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Supplementary Information

Direct visualisation of carbon dioxide adsorption in gate-opening zeolitic imidazolate framework ZIF-7

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1. Synthesis and characterisation of deuterated ZIF-7 (D-ZIF-7) sample

Synthesis: All chemicals employed were commercially available (Sigma-Aldrich, Acros Organics and Qmx Laboratories), with purity of 98 % or above, and were used as received. D-ZIF-7 sample was prepared following the procedure given by Gücüyener et al., 2010[1]: zinc nitrate hexahydrate ($Zn(NO_3)_2 \bullet 6H_2O$, 0.75 g, 2.52 mmol) and benzimidazole-4,5,6,7-d_4 (PhIm-d_4, 0.25 g, 2.05 mmol, Qmx Laboratories) were first dissolved in fresh dimethylformamide (DMF, 75 ml). The resultant solution was then filtered and sealed into a 100 ml teflon-lined Parr Bomb. A small amount of previously-synthesised hydrogenated ZIF-7 sample was added into the reaction solution as crystal seed, before the Parr Bomb was heated at 373 K for 48 hours. After naturally cooling to room temperature, white powdery crystals were isolated after the mother liquor was removed. The best yield was 0.14 g, 40.00 % based on PhIm-d_4. The product was then exchanged with methanol (for 24 hours at room temperature) and deuterium oxide (for 48 hours at room temperature); deuterated ZIF-7 (D-ZIF-7) sample was finally obtained after being dried under vacuum and back filled with nitrogen.

Characterisation: The D-ZIF-7 crystal structure was confirmed by ambient temperature X-ray powder diffraction using a flat glass plate sample holder on a laboratory PANalytical X'Pert Pro diffractome-

ter equipped with an X'Celerator RTMS detector and Ni-filtered CuKα radiation (λ=1.5418 Å). The generator was operated at 40 kV and 40 mA. Diffraction data were collected at room temperature in the range of 5-40° (2θ), in θ:2θ mode and step-scan with Δ2θ=0.02°, for 0.3 seconds per step.

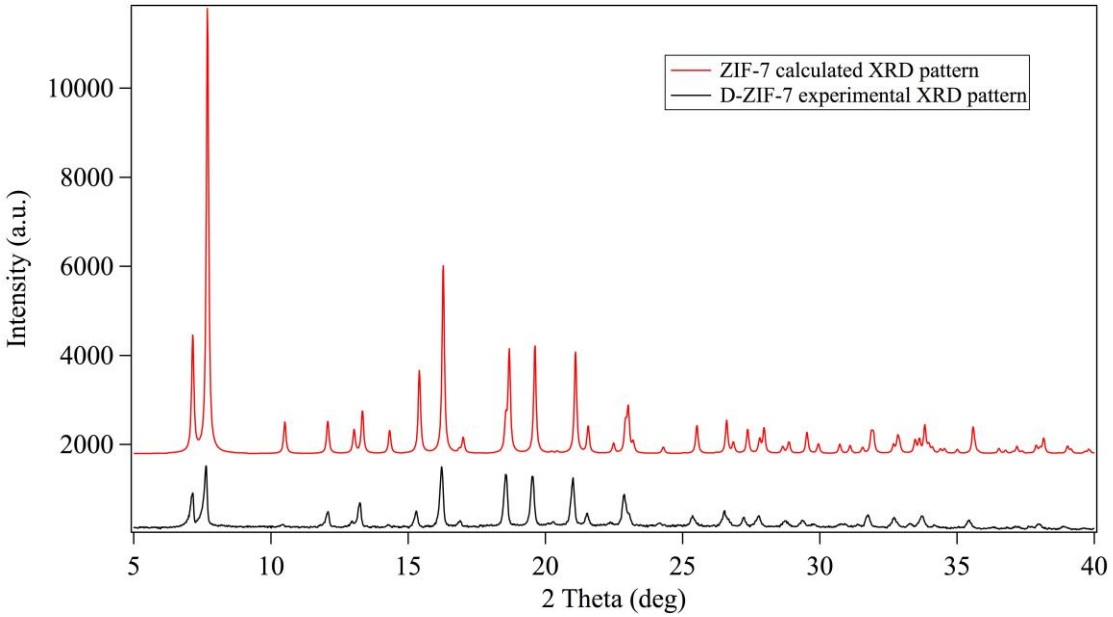

Figure SI 1. The calculated and experimental X-ray diffraction profiles of as-synthesised D-ZIF-7.

