# Supplementary Information for

# Structural dynamics of a metal-organic framework induced by CO<sub>2</sub> migration in its non-uniform porous structure

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#### **Supplementary Methods**

#### 1. Synthesis

ZIF-7 was synthesized using a solvothermal method. 0.75 g of zinc nitrate hexahydrate  $(Zn(NO_3)_2 \cdot 6H_2O, 2.52 \text{ mmol})$  and 0.25 g of benzimidazole (HbIm,  $C_7H_6N_2$ , 2.05 mmol) were first dissolved in 75 ml of fresh dimethylformamide (DMF). The resultant solution was then sealed into a 100 ml Teflon-lined stainless steel autoclave. The autoclave was heated at 400 K for 48 h. After naturally cooling to room temperature, white platy crystals were isolated after the mother liquor was removed. The solid product was washed thoroughly with methanol. The average yield was around 0.34 g (97% based on HbIm). All chemicals employed were commercially available (Sigma-Aldrich and Acros Organics), with purity of 98% or above, and were used as received.

#### 2. Laboratory characterization

The crystal structures of ZIF-7 samples were characterized by X-ray powder diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer operated at 40 kV and 40 mA with Cu K $\alpha_1$  radiation ( $\lambda = 1.54056$  Å). The XRD data of the as-synthesized sample were compared with that calculated from the ZIF-7-I crystallographic model in the literature<sup>1</sup>. ZIF-7-I purity was around 100%. The morphology of ZIF-7 samples was examined by scanning electron microscopy using a JEOL JSM-5510 microscope. CO<sub>2</sub> adsorption isotherms were measured by a Hiden Isochema IGA gravimetric analyzer. The as-synthesized sample was activated at 400 K in air for 48 h before each measurement. Before data collection, the sample was vacuumed *in situ* (~10<sup>-4</sup> mbar) at room temperature for 3 h to remove any remaining trace guest molecules.

# 3. In situ synchrotron X-ray powder diffraction (SXRD)

In situ SXRD data were collected at beamline I11, Diamond Light Source, Harwell, UK. The energy of the incident X-ray was set at ~15 keV<sup>2</sup>. The wavelength ( $\lambda = 0.82634(1)$  Å) and the 2 $\theta$  zero point were determined by fitting the diffraction data of a high-quality silicon powder (SRM640c).

The as-synthesized sample was first activated at 400 K in air for 24 h. The activated sample was then loaded into a quartz glass capillary (0.5 mm). Glass wool was packed on top of the sample and the capillary was then fixed onto a custom-made gas cell. Before data collection, the sample cell was evacuated to  $10^{-5}$  Pa at room temperature for 3 h to remove any remaining trace guest molecules from the sample. CO<sub>2</sub> pressure was controlled by a custom-made gas loading system. After each CO<sub>2</sub> loading, 2 min was allowed before data collection for the system to reach equilibrium.

Since sample spinning was prohibited due to the position of the gas cell, the sample was rocked through  $\pm 10^{\circ}$  about the  $\omega$ -axis to improve powder averaging. SXRD data were collected with Mythen II position sensitive detectors (PSD) over the 20 range of 2–90°, with two datasets offset by 0.25° (20) collected (each for 30 s). These datasets were subsequently automatically merged to remove gaps in the data where the microstrips (X-ray detection modules) join. PSD and data treatment have been described in detail in the literature<sup>3</sup>.

#### 4. Quasi-elastic neutron scattering (QENS)

QENS data were collected using the IRIS indirect geometry time-of-flight (TOF) spectrometer at ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Harwell, UK. At IRIS, the sample first got a white beam of neutrons containing a band of energy. After scattering, the crystal analyzer (the (002) plane of pyrolithic graphite) chose a single final energy (1.84 meV) to send to detectors. Scattered neutrons were detected over an angular range of  $2\theta = 25-160^{\circ}$ . The instrumental resolution and detector efficiencies were calibrated by fitting the spectrum of a vanadium standard. The elastic energy resolution was 17.5 µeV. The energy transfer range was -0.4–0.4 meV and the *Q* range was 0.42–1.85 Å<sup>-1</sup>. IRIS was also built with long-wavelength diffraction capability. The *d* range was 1-12 Å with  $\Delta d/d = 2.5 \times 10^{-3}$ .

