## SUPPORTING INFORMATION

# A Chemical Role for Trichloromethane: Room-Temperature Removal of Coordinated Solvents from Open Metal Sites in the Copper-Based Metal–Organic Frameworks

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## Section S1. Materials and Methods

Materials. All reagents were obtained from commercial sources (Sigma Aldrich, Alfa Aesar, CARLO ERBA, or Daejung). Copper (II) nitrate hemipentahydrate [Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O, 98.0-102%, Alfa Aesar], trimesic acid (1,3,5-bezenetricarboxylic acid, BTC, 95%, Sigma Aldrich), ethanol (EtOH, 94.5%, Daejung), N,N-dimethylformamide (DMF, 99.5%, Daejung), and distilled deionized water (DDW) were used for the synthesis of HKUST-1. 1,4-Benzenedicarboxylic acid (BDC, 98+%, Alfa Aesar) was used with copper (II) nitrate for the synthesis of Cu-MOF-2 powder. Methanol (MeOH, 99.5%, Daejung), EtOH (94.5%, Daejung), acetonitrile (MeCN, 99.9%, CARLO ERBA), and DMF (99.5%, Daejung) were employed as coordinating solvents, and the solvents were distilled and purified with zeolite 4A in a moisture-free argon-filled glove box prior to use. Sulfuric acid-d<sub>2</sub> (D<sub>2</sub>SO<sub>4</sub>, 96-98 wt% in D<sub>2</sub>O, 99.5 atomic % in deuterium, Sigma Aldrich) was used for dissolving HKUST-1 and Cu-MOF-2 prior to performing the <sup>1</sup>Hnuclear magnetic resonance (NMR) spectroscopic analysis of the samples. Polyvinylidene fluoride (PVDF, Mn = 71,000 g/mol, Sigma Aldrich) was employed for preparation of a mixed matrix membrane with HKUST-1 crystallites (pristine-MMM). Trichloromethane (CHCl<sub>3</sub>, TCM, 99%, Alfa Aesar) was employed as a reagent for chemical activation. TCM was also distilled and purified with zeolite 4A in the glove box prior to use. All synthesized MOFs were stored in a moisture-free argon-filled glove box prior to use.

**Synthesis of HKUST-1.** We synthesized HKUST-1 (HK) following the procedure described in our previous reports.<sup>S1-S2</sup> Briefly,  $Cu(NO_3)_2 \cdot 2.5H_2O(0.84 \text{ g}, 3.6 \text{ mmol})$  was dissolved in 10 mL of DDW in a vial. In a separate vial, BTC (0.21 g, 1.0 mmol) was dissolved in 10 mL of EtOH. The  $Cu(NO_3)_2$  solution was quickly added into the vial containing the BTC solution. After the mixed solution was continuously stirred for 10 min at room temperature, 1 mL of DMF was added to the mixed solution. Then, the vial was sealed with polytetrafluoroethylene (PTFE) tape. The vial was placed in an oven at 80 °C for 20 h to allow the mixture to react. After the product cooled down to room temperature, we collected and washed the crystalline solid (pristine-HK) with a mixed solvent of H<sub>2</sub>O and EtOH. The obtained HKUST-1 was kept placed in a moisture-free Ar-filled glove box prior to testing thermal activation (TA) and chemical activation (CA).

**Synthesis of Cu-MOF-2.** We also synthesized Cu-MOF-2 following the procedure described in our previous reports.<sup>S1</sup> Briefly,  $Cu(NO_3)_2 \cdot 2.5H_2O(0.23 \text{ g}, 1.0 \text{ mmol})$  was dissolved in 10 mL of DMF in a vial. In a separate vial, BDC (0.166 g, 1.0 mmol) was dissolved in 10 mL of DMF. The  $Cu(NO_3)_2$  solution was added to the BDC solution. After continuous stirring for 10 min at room temperature, the vial was sealed with PTFE tape. Then, the vial was placed in an oven at 110 °C for 48 h to allow the mixture to react. After allowing the vial to cool to room temperature, we collected and washed the crystalline solid (pristine Cu-MOF-2) with fresh DMF. The obtained Cu-MOF-2 was also kept placed in a moisture-free Ar-filled glove box prior to examining TA and CA.