2. Neutron powder diffraction

Neutron powder diffraction measurements were carried out on 0.14 g D-ZIF-7 sample using high-resolution neutron powder diffractometer D2B with gas injection system in the Institut Laue-Langevin. The 2D multi-detector of D2B is with a detection width of 147.5° (2θ) and a maximum detection range of 160° (2θ), the width of the detector window is 1.25°. Before the experiment, D-ZIF-7 sample was gently ground in an agate mortar and deposited into an annular aluminum sample holder with silicon wool on top; the sample holder was then fitted into the gas injection system in the beamline. Before data collection, the sample chamber was first equilibrated to 300 K for 6 hours under vacuum. The temperature was then raised to 393 K for 2 hours at a speed of 1 K min^{-1}, in order to get rid of all guest solvent molecules in the D-ZIF-7 structure. After the sample chamber was cooled to 300 K at a speed of 1K min^{-1}, the neutron diffraction data of bare D-ZIF-7 sample were collected in the range of 0-160° (2θ) with Δ2θ=0.05° for 12 hours; the incident beam wavelength λ=1.5946 Å. CO_2 was then

loaded into the sample chamber to reach the pressures of 50, 100 and 200 kPa after 30 minutes equilibration. The neutron diffraction data of D-ZIF-7 sample under each CO_2 pressure were collected for 12 hours respectively with the incident beam wavelength λ=1.5946 Å. The CO_2 pressure was reduced to 100 kPa afterwards and the neutron diffraction data of D-ZIF-7 sample were collected for 12 hours with the incident beam wavelength λ=2.3909 Å. Diffraction data collected in the center area of the 2D detector were integrated to generate high-resolution diffraction pattern. The neutron diffraction data of the aluminum sample holder was collected at 300 K after the removal of D-ZIF-7 sample, in order to exclude the strong aluminum peaks in the neutron diffraction patterns of D-ZIF-7.

3. The Rietveld refinement of the crystal structure of guest-free D-ZIF-7

The crystal structure of guest-free D-ZIF-7 was determined by applying Rietveld refinement[2, 3] on the neutron diffraction data of the bare sample using Topas 4.1,[4] in the 2θ range of 6-100° and with the crystallographic data of hydrogenated ZIF-7 given by Yaghi *et al.* as the starting model.[5] The background was described by an 8-term shifted Chebyschev function after being manually reduced in order to minimize its influence on the refinement. The diffraction peaks of aluminum sample holder were excluded from the refinement. Peak shape was modeled with a pseudo-Voigt function (TCHZ type). Spherical harmonics were used for preferred orientation correction. Benzimidazole-4,5,6,7-d_4 ligands were treated as rigid bodies using Cartesian coordinates to reduce the number of variables. Dummy atoms were added to define the origins of rigid bodies. Distance and angle restraints were set between zinc and the coordinating nitrogen atoms with reasonable weight factors. One single isotropic thermal factor was set for each element.

Rietveld refinement trial based on the hydrogenated ZIF-7 model given by Huang *et al.*[6] was also performed. The background was described by a 10-term shifted Chebyschev function after being reduced. Peak shape was modeled with a pseudo-Voigt function described by CS_G parameter for purely Gaussian-type crystallite size broadening. Spherical harmonics were used for preferred orientation correction. Benzimidazole-4,5,6,7-d_4 ligands were treated as rigid bodies using Z-matrix. Dummy atoms in special positions with respect to the symmetric elements were added for rigid body definition. Distance and angle restraints were set between zinc and the coordinating nitrogen atoms with reasona-

ble weight factors. One single isotropic thermal factor was set for each element. The resulting structure is similar with the D-ZIF-7 structure obtained from the Rietveld refinement based on the hydrogenated ZIF-7 model given by Yaghi *et al*.

