Electronic Supplementary Information

Two-step gas adsorption induced by the transmetallation in a two-dimensional metal-organic framework

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Analytical methods

Elemental analyses were performed with a Perkin-Elmer 2400 Series II CHN analyzer. Most PXRD data were obtained on a Bruker New D8 diffractometer at 40 kV and 40 mA for Cu Kα (λ = 1.54050 Å) with a scan speed of 5°/min and a step size of 0.02° in 2θ. The PXRD patterns for the as-synthesized, solvent-exchanged, and activated **1-Zn** samples were also measured using a Rigaku MiniFlex diffractometer with CuKα radiation (λ = 1.5418 Å). Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was performed on a Perkin-Elmer Optima-4300 DV instrument for the samples digested in concentrated nitric acid. Thermogravimetric analyses (TGA) were carried out using a PerkinElmer Pyris 1 TGA under air with a heating rate of 2 °C/min (25-250 °C) and 5 °C/min (250-600 °C). NMR spectra were obtained on a Bruker 400 MHz NMR spectrometer.

Gas sorption measurements

The gas adsorption-desorption experiments were performed by using an automated micropore gas analyzer Autosorb-3B (Quantachrome Instruments). All gases used were of 99.999% purity. Gas sorption isotherms for H_2, N_2, and O_2 were monitored at 77 K, and CO_2 and CH_4 gas sorption isotherms were conducted at 195 K at each equilibrium pressure by the static volumetric method. An exactly measured amount of the pre-desolvated solid was introduced into the gas-sorption apparatus, and the sample was reactivated at 60 °C under vacuum for 2 h. After each gas sorption measurement, the sample was precisely weighed again. Surface area and pore volume were determined from the N_2 gas isotherms at 77 K. Multipoint BET and the Langmuir surface areas were estimated by using the data recorded at P/P_0 = 0.0001 - 0.1 atm.

In-situ synchrotron X-ray powder diffraction analysis

1-Cu crystalline powder was packed in a capillary (Hampton Research, Glass Number 50; 0.4 mm in diameter) and its Debye-Scherrer Pattern was measured with the sample-to-detector distance of 150 mm in 50 sec exposure time with synchrotron radiation (λ = 1.00002 Å) on an ADSC Quantum-210 detector with a silicon (111) double crystal monochromator (DCM) at the 2D SMC beamline of the Pohang Accelerator Laboratory, Republic of Korea. In-situ variable pressure PXRD was measured with a custom-made vacuum manifold and goniometer head. CO_2 gas was extra-high purity quality (DAEHAN Gas Company, Korea, 99.999%). Prior to data collection, the **1-Cu** powder was outgassed at 331 K under a primary vacuum until its X-ray powder pattern showed a pure phase; then, the sample was cooled to 195 K by using a cryo-stream. Finally, CO_2 was introduced in the capillary. In each pressure step, the measurement pressure was adjusted by using a finely adjustable needle valve, and X-ray powder pattern was collected. The ADX program was used for data collection,[S2] and the Fit2D program was used to integrate 2D images to 1D patterns.[S3]

Table S1. Comparison of the various activation methods and the measured surface areas for **1-Zn**.

Ref.	Solvent exchange and activation conditions	$SA_{Langmuir}$ (N_2)	$SA_{Langmuir}$ (CO_2)	Thermal stability from PXRD data
13	Evacuation at 100 °C for 12 h	133 m^2/g	-	Stable up to 100 °C
14	$CHCl_3$ exchange for 3 d → Evacuation at 50 °C for 4 h	negligible	284 m^2/g	Amorphous at 80 °C
15	Acetone exchange → Evacuation with *gentle heat* for 24 h	375 m^2/g	-	-
16	MeOH exchange for 3 d → Evacuation at 130 °C for 10 h	negligible	573 m^2/g (SA_{BET})	Stable up to 150 °C
This work	MeOH exchange for 2 d → Evacuation at 60 °C for 2 h	786 m^2/g	739 m^2/g	-

Table S2. Compositions and gas sorption properties of **1-Zn**, **1-Zn/Cu**, and **1-Cu**.