The as-synthesized sample was first activated at 400 K in air for 24 h. The activated sample (*ca.* 4.6 g) was then wrapped into two pieces of aluminum foil to make a sample lining fitted into the annular space of an aluminum cylinder sample cell ( $\emptyset$  24/28 mm × *h* 65.6 mm). The thickness of the sample lining was about 2 mm. Glass wool was placed in the top of the sample cell. The sample cell was then sealed with indium and connected to a custom-made gas loading system. During data collection, the temperature of the sample was controlled by a helium cryostat and thermocouples. QENS spectra were first recorded when the sample was under vacuum. At 15 and 225 K, the accumulated proton current was 600  $\mu$ A for good statistics. At 298 K, the accumulated proton current was 1146.8  $\mu$ A. CO<sub>2</sub> was then loaded into the sample cell at 298 K to enable ZIF-7 to reach a CO<sub>2</sub> uptake of 1.3 mmol·g<sup>-1</sup>. For QENS data of the loaded sample collected at 15, 225 and 298 K, the accumulated proton current was 600  $\mu$ A. Diffraction data were collected simultaneously with QENS data collection.

 $CO_2$  loading was measured using the method employed in the literature<sup>4-6</sup>. A gas handling system shown in Supplementary Fig. 3 was used for gas loading. The volume of the system without the sample cell (i.e. to the valve on top of the cell) (V1) was measured using N<sub>2</sub>. A certain amount of N<sub>2</sub> (*n*0) was loaded into the vacuumed system at room temperature so that a pressure of *p*0 was reached (shown on the barometer). According to the ideal gas law, we can obtain the value of V1:

$$p0V1 = n0RT$$

p2V2 = n2RT

Supplementary Equation 1

The volume of the system including the sample cell (V2) was also measured using the same method. ZIF-7 has almost no N<sub>2</sub> adsorption capacity at 298 K<sup>7</sup>, so V2 is the actual volume of the system. After the sample was evacuated to  $10^{-5}$  Pa at room temperature for 16 h to remove any remaining trace guest molecules, the valve on top of the sample cell was closed. CO<sub>2</sub> was then loaded into the system to reach a pressure of *p*1. The amount of CO<sub>2</sub> in the system (*n*1) can be calculated:

$$p1V1 = n1RT$$
 Supplementary Equation 2

Then the valve on top of the sample cell was open,  $CO_2$  pressure will stabilize at p2. The amount of  $CO_2$  left in the system (n2) can also be calculated:

Supplementary Equation 3

3

The amount of  $CO_2$  adsorbed (*n*) by ZIF-7 is:

$$n = n1 - n2$$
 Supplementary Equation 4

As we know the amount of sample used in each experiment (*ca.* 4.6 g), we can precisely control the CO<sub>2</sub> loading to be 1.3 mmol·g<sup>-1</sup>.

#### 5. Inelastic neutron scattering (INS)

INS data were collected using the TOSCA TOF spectrometer at ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Harwell, UK. TOSCA has a wide energy transfer range of -2.5–1000 meV (-20–8050 cm<sup>-1</sup>) and a high energy resolution of *ca*. 1.25%  $\Delta E/E$ .

The sample environment at TOSCA was similar to that at IRIS. Before data collection, the as-synthesized sample was first activated at 400 K in air for 24 h. The activated sample (ca. 4.6 g) was then wrapped into two pieces of aluminum foil to make a sample lining for a stainless steel cylinder sample cell ( $\emptyset$  16 mm  $\times$  h 76 mm). Glass wool was placed in the top of the sample cell to prevent any sample spillage during the experiment. The sample cell was then sealed with a copper O-ring and connected to a custom-made gas loading system. The sample chamber was evacuated to  $10^{-5}$  Pa at room temperature for 16 h to remove any remaining trace guest molecules from the sample. During data collection, the temperature of the sample was controlled by a closed cycle refrigerator (CCR) and was kept below 10 K to minimize the thermal motion of CO<sub>2</sub> molecules and the host framework which influences the accuracy of the measurement. Namely, at higher temperatures the increase in Debye-Waller factor causes broadening of the spectral peaks, i.e. decrease in peak intensity or spectral resolution. INS spectra were first recorded when the sample was under vacuum. The accumulated proton current was 3604 µA for good statistics. CO<sub>2</sub> was then loaded into the sample cell at 298 K to enable ZIF-7 to reach a CO<sub>2</sub> uptake of 1.3 mmol $\cdot$ g<sup>-1</sup>. CO<sub>2</sub> loading was measured using the same method as that in the QENS experiment. During data collection of the loaded sample, the accumulated proton current was 3558.6 µA.