**TA of HKUST-1 and Cu-MOF-2 Crystals.** Precoordinated  $H_2O$  and EtOH solvents in pristine HKUST-1 were removed by thermal activation (TA) prior to the preparation of MeOH-, EtOH-, MeCN-, and DMF-coordinated HKUST-1 (MeOH-HK, EtOH-HK, MeCN-HK, and DMF-HK, respectively) (see the preparation below). For the TA of pristine HKUST-1, a pristine powder sample was placed in a glass vacuum tube. Then, the tube was heated at 150 °C for 12 h under vacuum (~10<sup>-3</sup> Torr). We also examined the TA of DMF-coordinated Cu-MOF-2 powders. For this examination, TA was also performed under similar conditions as described above except the applied temperatures were 200 °C. After activation, the tubes were transferred into a moisture-free Ar-filled glove box prior to use.

CA of HKUST-1 and Cu-MOF-2 crystals. 50 mg of pristine HKUST-1 powder were dispersed in 20 mL

of TCM in a vial. Then, the colloidal solution was shaken for 5 min to dissociate precoordinated H<sub>2</sub>O and EtOH. This process was repeated 5 times to successfully activate the HKUST-1. Finally, the TCM-treated HKUST-1 samples were dried under vacuum condition for 30 min prior to use. The chemical activation of MeOH-HK, EtOH-HK, and MeCN-HK samples was also performed with the same procedure (procedure for the preparation of MeOH-HK, EtOH-HK, and MeCN-HK was described below). The process for the chemical activation of Cu-MOF-2 was also same as the above procedure except that the number of repetitions of the TCM treatment was 20 times. The entire process was conducted under an inert atmosphere of the moisture-free Ar-filled glove box.

**Preparation of MeOH-HK, EtOH-HK, MeCN-HK, and DMF-HK.** The removal of precoordinated H<sub>2</sub>O and EtOH in pristine HKUST-1 was first performed via TA (see above). Initially, 1 g of the thermally activated HKUST-1 powder was placed in a 20-mL vial. After 10 mL of purified MeOH was added into the vial, MeOH was allowed to coordinate at the OCSs of the Cu<sup>2+</sup> centers for 1 h. Subsequently, the obtained MeOH-HK sample was collected by filtration and dried under vacuum prior to use. EtOH-HK, MeCN-HK, and DMF-HK samples were prepared following the same procedure described above except pure EtOH, MeCN, and DMF were used. The entire process was conducted under an inert atmosphere of a moisture-free argon-filled glove box.

**Preparation of pristine-MMM.** To prepare pristine MMM, first, 1 g of PVDF pellets was introduced into 10 mL of DMF in a 20-mL vial. Then, the vial was placed and stirred on a hot-plate at 80 °C to allow the PVDF pellets to completely dissolve in DMF. After 3 g of DMF-HK powder was added into the viscous PVDF/DMF solution, the powder was allowed to homogenously disperse in the polymer solution with vigorous stirring for 5 min. Then, the mixed solution was transferred and spread onto a pre-heated (ca. 40 °C) flat stainless steel plate which size was  $15 \times 20 \text{ cm}^2$ . After the plate was placed in an oven at 80 °C for 10 min, the plate was allowed to cool to -15 °C in a refrigerator. Subsequently, the pristine-MMM was obtained by detaching it from the plate. The membrane was cut into a size of ca.  $10 \times 10 \text{ cm}^2$  prior to use.

**TA of pristine-MMM.** To examine gas (N<sub>2</sub>, H<sub>2</sub>O, and NO) sorption, <sup>1</sup>H-NMR, and powder X-ray diffraction (PXRD) of thermally activated MMMs, we performed the thermal activation with pristine-MMMs at 105, 150, and 200 °C ( $TA^{105}$ -MMM,  $TA^{150}$ -MMM, and  $TA^{200}$ -MMM, respectively) for 12 h under vacuum (ca. 10<sup>-3</sup> Torr) conditions. Then, the obtained TA<sup>105</sup>-MMM, TA<sup>150</sup>-MMM, and TA<sup>200</sup>-MMM, and TA<sup>200</sup>-MMM samples were transferred into a moisture-free Ar-charged glove box prior to testing the measurements.

**CA of pristine-MMM.** To examine gas ( $N_2$ ,  $H_2O$ , and NO) adsorption, <sup>1</sup>H-NMR, and PXRD of chemically activated MMM, we prepared TCM-treated MMM (TCM-MMM). Precisely, the chemical activation was achieved by dipping a piece (75 mg) of pristine-MMM into 20 mL of fresh TCM solvent for 10 min. This procedure was also repeated 25 times to successfully activate the membranes. Subsequently, the TCM-treated MMM samples were dried under vacuum condition for 30 min prior to use. The entire process conducted under an inert atmosphere of the moisture-free Ar-charged glove box.