MOF	Metal contents in the M_3 cluster (Zn : Cu) [a]	S_{BET}, m^2g^{-1}	Uptake capacity, mmol/g		
			N_2 [b]	O_2 [c]	CO_2 [d]
1-Zn	3 : 0	725	9.25	10.9	8.55
1-Zn/Cu (1h)	2.12 : 0.88	746	9.74	11.0	8.63
1-Zn/Cu (3h)	1.93 : 1.07	737	10.6	11.2	9.15
1-Zn/Cu (6h)	1.19 : 1.81	714	11.4	12.8	10.6
1-Zn/Cu (12h)	0.81 : 2.19	698	12.1	14.4	11.6
1-Zn/Cu (24h)	0.57 : 2.43	679	13.7	16.0	13.1
1-Zn/Cu (48h)	0.42 : 2.58	656	13.9	17.7	16.9
1-Cu	0 : 3	522	14.8	20.2	17.7

[a] Determined by ICP-AES and elemental analysis, [b] at 77 K and 0.9 atm, [c] at 77 K and 0.2 atm, [d] at 195 K and 1 atm.

Synthesis of 1,3,5-tri(4-carboxyphenoxy)benzene (H_3TCPB)

H_3TCPB was synthesized by following a literature method with slight modification.[S1] Phloroglucinol (0.63 g, 5 mmol), *p*-fluorobenzonitrile (1.91 g, 15.8 mmol), and K_2CO_3 (3.11 g, 22.5 mmol) were sequentially placed in a 100 mL two-neck round-bottom flask equipped with a magnetic stirring bar and a Dean-Stark trap. NMP (10 mL) and toluene (10 mL) were respectively purged with nitrogen for 30 min, and added into the flask under nitrogen atmosphere. The reaction mixture was heated at 150 °C for 3 h under nitrogen atmosphere. After the removal of toluene, the reaction mixture was further heated at 180 °C for 16 h. After cooling to room temperature, the mixture was poured into distilled water (30 mL) and acidified with 1 M HCl (35 mL) to give dark brown precipitates. The collected solid was put in a round-bottom flask containing KOH (13 g, 0.2 mol), distilled water (50 mL), and ethanol (50 mL). The mixture was heated at 80 °C for about 12 h. After removal of ethanol by distillation, the mixture was cooled to room temperature and poured into water (100 mL). When acidified with concentrated HCl (25 mL), off-white precipitates were produced. The solid was separated, thoroughly washed with distilled water, and dried under reduced pressure to give 1.90 g (Yield, 78 %). The ligand was used for the syntheses of MOFs without further purification. ^{1}H-NMR (DMSO-d_6, δ, ppm): 6.64 (s, 3 H), 7.16 (d, 6H), 7.96 (d, 6H).