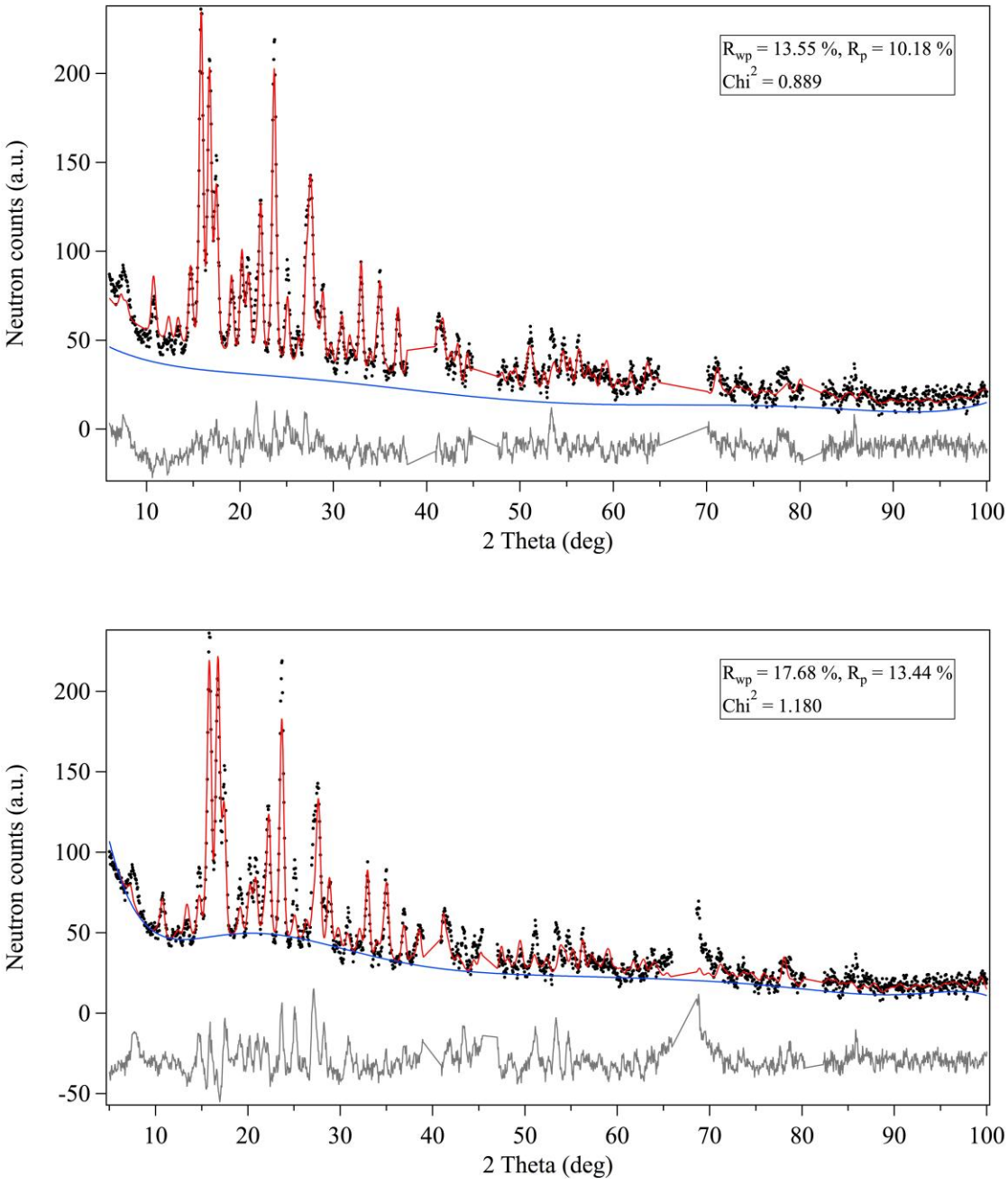

Figure SI 2. The observed and refined neutron diffraction profiles of guest-free D-ZIF-7 structure based on the hydrogenated ZIF-7 models given by Yaghi *et al.* (above) and Huang *et al.* (below).