#### 6. Density functional theory (DFT) calculation

Models for the DFT calculations were built based on the crystal structures from the literature<sup>8,9</sup>. One ZIF-7 unit cell was used with a chemical formula of  $Zn_{18}C_{252}N_{72}H_{180}$ . Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA)<sup>10</sup> implemented in the VASP package<sup>11</sup> was used. The projector augmented wave (PAW)<sup>12</sup> pseudopotential method was employed. Due to the large unit cell of ZIF-7, only Gamma point was sampled. The cutoff energy was 400 eV. The shape of the unit cell and atomic positions were allowed fully relaxed during the optimization. The energy convergence for the self-consistent electronic relaxation was set to be  $10^{-6}$  eV and the force convergence was set to be 0.01 eV·Å<sup>-1</sup>. To count in the weak dispersive interaction, van der Waals interactions (as implemented in the DFT-D2 scheme<sup>13,14</sup>) were considered during the calculations. We included a typical input file of our DFT calculations as a supporting file (Supplementary Data 1). Details of the calculation can be found in this file.

#### 7. Grand canonical Monte Carlo (GCMC) molecular simulations

CO<sub>2</sub> adsorption isotherms in ZIF-7 were investigated using grand canonical Monte Carlo (GCMC) simulations performed in the multi-purpose code RASPA<sup>15</sup>. ZIF-7-I and ZIF-7-II models were built based on the crystal structures from the literature<sup>8,9</sup>. Framework atoms were kept fixed at the crystallographic positions. In order to correctly describe the absence of CO<sub>2</sub> molecules in pores A before the ZIF-7-II to ZIF-7-I phase transition, pores A were all blocked in ZIF-7-II during the simulation. We used the standard Lennard-Jones (LJ) 12-6 potential to model the interactions between the framework and fluid atoms. In addition, a Coulomb potential was used for fluid-fluid interactions. The parameters for framework atoms were derived from the Universal Force Field<sup>16</sup> and those previously developed for ZIF-8<sup>17</sup>. CO<sub>2</sub> molecules were modeled using the TraPPE potential with charges placed on each atom and at the center of mass (Supplementary Table 5)<sup>18</sup>. EQeq was used to assign the partial charges of the framework. The Lorentz-Berthelot mixing rules were employed to calculate fluid-solid LJ parameters, and LJ interactions beyond 12.8 Å were neglected. The Ewald summations method was used to compute the electrostatic interactions. Up to 50,000 Monte Carlo cycles were performed, the first 50% of which were used for equilibration, and the remaining steps were used to calculate the ensemble averages. Monte Carlo moves consisted of insertions, deletions, displacements, and rotations. In a cycle, N Monte Carlo moves are attempted, where N is defined as the maximum of 20 or the number of adsorbates in the system. To calculate the gas-phase fugacity we used the Peng-Robinson equation of state<sup>19</sup>. The isosteric heat of adsorption ( $Q_{st}$ ) was calculates using the fluctuation theory<sup>20</sup>. Input files are included in Supplementary Data 2.

#### **Supplementary Discussion**

#### 1. QENS data analysis

TOF data were converted to energy transfer using the Mantid software<sup>21</sup>. In each measurement, 50 QENS spectra were recorded over the energy transfer range (-0.4–0.4 meV, 0.42–1.85 Å<sup>-1</sup> in *Q*). To fit each QENS spectrum, a delta function and a Lorentzian function were used to describe the elastic and coherent quasi-elastic scattering from the sample, respectively (Supplementary Fig. 4). They were convolved by the scattering function of the vanadium standard, which is close to a Lorentzian function. The baseline was regarded as a straight line. Sequential fitting was conducted. The QENS spectrum collected at Q = 0.44 Å<sup>-1</sup> was first manually fitted. The starting functions used for fitting each following spectrum at Q = 0.48-1.85 Å<sup>-1</sup> were the calculated results from the previous spectrum in the sequence.

No coherent quasi-elastic scattering signal can be found in the QENS spectra of ZIF-7 under vacuum. This indicates that the dynamics of ZIF-7 do not contribute to the QENS spectra of CO<sub>2</sub>-loaded ZIF-7, regardless of the ZIF-7-II to ZIF-7-I phase transition observed by simultaneous neutron powder diffraction. No coherent quasi-elastic scattering signal can be found in the QENS spectra of CO<sub>2</sub>-loaded ZIF-7 at 15 K. This suggests that CO<sub>2</sub> was frozen in ZIF-7 at 15 K.