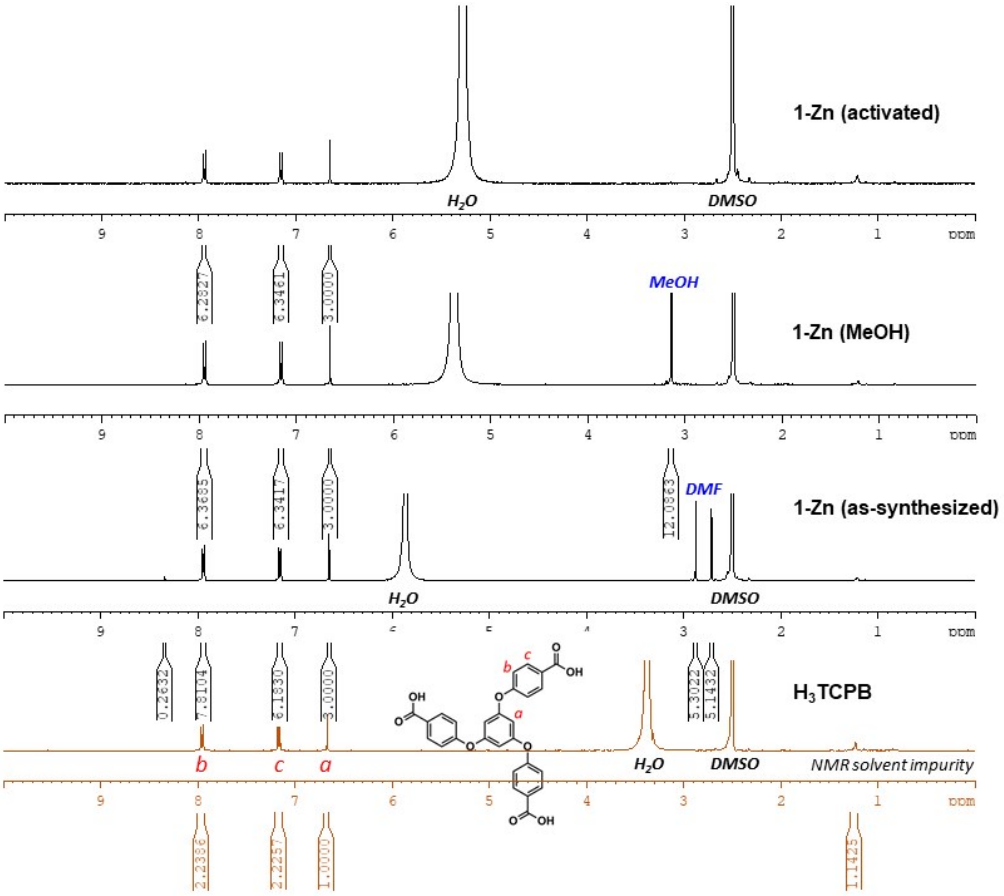

Figure S1. ^{1}H-NMR spectra of ligand and **1-Zn** samples. The **1-Zn** MOF samples were dissolved in DCl/DMSO-d_6.

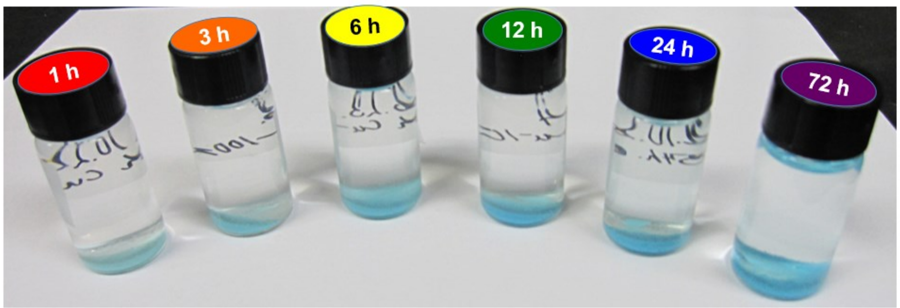

Figure S2. The picture of the **1-Zn/Cu** crystals collected after transmetallation.

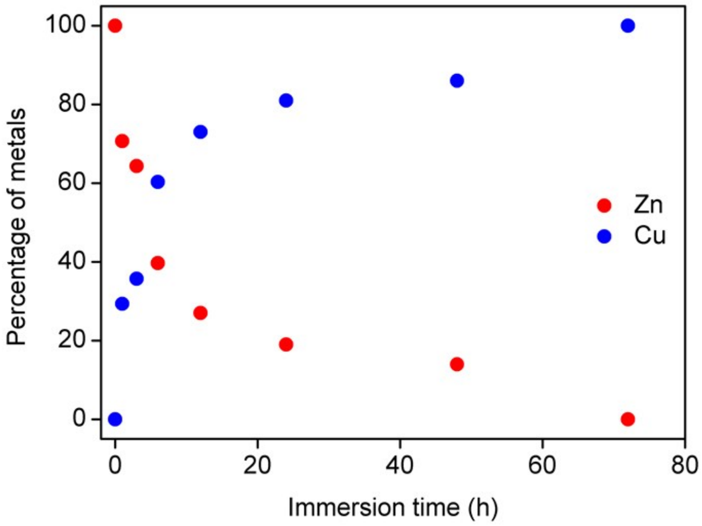

Figure S3. Kinetic profiles for the exchange of the framework Zn^{2+} ions in **1-Zn** with Cu^{2+}, as determined by ICP-AES data.