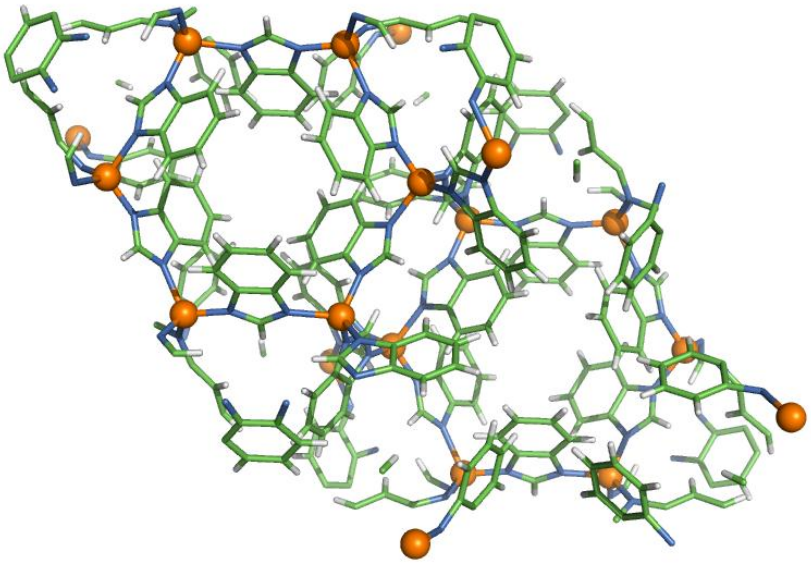

Figure SI 3. The refined guest-free D-ZIF-7 structure based on the hydrogenated ZIF-7 model given by Yaghi *et al*. Zn: orange, C: cyan, N: blue, H/D: silver.

4. **The internal structures of D-ZIF-7 (CO_2) under pCO_2=50, 100, 200 kPa**

The determination of the location of CO_2 molecules in the D-ZIF-7 (CO_2) structure under pCO_2=50 kPa was carried out by using the Fourier difference map generated by GSAS.[7, 8] The background was described by an 8-term shifted Chebyschev function after being manually reduced. The diffraction peaks of the aluminum sample holder were excluded. Peak shape was modeled with a pseudo-Voigt function (type IV). Spherical harmonics was used for preferred orientation correction. Guest-free D-ZIF-7 structure was used as the starting model and no structural parameter was refined.

Eight Fourier difference peaks were found with the highest intensities. Each of them was treated as a single CO_2 molecule and added to the guest-free D-ZIF-7 structure for Rietveld refinement using Topas 4.1. The preferred orientation parameters were set the same value as determined for the guest-free D-ZIF-7 structure and fixed for all the following refinements. CO_2 molecule was defined as a rigid body described by Z-matrix with O-C-O angle limited in the range of 140-180° and thermal parameters, occupancy of C and O atoms constrained. Distance and "anti-bump" restraints were used as needed between CO_2 molecule and D-ZIF-7 structure.

Based on DFT calculation, two CO_2 adsorption sites were finally selected for further refinement. Starting from the refined D-ZIF-7 (CO_2) structure (pCO_2=50 kPa), the determination of the internal structure of D-ZIF-7 (CO_2) under pCO_2=100 kPa were carried out by a combined-Rietveld refinement on two neutron diffraction datasets obtained using different incident neutron beam wavelengths λ=1.5946 and 2.3909 Å. The resulting structure was then used as the starting model in the Rietveld refinement for the determination of the atomic positions in D-ZIF-7 (CO_2) structure (pCO_2=200 kPa). Considering the temperature was fixed when CO_2 pressure increased, thermal parameters of the atoms in D-ZIF-7 host were kept the same as they were under pCO_2=50 kPa.

