Supporting Information

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Sorption metastable state of a metal-organic porous material obtained by in situ synchrotron powder diffraction

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Adsorption isotherm

The adsorption isotherm for acetylene in CPL-1 was measured with an automatic volumetric adsorption apparatus BELSORP18 (BEL JAPAN, INC).

Figure S1. Adsorption isotherm for acetylene on CPL-1 at 270 K. Gas pressure ranges were a) from 0 to 100 kPa and b) from 0 to 5 kPa.
In situ diffraction patterns for the acetylene adsorption at 10k Pa.

Under these conditions, a single phase M could not be obtained and the co-existence of phases M and S were observed around 300 K as shown in Figure S2. A reflection peak not assigned to any of the known three phases (about 4.9° in 2θ) was observed between 326 K and 320 K. This may be due to another intermediate phase. In the adsorption isotherm (Figure S1), there exists a small step below 1.0 kPa that may correspond to the phase.

Figure S2. Temperature dependence of diffraction patterns of CPL-1 with the adsorption of acetylene at 10 kPa (adsorption process).
MEM/Rietveld analysis\textsuperscript{[1,2]}

The crystal structure of CPL-1 has been determined by the single crystal X-ray diffraction study.\textsuperscript{[3]} In the preliminary Rietveld refinement of phase M of CPL-1 with the adsorption of acetylene at 150 kPa and 360 K, the structural model of the anhydrous hollow CPL-1 framework was assumed as an initial model. The structural parameters of the CPL framework were refined with soft constraints on bond distances and bond angles throughout the refinement. The preliminary Rietveld fitting of phase M is shown in Figure S3. The integrated intensities of each reflection were evaluated by dividing the observed profile intensities of each data point, using the result of the Rietveld fitting. The MEM analysis was carried out using the structure factors obtained from the integrated intensities. In the MEM analysis, $\sin \theta/\lambda \leq 0.45$ Å\textsuperscript{-1} was used. The unit cell was divided into 32×128×64 pixels in the calculation. Figure S4 shows the preliminary MEM charge density of phase M of CPL-1 with the adsorption of acetylene. In the MEM charge density map, the electron density of the framework structure of CPL-1 was clearly observed. The peak maxima were also seen in the centre of the nanochannels despite the structural model having no guest molecules. These were considered to be the electron densities due to the adsorbed acetylene molecules. A modified structural model in which the acetylene molecule was placed on the peak position of the electron density was used for further Rietveld analysis. From the limitation of site symmetry and consideration of the crystal structure of phase S,\textsuperscript{[4]} the position of the centre of gravity of the acetylene molecule was fixed at the centre of the nanochannel. The bond distances in an acetylene molecule are fixed and only the orientation was refined. The occupancy parameter of the acetylene molecule was refined. After the final Rietveld refinement (Figure S5), we obtained the final MEM charge density.

The three-dimensional MEM charge density as an equi-contour surface of phase M is shown in Figure S6. The section MEM charge density containing the molecular axis of acetylene is shown in Figure 3 in the main body text. The section MEM charge density containing the hydrogen atom in acetylene and the non-coordinated oxygen (O2) atom of carboxylate is shown in Figure S7. A few electron densities are also observed between the adsorbed acetylene molecule and the O2 atom.
Figure S3. Preliminary Rietveld fitting of phase M of CPL-1 with the adsorption of acetylene at 150 kPa and 360 K using a structural model of the hollow framework of CPL-1. The reliability ($R$) factors based on the powder profile $R_{wp}$ and the Bragg integrated intensities $R_I$ were 6.21% and 14.55%, respectively.

Figure S4. Preliminary MEM charge density of phase M of CPL-1 with the adsorption of acetylene as an equi-contour surface. Views from a) side and b) front of the nanochannel directions. The equi-contour level is 1.0 eÅ$^{-3}$. The peak maxima in the centre of the nanochannels are coloured orange.
Figure S5. Final Rietveld fitting of phase M of CPL-1 with the adsorption of acetylene. The reliability ($R$) factors based on the powder profile $R_{WP}$ and the Bragg integrated intensities $R_1$ were 3.27% and 4.70%, respectively.

Figure S6. Final MEM charge density of phase M of CPL-1 with the adsorption of acetylene as an equi-contour surface. Views from a) side and b) front of the nanochannel directions. The equi-contour level is 1.0 eÅ$^{-3}$. The electron densities of acetylene molecules are coloured orange.
Figure S7. Section MEM charge density of phase M containing the hydrogen atom in acetylene, the non-coordinated oxygen atom (O2) of carboxylate and the a-axis.

References