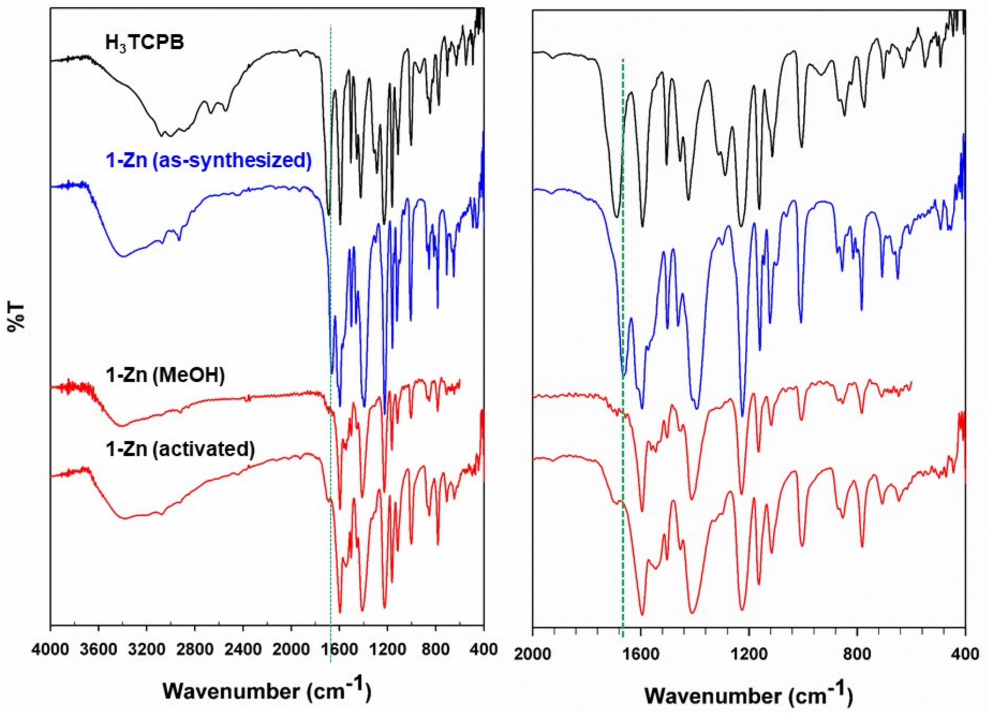

Figure S4. IR spectra of ligand and **1-Zn** samples. The green dotted line indicates the wavenumber of the DMF carbonyl in **1-Zn** (as-synthesized).

