>
</tr>
<tr>
<td>OA^b</td>
<td>1.208</td>
<td>2.99429</td>
<td>46.47457</td>
<td>0.00000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

^a refers to the distance from the molecular centre-of-mass.
^b refers to the off-atom positions.
Figure S1. Room temperature PXRD patterns of SIFSIX-2-Cu.
Figure S2. Room temperature PXRD patterns of SIFSIX-2-Cu-i.
Figure S3. Room temperature PXRD patterns of SIFSix-3-Zn.
Figure S4. N\textsubscript{2} adsorption isotherms of SIF\textsubscript{SIX-2-Cu} (red) and SIF\textsubscript{SIX-2-Cu-i} (blue) at 77 K. Adsorption and desorption are represented by closed and open symbols, respectively.
Figure S5.  

a) Low pressure isotherms at 298 K for SIFSIX-2-Cu (red) and SIFSIX-2-Cu-i (purple).  
b) CO$_2$/N$_2$ (10/90 mixture) and CO$_2$/CH$_4$ (50/50 mixture) IAST selectivity of SIFSIX-2-Cu and SIFSIX-2-Cu-i, calculated from the low pressure isotherms at 298 K.  
c) CO$_2$ $Q_{st}$ of SIFSIX-2-Cu and SIFSIX-2-Cu-i, estimated from low pressure isotherms at 273 and 298 K by applying the virial equation.
Figure S6. Column breakthrough experiments for a) CO₂/N₂: 10/90; b) CO₂/CH₄: 50/50; and c) CO₂/H₂: 30/70 binary gas system at 298 K and 1 bar on SIFSIX-2-Cu-i.
Figure S7. Relationship between cost of CO$_2$ capture, CO$_2$ selectivity, and working CO$_2$ capacity for solid sorbents.$^{21}$
Figure S8. Low pressure, variable temperature CO$_2$ isotherms for SIFSIX-3-Zn.
Figure S9. High pressure single gas CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}, O\textsubscript{2}, and H\textsubscript{2} adsorption isotherms for (a) SIFSIX-3-Zn and (b) SIFSIX-2-Cu-i.
Figure S10. Experimental CO₂/H₂:30:70 adsorption isotherms as compared to experimental pure CO₂ and H₂ isotherms at 298 K for SIFSIX-3-Zn.
Figure S11. Fractional uptake of CO$_2$, N$_2$, O$_2$, CH$_4$ and H$_2$ on SIFIX-3-Zn at 0.5 bar and 298 K.
Figure S12. Virial fit of CO$_2$ isotherms of SIFSIX-2-Cu at 273 and 298 K (see Figure S5a and S5c).
Figure S13. Virial fit of CO₂ isotherms of SIF SIX-2-Cu-i at 273 and 298 K (see Figure S5a and S5c).
**Figure S14.** Cyclic CO$_2$ adsorption on SIFSIX-3-Zn using vacuum swing regeneration mode at 323 K and 0.15 bar.

**Figure S15(a).** Example of one cycle column breakthrough experiment for CO$_2$/N$_2$:10/90 binary gas systems at 298 K and 1 bar under dry conditions and in the presence of 74%RH carried out on SIFSIX-2-Cu-i.
**Figure S15(b).** Example of one cycle column breakthrough experiment for CO$_2$/H$_2$:30/70 binary gas systems at 298 K and 1 bar under dry conditions and in the presence of 74%RH carried out on SIFSIX-2-Cu-i.

**Figure S16(a).** Example of one cycle column breakthrough experiment for CO$_2$/N$_2$:10/90 binary gas system at 298 K and 1 bar under dry conditions and in the presence of 74%RH carried out on SIFSIX-3-Zn.
**Figure S16(b).** Example of one cycle column breakthrough experiment for CO$_2$/H$_2$:30/70 binary gas system at 298 K and 1 bar under dry conditions and in the presence of 74%RH carried out on SIFSIX-3-Zn.
**Figure S17.** PXRD patterns of SIFSiX-2-Cu-i when exposed to varying relative humidity in a nitrogen atmosphere.

**Figure S18.** VT-PXRD patterns of SIFSiX-2-Cu-i under vacuum at non-ambient temperatures (173 K - 573 K).
**Figure S19.** PXRD patterns of SIFSIX-3-Zn when exposed to varying relative humidity in a nitrogen atmosphere.

**Figure S20.** PXRD of SIFSIX-3-Zn after humidity PXRD experiment and regeneration by heating under vacuum.
Figure S21. PXRD of SIFSIX-3-Zn after multiple cycles of humid breakthrough experiments and high pressure sorption experiments compared to the calculated powder pattern.

Figure S22. VT-PXRD patterns of SIFSIX-3-Zn under vacuum and at non-ambient temperatures (173 K - 573 K).
Figure S23. CO$_2$ volumetric adsorption capacity at low pressure (0-0.25 bar) and 298 K for SIFSIX-3-Zn, Mg-dobdc (313 K), UTSA-16 and SIFSIX-2-Cu-i.

Figure S24. Water adsorption isotherm on SIFSIX-2-Cu-i and SIFSIX-3-Zn at 298 K after activation at 323 K.
Figure S25. GCMC-generated CO₂ sorption isotherms for SIFSIX-3-Zn.
Figure S26. Calculations show CO$_2$ molecules adsorbed in the pores of SIFSIX-3-Zn with the electropositive carbon atoms attracted to the SiF$_6^{2-}$ pillaring anions.
Figure S27. Simulated and experimental $Q_{st}$ plots for SIFSIX-3-Zn.
Figure S28. Pressure-density isotherm for CO$_2$ at 298.15 K for the CO$_2$ model used in this work (red) compared to experimental data (black).
References