Thus the coherent quasi-elastic scattering signal in the QENS spectra of CO<sub>2</sub>-loaded ZIF-7 at 225 and 298 K predominantly reflects the collective motion of CO<sub>2</sub> molecules in ZIF-7 at these temperatures. The contribution from the vibrational and rotational motions of CO<sub>2</sub> molecules is negligible: the vibrational motion only affects the measured intensity through a Debye-Waller factor; for a linear and symmetrical molecule like CO<sub>2</sub>, the influence of the rotational motion is very small in the QENS domain<sup>22</sup>. We can say that the coherent quasi-elastic scattering signal in the QENS spectra of CO<sub>2</sub>-loaded ZIF-7 at 225 and 298 K predominantly reflects the collective translational motion of CO<sub>2</sub> molecules, i.e. CO<sub>2</sub> transport diffusion at these temperatures.

Over a small Q range (i.e. large length scales), assuming CO<sub>2</sub> transport diffusion is isotropic, the coherent quasi-elastic scattering function has the form<sup>22</sup>:

$$S_{Coh}(Q,\omega) = \frac{S(Q)}{\pi} \times \frac{D(Q)Q^2}{\omega^2 + (D(Q)Q^2)^2} = S(Q)L$$
 Supplementary Equation 5

where D(Q) is CO<sub>2</sub> transport diffusion coefficient and *L* corresponds to a Lorentzian function. The half-width at half-maximum (HWHM) of *L* is the product of D(Q) and  $Q^2$ :

$$HWHM = D(Q)Q^2$$
 Supplementary Equation 6

where HWHM is in s<sup>-1</sup>, Q is in m<sup>-1</sup> and  $D_t$  is in m<sup>2</sup>·s<sup>-1</sup>. At larger Q values (*i.e.* over smaller length scales), the relationship between HWHM and  $Q^2$  is no longer linear due to CO<sub>2</sub> elementary jumps between adsorption sites (Supplementary Fig. 5). Since we are simply interested in CO<sub>2</sub> long-range diffusion (i.e. small Q range), the calculation of D(Q) can be based on Supplementary Equation 6. Fitting the QENS spectra of CO<sub>2</sub>-loaded ZIF-7 at 225 and 298 K allows the calculation of D(Q) over the whole Q range. By fitting D(Q) with a polynomial function, D(0), i.e. macroscopic CO<sub>2</sub> transport diffusivity  $D_t$ , can be determined<sup>22</sup>. CO<sub>2</sub> transport diffusivity in zeolites usually ranges from  $10^{-10}$  to  $10^{-8}$  m<sup>2</sup>·s<sup>-1</sup> <sup>23,24</sup>. CO<sub>2</sub> transport diffusivities in ZIF-7 at 225 and 298 K (6.3(7) ×  $10^{-9}$  m<sup>2</sup>·s<sup>-1</sup> and 4(2) ×  $10^{-11}$  m<sup>2</sup>·s<sup>-1</sup>, respectively) are comparable with those in zeolites.

While transport diffusion reflects the collective motion of  $CO_2$  molecules caused by local concentration gradients, self-diffusion often describes the displacement of individual  $CO_2$  molecules, i.e. elementary jumps between adsorption sites. In zeolites,  $D_t$  has a close relationship with self-diffusivity  $D_s^{22}$ :

$$D_t = D_s(\frac{\partial \ln p}{\partial \ln c})$$
 Supplementary Equation 7

where  $\partial \ln p / \partial \ln c$  is the thermodynamic correction factor and can be calculated directly from the CO<sub>2</sub> adsorption isotherm. *p* is CO<sub>2</sub> pressure in kPa and *c* is CO<sub>2</sub> uptake at *p* in mmol·g<sup>-1</sup>. Considering the similarity between zeolites and ZIFs (zeolitic imidazolate frameworks), CO<sub>2</sub> self-diffusivities in ZIF-7 at 225 and 298 K can be calculated based on Supplementary Equation 7. At CO<sub>2</sub> loading = 1.3 mmol·g<sup>-1</sup> and *T* = 195 K,  $\partial \ln p / \partial \ln c = 2.6$  from Fig. 1a. Assuming  $\partial \ln p / \partial \ln c$  is still 2.6 at 225 K, considering  $D_t = 4(2) \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ ,  $D_s = 1.5(8) \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ . At CO<sub>2</sub> loading = 1.3 mmol·g<sup>-1</sup> and *T* = 298 K,  $\partial \ln p / \partial \ln c = 33.3$  from Fig. 1a and  $D_t = 6.3(7) \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ , thus  $D_s = 1.9(2) \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ .