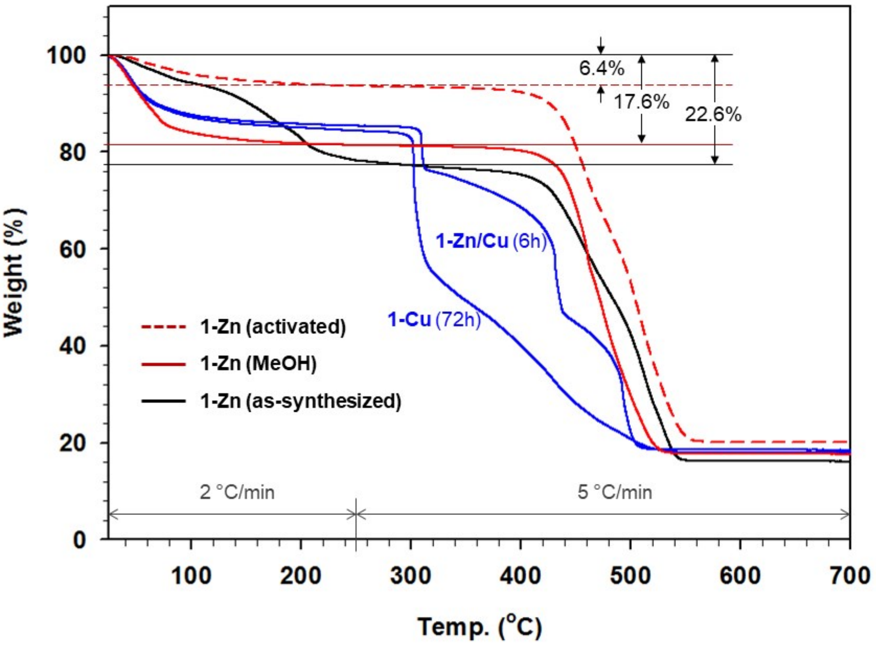

Figure S5. TGA curves for **1-Zn**, **1-Zn/Cu**, and **1-Cu** samples. The samples were heated in the air with changing heating rates, as shown in the figure.

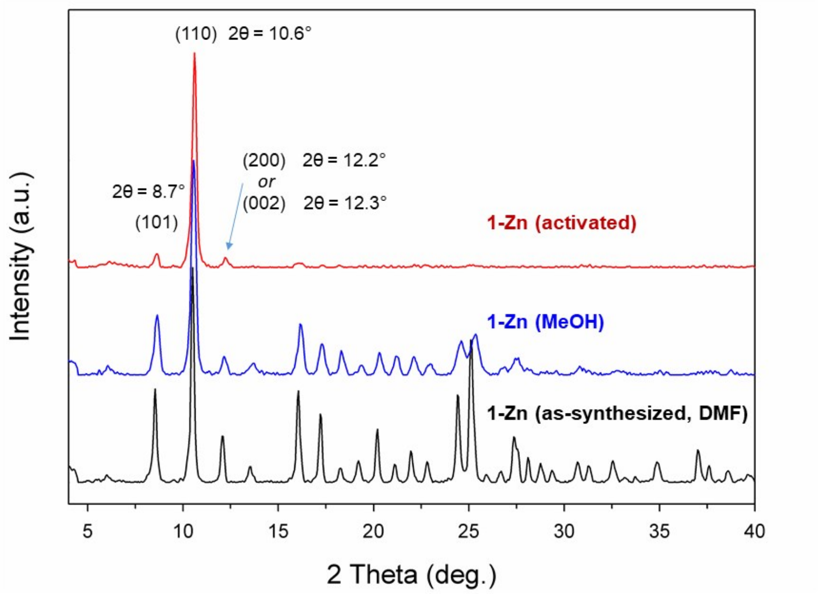

Figure S6. PXRD patterns for **1-Zn** samples. The peaks for (200) and (002) planes appear close to each other, and thus cannot be identified with the current data.

Structural modelling

The conformational change of the TCPBs in **1-Zn** was investigated using Visulalizer of BIOVIA Materials Studio 2020 software package. The coordinate of $[Zn_3(TCPB)_2 \cdot 2H_2O] \cdot 2H_2O \cdot 4DMF$ (reported as CCDC 879381 or GICNIR) was loaded into Visulalizer. Since the occluded DMF and water molecules were simply assigned as O atoms due to disorder, they were deleted to give an empty framework. Then, the original space group (a trigonal *P*(-3)1*c*, No. 163) was changed to its subgroup, *P*(-3) (No. 147), to vary independently two torsion angles (ϕ_1 and ϕ_2) of the paired TCPB linkers (Figure S3). If the symmetry is reduced further to *P*(-1) or *P*1, possible combinations of torsion angles are numerous and cannot be investigated. Therefore, the choice of the *P*(-3) space group was inevitable.

There was no automatic method of changing the torsion angles systematically in the extended structure. Therefore, each torsion angle was changed manually by 10°. In detail, all possible combinations of the torsion angles (ϕ_1 and ϕ_2) were generated using the torsion-angle measurement and editing utility of Visualizer. At the same time, the shortest H···H interatomic distances between neighboring benzene rings, including A and B, were monitored by the distance measurement utility of Visualizer. In the resulting conformation map shown in Figure S7, the regions for possible **1-Zn** structures that did not involve bad H···H contacts (< 2.0 Å) were identified.