**Sample preparation for the** <sup>1</sup>**H-NMR measurements.** A tiny amount of HKUST-1 or Cu-MOF-2 powder samples was dried under vacuum at room temperature only to evacuate pore-filling solvent prior to the preparation of an NMR sample. After the sample was completely dissolved in 1 mL of D<sub>2</sub>SO<sub>4</sub>, then, the solution was transferred into an NMR tube. The sample preparation of pristine-MMM, TA<sup>105</sup>-MMM, TA<sup>150</sup>-MMM, TA<sup>200</sup>-MMM, and TCM-MMM for NMR was also achieved by completely dissolving small piece of a corresponding membrane in 1 mL of D<sub>2</sub>SO<sub>4</sub>. Undissolved PVDF suspension was

removed by filtration prior to transferring the solution into an NMR tube. These procedures were also conducted in an Ar-charged glove box. Additionally, the tubes were kept sealed with plastic caps and acrylic Parafilm<sup>®</sup> prior to measuring the NMR spectra.

**Sample preparation for the measurement of UV-vis absorption spectra.** Prior to taking UV-vis absorption spectra, HKUST-1 or Cu-MOF-2 powder samples were contained in cylindrical quartz cells (Starna, Type 37GS Cylindrical Cells with Quartz to Borofloat graded seal). The preparation was performed in a moisture-free Ar-charged glove box, and the quartz cells were sealed with a glass cork using a grease (Apiezon, H, high temperature Vacuum Greases) prior to the measurements.

In situ Raman measurements. Prior to taking in situ Raman measurements, several tens of large EtOH-HK crystals (approximately 100–200  $\mu$ m) were introduced into the cylindrical quartz cell that was used for the UV-vis absorption measurements. After taking the Raman spectrum of EtOH-HK, we introduced approximately 0.25 mL of TCM into the cell. We repeated this process five times to monitor the continuous change of the Raman shift of the Cu–Cu vibration. After picking out the crystals from the quartz cell, we placed the crystals on a clean glass plate and allowed the crystals to be exposed to the moist atmosphere. The Raman spectra were continuously recorded every 30 s during the process.

**Instrumentation.** DDW was obtained from a water purification system (Merck Millipore, MQ Direct 8). Diffuse reflectance UV-vis spectra of samples were recorded using an Agilent Cary 5000 UV-VIS-NIR spectrophotometer. PXRD patterns were obtained using a PANalytical diffractometer (Empyrean) with a monochromatic nickel-filtered Cu K<sub>a</sub> beam. <sup>1</sup>H-NMR spectra were recorded using an AVANCE III HD FT-NMR spectrometer (Bruker, 400 MHz for <sup>1</sup>H). The <sup>1</sup>H chemical shifts were referenced to the residual proton resonance of the solvent. N<sub>2</sub> adsorption/desorption isotherms were obtained at 77 K using a BELSORP-max (BEL Japan, Inc.). Using the BELSORP-max equipment, NO and H<sub>2</sub>O adsorption isotherms were also obtained at 0 and 25 °C, respectively. Optical microscope images were taken using an S43T microscope (Bimeince). Raman spectra were recorded using a Nicolet Almega XR dispersive Raman spectrometer (Thermo Scientific). Excitation of the samples was performed by focusing a 0.5-mW 532-nm-wavelength laser beam on a crystal with a 10× magnifying objective lens. Scanning electron microscopy (SEM) images were obtained from an FE-SEM (Hitachi S-4800) operated at an acceleration voltage of 3 kV, after samples were coated by Au-Pt alloys with a thickness of 3 nm.

#### Section S2. Changes in UV-vis Absorption Spectra of HKUST-1 After Activation



**Figure S1.** Diffuse-reflectance UV-vis absorption spectra of pristine-HK (black curve), TA-HK (red curve), and TCM-treated HK (blue curve). The absorption spectrum of HK-wet-in-TCM (green curve) is also displayed for comparison. The circular insets show optical microscope images of the samples as indicated.

#### Section S3. Sample Preparation for <sup>1</sup>H-NMR Measurements



**Figure S2.** Photograph images of a tiny amount of HKUST-1 powder sample added into 1 mL of  $D_2SO_4$  in a <sup>1</sup>H-NMR tube (a) before and (b) after sonication for 10 min. The HKUST-1 crystals are completely dissolved in  $D_2SO_4$  after sonication for 10 min.





Figure S3. (a) <sup>1</sup>H NMR spectra and (b) PXRD patterns of pristine-HK and TA-HK powder samples. The TA was performed

at 150 °C for 12 h. The NMR spectra were taken after completely dissolving the powder samples in  $D_2SO_4$ .