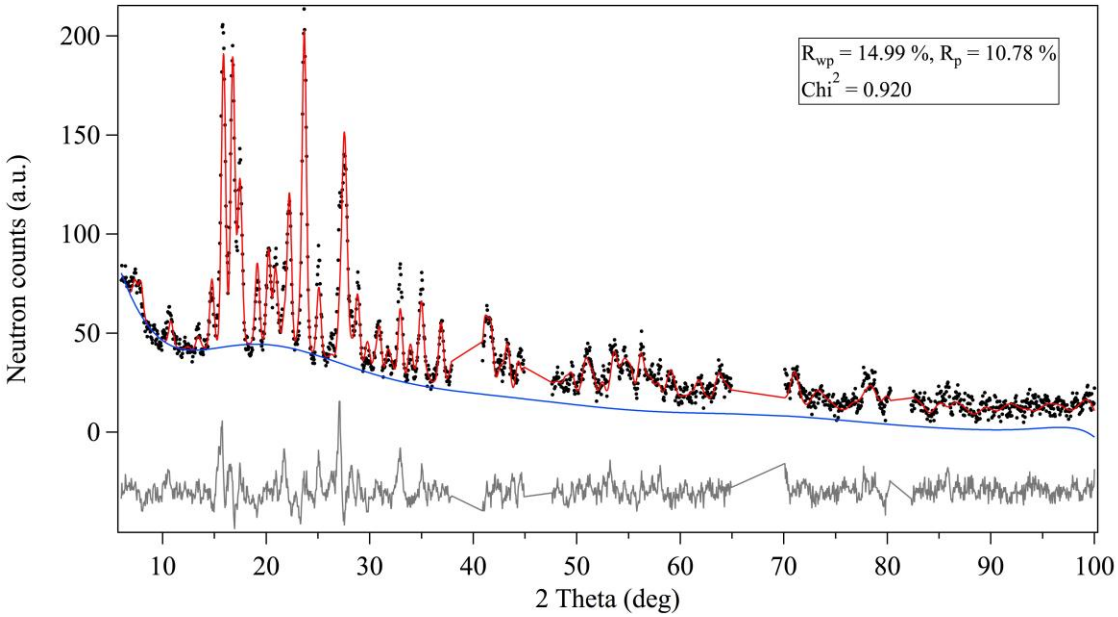

Figure SI 4. The observed and refined neutron diffraction of the D-ZIF-7 (CO_2) structure under pCO_2=50 kPa.

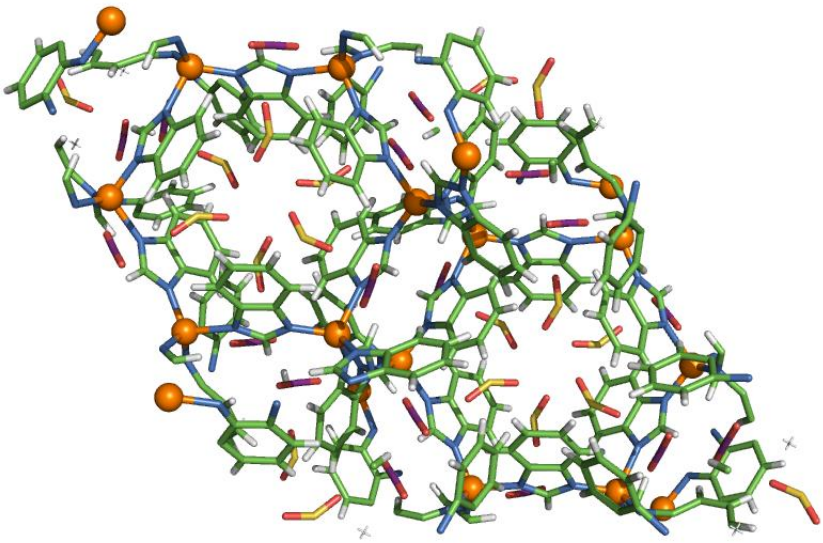

Figure SI 5. The D-ZIF-7 (CO_2) structure under pCO_2=50 kPa. Zn: orange, C: cyan, N: blue, H/D: silver. CO_2: C in Site A wheat, in Site B purple; O, red.