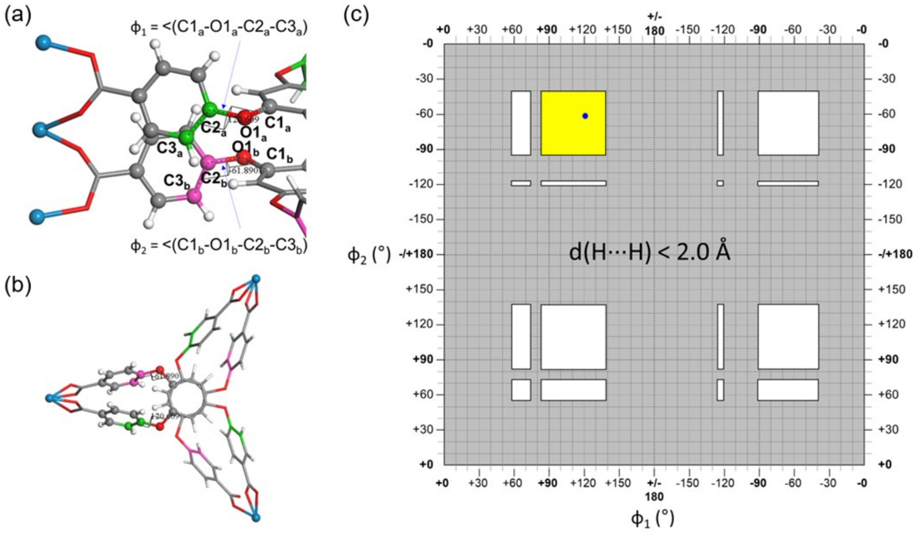

Figure S7. (a) Torsion angles, ϕ_1 and ϕ_2 of the paired TCPB linkers in **1-Zn**. (b) The symmetry-related atoms in the *P*(-3) space group are respectively shown with green and pink colours. Therefore, for example, when a torsion angle ϕ_1 is changed, the other two symmetry-related torsion angles are also changed with the same angles. (c) A conformation map obtained with combinations of the torsion angles ϕ_1 and ϕ_2. The white or yellow rectangular boxes are regions without involving bad H···H interatomic contacts. The blue circle in the yellow box denotes the 1-O structure with (ϕ_1, ϕ_2) = (120.6°, -61.9°) that corresponds to the reported crystal structure of **1-Zn**. The conformation map should be drawn symmetrically but is not here because the benzene rings in the original crystal structure (CCDC 879381.cif or GICNIR) are not completely flat.

In the next step, one of the regions that contained a combination, (ϕ_1, ϕ_2) = (120.6°, -61.9°) was defined as a representative **1-O** and used as a starting structure for further models. We assumed that the conformational changes between the isolated yellow or white boxes were forbidden due to large rotational barriers, that is, bad contacts. With changing the torsion angles, the shortest interatomic (C···C) distances between neighboring benzene rings were monitored. When the C···C distances were less than 3.40 Å, the sum of van der Waals radii, the structures were not allowed as depicted as an orange-coloured region in Figure S4(a). The grey circles on the borderline between orange and white regions have minimum C···C contact of 3.4 Å, and thus, all conformations in the orange area have 'bad C···C contacts'. Then, the possible structures in the allowed region were generated. That is, the CIF files for the structures marked with circles in Figure S4(a) were generated and used for the calculations of void volumes using the Mecury program. The void volumes in % were calculated and displayed with the Display-Voids utility of Mercury; a probe radius of 1.8 Å (the kinetic radius of N_2) and a grid spacing of

0.3 Å were chosen for the calculations. The structural models accompanied by the disconnection of the channels in **1-Zn** were considered as **1-C** states. In other words, all structures that belong to the small yellow area at the top-right corner in the map are possible **1-C** structures while the remaining white area was for possible **1-O** structures. In the map, the black circles on the borderline denote **1-C** structures with disconnected channels. Among the possible **1-C** structures, the structure with ϕ_1 = 137.0° and ϕ_2 = -40.0° had the smallest void volume of 26.6% and was chosen as a representative **1-C**.