#### Section S5. Chemical Activation of Cu-MOF-2

We also tested Cu-MOF-2 to address whether the chemical activation behavior of TCM could be adopted to other MOFs. We observed that the color of Cu-MOF-2 changed from light green to dark blue after the sample was thermally activated. The TCM treatment also exhibited a similar color change, thus implying the activation function of TCM even in Cu-MOF-2 (see Figure S3). UV-vis absorption spectra of the MOF-2 samples clearly indicate that the color change is caused by the blueshift of the d-d transition, similar to the pattern observed in HKUST-1 (see Figure S1).

To further understand this behavior, we examined <sup>1</sup>H NMR analysis. The <sup>1</sup>H NMR spectrum of pristine MOF-2 powder shows that it contains DMF as a coordinating component at the OCSs (see Figure S4). Consistent with the above result, the coordinated DMF was dissociated after TCM treatment (the experimental details are presented in Section S1).



**Figure S4.** Diffuse reflectance UV-vis absorption spectra of pristine-MOF-2 (black curve), TA-MOF-2 (pink curve), and TCM-MOF-2 (blue curve) crystalline powders. The optical microscope images in the circular insets display the colors of the powder samples.



**Figure S5.** <sup>1</sup>H NMR spectra of pristine-MOF-2, TA-MOF-2, and TCM-MOF-2 taken after the samples were dissolved in D<sub>2</sub>SO<sub>4</sub>.

The phase of MOF-2 was transformed after the TA process, as previously reported in literature (see Figure S5).<sup>S1</sup> To check whether the chemical activation of Cu-MOF-2 engenders behavior similar to TA, we also monitored the change in the PXRD pattern of TCM-treated MOF-2. The PXRD pattern indicated that although the crystalline phase of the MOF-2 was transformed after TCM treatment, the superficial result of the chemical activation was the same as that of the TA (see Figure S5). It also indicates that its 2-dimensional framework was not collapsed or damaged after the chemical activation. Although more comprehensive studies are required to fully understand the phase transition behavior, this feature has often been observed.<sup>S3-S6</sup>



Figure S6. PXRD patterns of pristine-MOF-2, TA-MOF-2, and TCM-MOF-2 powder samples, as indicated.

In terms of the Raman spectra, MOF-2 exhibited behavior that differed from that of HKUST-1 in two aspects (see Figure S6). One aspect is that the Raman shift involving the Cu–Cu stretching vibration appeared as a doublet mode at 189 and 205 cm<sup>-1</sup>. The other aspect is that whereas HKUST-1 exhibited a blue-shift in the Cu–Cu vibration after activation (from 185 to 228 cm<sup>-1</sup>), MOF-2 exhibited red-shifts in both peaks of the doublet (from 189 to 184 cm<sup>-1</sup> and from 205 to 197 cm<sup>-1</sup>). Although more comprehensive studies are required to fully understand this behavior, our observation is in good agreement with the pattern reported in the literatures.<sup>S1,S4</sup> Regardless, an important fact is that the pattern of the shift after chemical activation is exactly same as the pattern of the shift after TA. This evidence strongly supports our demonstration of the chemical activation behavior of TCM in Cu-MOF-2.



**Figure S7.** Expanded (left panel) and wide (right panel) views of the Raman spectra of pristine-MOF-2, TA-MOF-2, and TCM-MOF-2 powder samples. The Raman spectra were taken after the samples were sealed in a moisture-free argon-charged glovebox.



**Figure S8.** <sup>1</sup>H NMR spectra of a MeOH-HK sample treated with (a, b) DCM at (a) 25 °C and (b) 35 °C and (c, d) TCM at (c) 25 °C and (d) 55 °C



**Figure S9.** Changes in the amount of MeOH dissociated from MeOH-HK with respect to the number of DCM- and TCM-treatments. DCM-treatments were performed at 25 °C (sky blue plot) and 35 °C (blue plot), and TCM-treatments were performed at 25 °C (orange plot) and 55 °C (pink plot). Each treatment was conducted by soaking a powder sample in a corresponding pure solvent for 5 min.

# Section S7. Microscopic Analysis of HKUST-1–PVDF MMM After Thermal and Chemical Activation



**Figure S10.** Top, bottom, and cross-sectional view SEM images of pristine-MMM, TA<sup>105</sup>-MMM, TA<sup>150</sup>-MMM, TA<sup>200</sup>-MMM, and TCM-MMMs. The insets show magnified top-view SEM images of the samples.

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