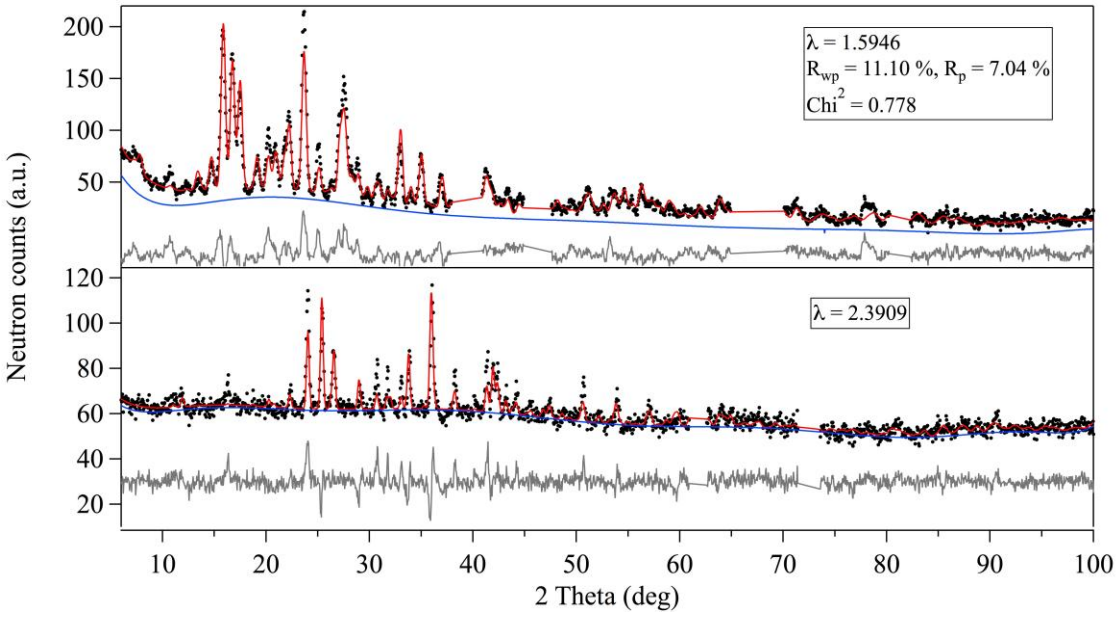

Figure SI 6. The observed and refined neutron diffraction of the D-ZIF-7 (CO_2) structure under pCO_2=100 kPa.

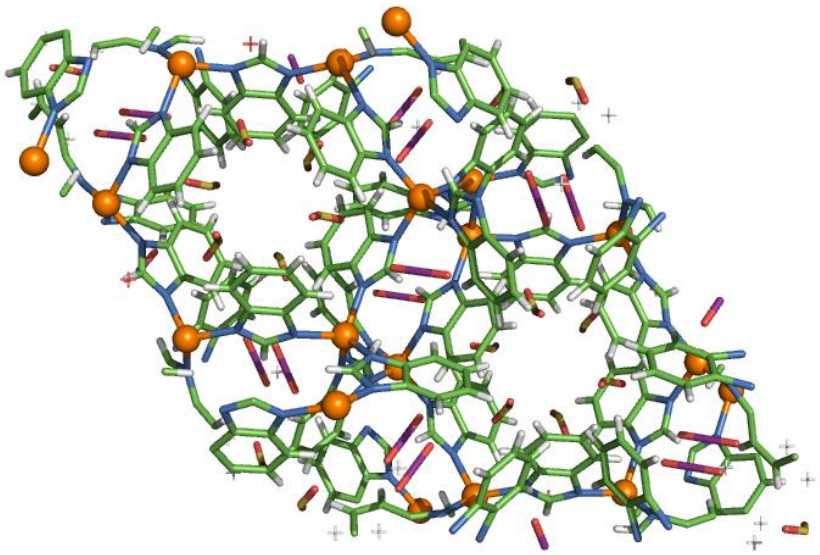

Figure SI 7. The D-ZIF-7 (CO_2) structure under pCO_2=100 kPa. Zn: orange, C: cyan, N: blue, H/D: silver. CO_2: C in Site A wheat, in Site B purple; O, red.