Although there was a significant difference in the calculated void volumes, the overlap of **1-O** (blue circle; 33.2%) and **1-C** (yellow circle; 26.6%) structures were overlapped, both structures seem almost similar. In fact, the simulated PXRD patterns generated using Mercury were almost the same except for some intensity changes, as shown in Figure S8c.

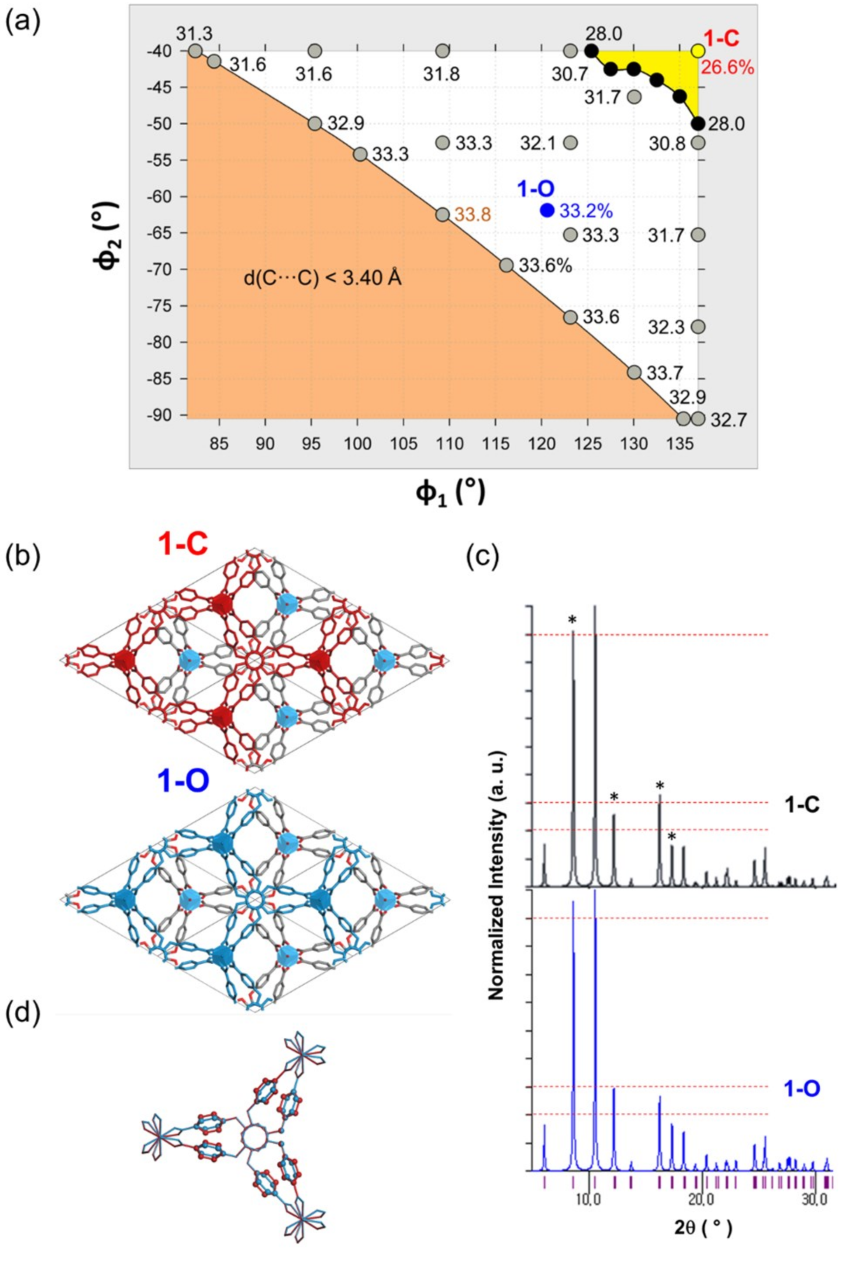

Figure S8. (a) A detailed conformation map of the yellow box in Fig. S3 shown with the calculated void volumes against torsion angles. (b) The structures of **1-C** (yellow circle) and **1-O** (blue circle) along the [001] direction, respectively. (c) Comparison of the simulated PXRD patterns of **1-C** and **1-O**, where the **1-C** peaks marked with asterisks show different intensities from those of **1-O**. (d) Overlap of the fragments of the **1-O** and **1-C** structures.