# 2. INS data analysis

The INS spectrum of ZIF-7 at a CO<sub>2</sub> loading of 1.3 mmol·g<sup>-1</sup> was compared with that of ZIF-7 without CO<sub>2</sub> loaded (ZIF-7-II) (Supplementary Fig. 7A). Peaks were assigned based on previous works<sup>25-27</sup> (Supplementary Table 4). In the ZIF-7-II spectrum, a doublet at 230–245 cm<sup>-1</sup> represents the out-of-plane bending motion of bIm linkers at the bridge of the imidazole ring (Im) and the benzene ring (Bz) (Supplementary Fig. 7B). The ratio between peak areas at 242 cm<sup>-1</sup> and 234 cm<sup>-1</sup> is 1:2.3. As shown in Fig. 1d, linkers in ZIF-7-II are distributed in two types of pore B. The ratio between the number of type I and II pore B is 1:2, thus the INS peak at 242 cm<sup>-1</sup> corresponds to the out-of-plane bending motion of the linkers in type I pore B. After CO<sub>2</sub> loading, the 242 cm<sup>-1</sup> peak merges into the 234 cm<sup>-1</sup> peak, this peak shift matches well with what is expected when 0.5 CO<sub>2</sub> molecule is adsorbed per linker in type I pore B, as predicted by neutron powder diffraction results<sup>9</sup>. According to Hooke's Law,

$$\varpi \propto \sqrt{\frac{k}{m}}$$

Supplementary Equation 8

where  $\omega$  is wavenumber, k is the elastic constant, m is mass. Thus,

$$\frac{\overline{\omega}_0}{\overline{\omega}_{\rm f}} = \sqrt{\frac{m_0 + N\Delta m}{m_0}}$$

Supplementary Equation 9

where  $\omega_0$  is the wavenumber when the linker is without CO<sub>2</sub> adsorbed,  $\omega_f$  is the wavenumber when the linker is adsorbed with CO<sub>2</sub>,  $m_0$  is the mass of one bIm linker,  $\Delta m$  is mass of one CO<sub>2</sub> molecule, N is the number of CO<sub>2</sub> molecules adsorbed per linker. When N = 0.5,  $\omega_0 = 242$  cm<sup>-1</sup> and  $\omega_f = 234$  cm<sup>-1</sup>,

$$\sqrt{\frac{m_0 + N\Delta m}{m_0}} = 1.08 \approx \frac{\varpi_0}{\varpi_{\rm f}}$$

Supplementary Equation 10

Thus we can conclude that the linkers of type I pore B are mainly responsible for the initial  $CO_2$  adsorption, rather than those of type II pore B.

A higher-frequency peak occurs after  $CO_2$  loading in the energy ranges corresponding to Im torsion (644 cm<sup>-1</sup>) and the out-of-plane bending motion of Im C–H (843 cm<sup>-1</sup>) (Supplementary Fig. 7D). The occurrence of higher-frequency peaks could be due to the formation of hydrogen bonds between  $CO_2$  and Im C–H. The ratio between peak areas at two frequencies is approximately 1:1. This is because only half of the linkers can adsorb  $CO_2$  on its Im (Supplementary Fig. 7E).

Admittedly, ZIF-7-II to ZIF-7-I phase transition can also induce peak shift and affect that induced by  $CO_2$  adsorption. For the torsion motion of Bz (415–435 cm<sup>-1</sup>, Supplementary Fig. 7C), the ratio between peak areas at 419 cm<sup>-1</sup> and 429 cm<sup>-1</sup> is 1:1.6. Bz in type I pore B is more relaxed since they are further away from each other when compared with those in type II pore B. After  $CO_2$  loading, two peaks merge into one, indicating type I and II pore B became one structure (Fig. 1d). The narrowing of 898 cm<sup>-1</sup> peak (the out-of-plane bending motion of Bz C–H) is also due to the same reason.



**Supplementary Figure 1** Pore size distribution of ZIF-7-I, ZIF-7-II, and ZIF-8, measured by CrystalMaker 10.3 software using their crystal structures<sup>1,8</sup>. The probe radius was 1.55 Å, the same as the van der Waals radius of a N<sub>2</sub> molecule. SOD: sodalite cage, 4M: four-memberring pore. Values of pore sizes are listed in Supplementary Table 1.

From the analysis results, it is clear that there is only one type of pores in ZIF-8 (7.1 Å), which corresponds to the sodalite cage of ZIF-8. This indicates that ZIF-8 has a uniform porous structure. In ZIF-7-I, four types of pores with distinct radius were found: pore A (4.0 Å), sodalite cage (3.8 Å), pore B (3.2 Å), and four-member-ring pore (2.4 Å). The pore distribution in ZIF-7-II is very different from that in ZIF-7-I. During ZIF-7-II to ZIF-7-I phase transition, the radius of pore B decrease from 3.5 - 4.7 Å to 3.2 Å, whereas the radii of pore A and sodalite cage increase from 2.3 - 2.5 Å and 2.8 - 3.1 Å to 4.0 Å and 3.8 Å, respectively. The radius of four-member-ring pore remains unchanged (2.5 - 2.9 Å to 2.4 Å).