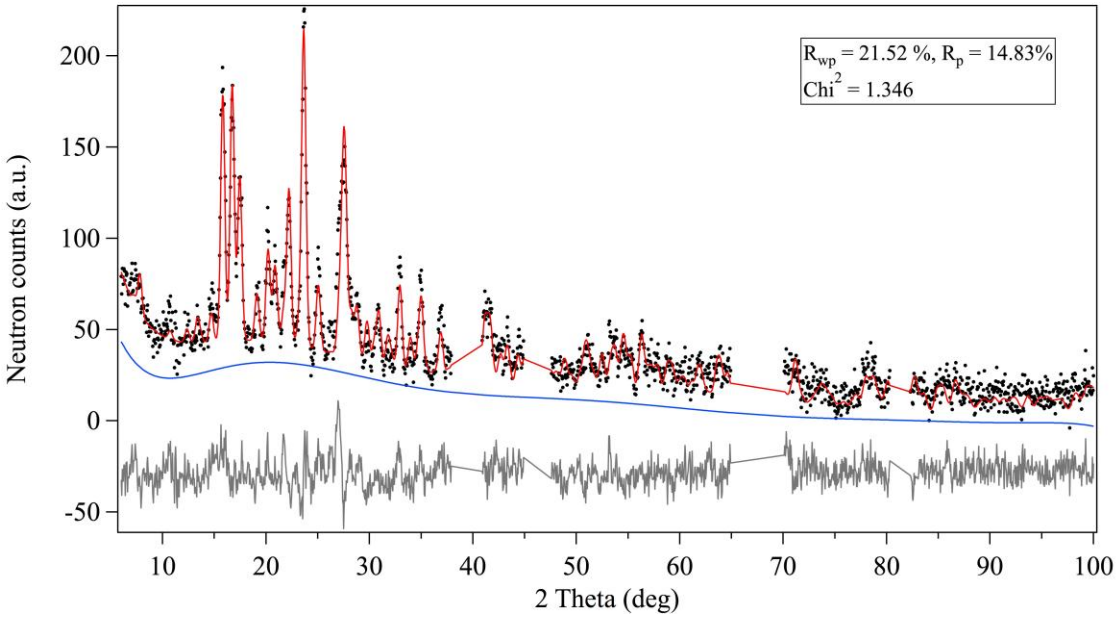

Figure SI 8. The observed and refined neutron diffraction of the D-ZIF-7 (CO_2) structure under pCO_2=200 kPa.

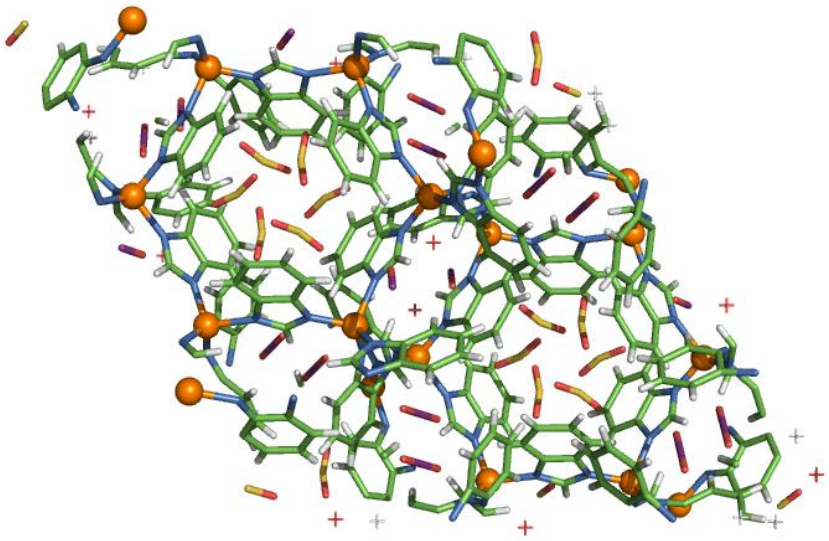

Figure SI 9. The D-ZIF-7 (CO_2) structure under pCO_2=200 kPa. Zn: orange, C: cyan, N: blue, H/D: silver. CO_2: C in Site A wheat, in Site B purple; O, red.

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