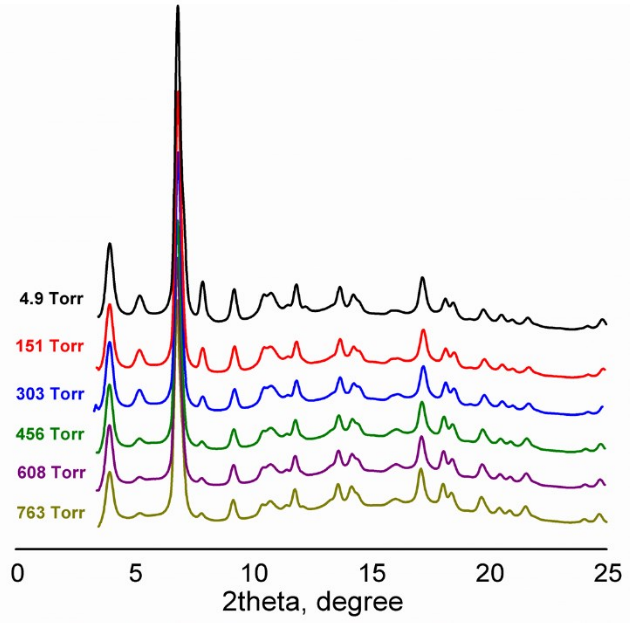

Figure S9. PXRD patterns of **1-Cu** observed under varying CO_2 pressure at 195 K using a synchrotron light source ($\lambda = 1.00002$ Å).

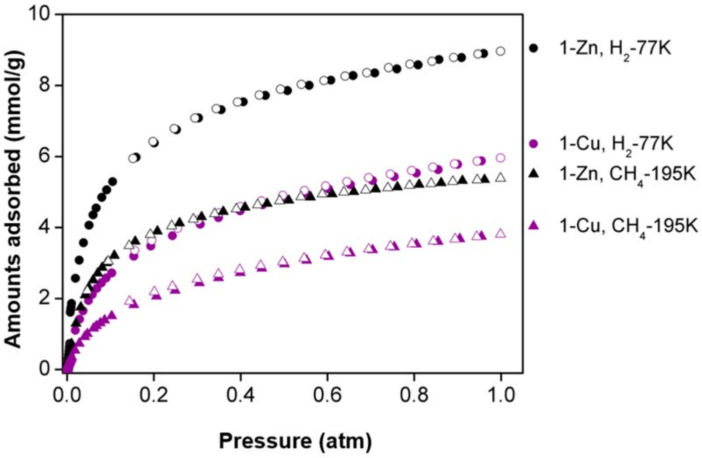

Figure S10. H_2 and CH_4 adsorption-desorption isotherms of **1-Zn** (black) and **1-Cu** (purple).

S1. K. Matsumoto, T. Higashihara and M. Ueda, *Macromolecules*, 2008, **41**, 7560–7565.

S2. Arvai, A. J.; Nielsen, C. ADSC Quantum-210 ADX Program; Area Detector System Corporation; Poway, CA, USA, 1983.

S3. Fit2D program: Andy Hammersley (E-mail: hammersley@esrf.fr), ESRF; 6 rue Jules Horowitz, BP 220, 38043 Grenoble Cedex 9, France.