As ZIF-7-II to ZIF-7-I phase transition is induced by  $CO_2$  adsorption, it can be said that with the filling of  $CO_2$ , pore B decreases in size whereas pore A increases in size. This strengthens our proposed mechanism on the sequential  $CO_2$  filling of pore B (first) and pore A (last). The filling of pore A with  $CO_2$  requires pore deformation which is induced by the interaction between  $CO_2$  and pore B.



**Supplementary Figure 2** The crystal structures of ZIF-7-I and ZIF-7-II. One pore A is shown. The other part of the framework is simplified by replacing Zn–bIm–Zn with Zn–Zn (Zn: grey).



Supplementary Figure 3 A sketch of the setup of QENS and INS experiments.



**Supplementary Figure 4** A fitted QENS spectrum of CO<sub>2</sub>-adsorbed ZIF-7. CO<sub>2</sub> loading = 1.3 mmol·g<sup>-1</sup>, T = 298 K, Q = 0.44 Å<sup>-1</sup>. The contribution from elastic and quasi-elastic scattering is illustrated in the enlarged figure on the right side.



**Supplementary Figure 5** The  $Q^2$  dependence of the HWHM of the Lorentzian component of each QENS spectrum at 225 and 298 K. The non-linear dependence suggests non-Fickian diffusion.



**Supplementary Figure 6** The building unit, sodalite cage, of ZIF-8 (A) and ZIF-7 (B). The six-member-ring of ZIF-8 resembles the geometry of pore A in the ZIF-7. Its window size (diameter 3.4 - 4.1 Å) is similar to that of pore A (3 Å).



**Supplementary Figure 7** (A) INS spectra of ZIF-7-II and CO<sub>2</sub>-adsorbed ZIF-7. Difference between ZIF-7 (CO<sub>2</sub>) and ZIF-7-II spectra is shown at the bottom of the figure: ZIF-7 (CO<sub>2</sub>) spectrum subtracted by ZIF-7-II spectrum. v: stretching;  $\delta$ : bending ( $\delta$ 1: in-plane,  $\delta$ 2: out-of-plane);  $\tau$ : torsion. Bz: benzene ring; Im: imidazole ring. The inset shows the atom nomenclature used for linker; H is omitted for clarity.1 meV  $\equiv$  8.05 cm<sup>-1</sup>. (**B**–**D**) Detailed INS spectra with peak(s) fitted. ZIF-7-II: black dots, CO<sub>2</sub>-adsorbed ZIF-7: blue dots. (**E**) The asymmetric unit of CO<sub>2</sub>-adsorbed ZIF-7 crystal structure. Linker: N, blue; C, green; H/D, pink. C of CO<sub>2</sub> in pore A: yellow, C of CO<sub>2</sub> in pore B: purple, O: red. The linker not interacting with CO<sub>2</sub> is shown in grey.



**Supplementary Figure 8** Models used in DFT calculations.  $CO_2$  is adsorbed (A) in pore B or (B) in the channel between pores A and B before the ZIF-7-II to ZIF-7-I phase transition.  $CO_2$  is adsorbed (C) in pore A or (D) in both A and B pores after phase transition.



**Supplementary Figure 9** (**A**) The XRD data of an as-synthesized ZIF-7 sample, compared with the simulated data using the ZIF-7-I crystal structure from the literature<sup>1</sup>. (**B**) The XRD data of ZIF-7-I and ZIF-7-II.



**Supplementary Figure 10** The SEM images of an as-synthesized ZIF-7 sample, showing rhombohedral morphology, in line with the crystal system of ZIF-7-I phase (*R*-3). The crystal size is estimated to be around  $17 \mu m$ .



**Supplementary Figure 11** The SEM image of an activated ZIF-7 sample, showing triclinic morphology, in line with the crystal system of ZIF-7-II phase (*P*-1). The crystal size is estimated to be around 7  $\mu$ m. The crystal size refers to the long edge length of the crystals.

The adsorption behaviors of flexible MOFs are recently found to strongly depend on their crystal sizes. For DUT-49 and ZIF-8 mentioned in the main text, it has been demonstrated that the adsorption-induced flexibility of samples with nanometer-scaled crystal sizes is suppressed or the transition pressure is significantly higher than that for those with micrometer-scaled crystal sizes<sup>28-31</sup>. Our activated ZIF-7 sample contains micrometer-scaled crystals, which allows it well exhibiting adsorption-induced flexibility under our experimental conditions. The crystal sizes of all activated samples analyzed by various techniques in this manuscript are the same, so the crystal size effect is not discussed in the main text.

**Supplementary Table 1** Pore size distribution of ZIF-7-I, ZIF-7-II, and ZIF-8, measured by CrystalMaker 10.3 software using their crystal structures<sup>1,8</sup>. The probe radius was 1.55 Å, the same as the van der Waals radius of a  $N_2$  molecule. SOD: sodalite cage, 4M: four-memberring pore.

Pore center	Identity	Radius [Å]	Volume [Å <sup>3</sup> ]
(0, 0, 0)	Pore A	3.99	266
(0.33, 0.67, 0.16)	SOD	3.76	223
(0.51, 0.49, 0.06)	Pore B	3.22	140
(0.66, 0.84, 0.85)	4M	2.42	60

# ZIF-7-I

# ZIF-7-II

Pore center	Identity	Radius [Å]	Volume [Å <sup>3</sup> ]
(0.98, 0.02, 0.50)	Pore B	4.70	436
(0.57, 0, 0.45)	Pore B	4.20	309
(0.34, 0.66, 0.20)	Pore B	3.98	264
(0, 0.52, 0.52)	Pore B	3.84	237
(0.70, 0.89, 0.87)	Pore B	3.70	212
(0.81, 0.67, 0.22)	Pore B	3.53	184
(0.53, 0.45, 0.19)	SOD	3.07	121
(0.02, 0.98, 0)	4M	2.85	97
(0.11, 0.79, 0.16)	SOD	2.77	89
(-0.02, 0.48, 0.97)	4M	2.61	74
(0.79, 0.65, 0.73)	4M	2.55	69
(0.32, 0.67, 0.63)	4M	2.52	67
(0.60, 0.62, 0.53)	Pore A	2.50	66
(0.23, 0.83, 0.91)	Pore A	2.33	53
(0.96, 0.26, 0.22)	Pore A	2.28	50
(0.51, 0, 0)	4M	2.24	47
(0.38, 0.24, 0.78)	4M	2.02	34
(0.19, 0.79, 0.59)	SOD	1.94	31

# ZIF-8

Pore center	Identity	Radius [Å]	Volume [Å <sup>3</sup> ]
(0, 0, 0)	SOD	7.11	1503

**Supplementary Table 2** The relationship between pressure and CO<sub>2</sub> uptake by ZIF-7 at 195 and 298 K.

 $CO_2$  uptake (*X*, mmol·g<sup>-1</sup>) is given by

$$X = \frac{m - m_0}{44 \times m_0} \times 10^3$$

Supplementary Equation 11

where  $m_0$  is the sample weight measured under vacuum, m is the sample weight measured under CO<sub>2</sub>.

	p (kPa)	$CO_2$ uptake (mmol·g <sup>-1</sup> )	p (kPa)	$CO_2$ uptake (mmol·g <sup>-1</sup> )
-	0.0482	0.02237	31.283	4.19432
	1.0821	0.91892	32.7522	4.20277
	2.32	1.53877	34.2622	4.21099
	3.5444	1.94028	34.956	4.21516
	4.7824	2.19601	36.3028	4.22204
	5.9523	2.34844	37.8129	4.23003
	7.2447	2.47641	39.3093	4.23607
	8.4418	2.56530	42.3702	4.24698
	9.6662	2.63876	44.9958	4.25525
	11.8156	2.71995	47.4173	4.26260
	13.3121	2.78200	49.8932	4.27108
	14.8085	2.85341	54.9267	4.28506
	16.305	2.93317	59.9602	4.29735
	17.815	3.07060	65.0073	4.30815
	19.3795	3.31271	69.8639	4.31822
	20.7943	3.52878	74.9518	4.32843
	22.2907	3.79742	79.9581	4.33817
	23.7736	4.06606	84.9916	4.34836
	25.2836	4.14341	89.8754	4.35759
	26.78	4.16542	94.9361	4.36728
	28.2765	4.17736	104.3637	4.38161
	29.7865	4.18617	100.3505	4.37568

T = 195 K

T =	298	K
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p (kPa)	$CO_2$ uptake (mmol·g <sup>-1</sup> )	p (kPa)	$CO_2$ uptake (mmol·g <sup>-1</sup> )
-0.0607	0.00344	51.2536	0.77531
1.0549	0.01169	52.478	0.88821
2.2792	0.01870	53.7024	1.02912
3.5036	0.02510	54.9403	1.14016
4.7416	0.03096	56.1783	1.19315
5.9795	0.03666	57.3891	1.24289
7.1631	0.04221	58.5998	1.29106
8.401	0.04775	59.8106	1.32397
9.6254	0.05309	61.0485	1.35679
10.8498	0.05834	62.2865	1.37792
12.0741	0.06359	63.4972	1.40373
13.2985	0.06841	64.7352	1.42569
14.5228	0.07348	65.946	1.44353
15.7472	0.07856	67.1703	1.46212
16.9852	0.08384	68.4083	1.47728
18.2095	0.08891	69.6055	1.49410
19.4203	0.09410	70.857	1.50690
20.631	0.09937	72.0678	1.51815
21.869	0.10459	73.2785	1.53037
23.107	0.11030	74.5165	1.53964
24.3177	0.11590	75.7409	1.54739
25.5285	0.12122	76.9788	1.55363
26.7664	0.12528	78.1896	1.55984
27.9908	0.12863	79.4003	1.56596
29.2016	0.13360	80.6247	1.57170
30.4395	0.13947	81.8763	1.57658
31.6639	0.14648	83.0734	1.58113
32.8746	0.15354	84.3114	1.58628
34.1262	0.16123	85.5357	1.59037
35.337	0.16947	86.7601	1.59417
36.5477	0.17871	87.9845	1.59765
37.7993	0.18736	89.168	1.60141
39.01	0.19563	90.4468	1.60509
40.2208	0.20643	91.6439	1.60874
41.4588	0.22072	92.9091	1.61222
42.6831	0.23830	94.0927	1.61535
43.9075	0.26401	95.3306	1.61888
45.1454	0.29539	96.5414	1.62187
46.3562	0.33953	97.7929	1.62537
4/.5534	0.40062	99.0445	1.62816
48.8049	0.49391	100.2281	1.03110
50.0429	0.00723	101.4324	1.03329

	ZIF-7-I	ZIF-7-II
Formula	Zn(bIm) <sub>2</sub>	Zn <sub>9</sub> (bIm) <sub>18</sub>
Crystal system	Rhombohedral	Triclinic
Space group	<i>R</i> -3	<i>P</i> -1
<i>a</i> [Å]	22.989(3)	23.948(6)
<i>b</i> [Å]	22.989(3)	21.354(6)
<i>c</i> [Å]	15.763(3)	16.349(4)
α [deg]	90	90.28(2)
β[deg]	90	93.28(2)
γ [deg]	120	108.41(1)
V [Å <sup>3</sup> ]	7214(2)	7917(3)

Supplementary Table 3 Crystallographic information of ZIF-7-I and ZIF-7-II<sup>8</sup>.

Wavenumber (cm <sup>-1</sup> )	Band assignment
50-150	Zn ring deformation; linker rotation
150–215	δ N–Zn–N; v Zn–N
230–245 (doublet)	δ2 linker at C2–C6
270–290	v Zn–N
290–330	τ linker
415–435 (doublet)	τ Bz (raised by C3–H & C7–H wagging)
460–464	δ Zn–N–C2/6
471	δ N–C2/6–C
550	τ Bz & Im
583	δ2 Bz C4–H & C5–H (wagging)
644	τ Im
744–747	δ2 Bz C–H
771	δ1 Bz & Im
844-847	δ2 Im C1–H
895–900	δ2 Bz C3–H, C4–H & C7–H
1003–1006	δ1 Bz C–H

Supplementary Table 4 Band assignment of ZIF-7-II INS spectra.

<sup>1</sup> ν: stretching; δ: bending ( $\delta$ 1: in-plane,  $\delta$ 2: out-of-plane); τ: torsion.

 $^{2}$  Bz: benzene ring; Im: imidazole ring. Below shows the atom nomenclature used for the linker, H is omitted for clarity.



**Supplementary Table 5** Force field parameters for UFF+, derived from the Universal Force Field, and used to model the framework atoms of ZIF-7-I and ZIF-7-II<sup>16,17</sup>. TraPPE parameters used to model CO<sub>2</sub><sup>18</sup>.

UFF+

	σ (Å)	ε (K)
С	3.431	31.270
Ν	3.261	20.549
Н	2.571	13.103
Zn	2.462	36.928

# TraPPE

	σ(A)	$\epsilon(K)$
O <sub>CO2</sub>	3.05	79.0
C <sub>CO2</sub>	2.80	27.0

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