Electronic Supplementary Information

Water-triggered Macroscopic Structural Transformation of a Metal-Organic Framework

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Table of Contents

1. Materials

All the reagents and chemicals used were obtained from commercial sources and used as received, unless otherwise noted. Methanol (MeOH), *N*,*N*-dimethylformamide (DMF), 2-propanol, hexane, zinc (II) acetate hexahydrate ($Zn(OAc)_2 \cdot 6H_2O$), and ortho-phthalic acid were purchased from Wako Pure Chemical Industries Co. Ltd.

2. Experimental Procedure

2.1 Synthesis of Zn-phthalate metal-organic framework (MOF)

$Zn(OAc)_2 \cdot 6H_2O$ (175 μmol) and Phthalic acid (875 μmol) were dissolved in MeOH (3.5 mL). The resultant precursor solution was transferred to an SUS-316 stainless steel tubular reactor of 10 mL inner volume, and then, the reactor was sealed with an SUS-316 screw cap. The sealed reactor was placed in a molten-salt bath, which was pre-heated and maintained at 300 °C (***CAUTION!*** *In this experiment, maximum heating rate is reached to >500 ºC/min. Thus, the inner pressure of the system is drastically increasing within 30 seconds. It should be carefully treated with protection gloves, lab coat, and eye shield to avoid unexpected accident.*). After appropriate time period (10 min), the reaction was immediately quenched by placing the reactor in an ice-water bath (0 ºC). The obtained mixture was centrifuged (6,600 rpm, 30 min), washed three times with MeOH, and dried under vacuum (30 ºC, 24 hour) to give a powdery product (white powder, 64.9 mg).

2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) images were measured on a JEOL JEM-7300F microscope. A specimen was prepared by directly placing the bulk powder on a conducting carbon tape.

2.3 Transmission Electron Microscopy

Transmission electron microscopy (TEM) images were measured on a JEOL JEM-2100F microscope. For the preparation of the specimen, first, the powdery sample was dispersed in solvent (DMF, methanol, 2-propanol, or hexane) with sonication (30 min). Then, 10 μL of resultant dispersion was drop-casted on a carbon-coted copper micro grid and the solvent was vaporized under atmospheric (dry air or wet air) or vacuum conditions.

2.4 Powder X-ray diffraction (XRD) measurement

Powder X-ray diffraction (XRD) measurements were performed using a Rigaku SmartLab diffractometer with graphite-monochromatized Cu-K_α radiation (X-ray wavelength: 1.5418 Å) in steps of 0.02° over the 2θ range of 10–90°. A sample was set in a standard glass holder or a nonrefractive silicon holder (Overseas X-Ray Service, Saitama, Japan).

2.5 Optical microscopy

Optical microscopic observation was carried out with a Olympus BX50F4 fitted with a digital camera. For the preparation of the specimen, the powdery MOF sample was dispersed in solvent DMF with sonication. The resultant dispersion was drop-casted on a glass plate. The solvent was vaporized under dry or wet air conditions.

2.6 Infrared (IR) Spectroscopy

The IR measurements were performed on a Shimadzu IRAffinity-1 equipped with ATR module. Prior to the measurements, the samples were dried at 30 ℃ in a vacuum chamber with continuous pumping overnight.

2.7 Thermogravimetric (TG) measurement

The thermogravimetric analysis was performed with a Seiko Instruments Inc. Exstar TG/DTA 6200 instrument. Samples were placed on an open platinum sample pan. The experiment was conducted in synthetic air at 2 ℃/min heating rate.

2.8 Synchrotron X-ray single-crystal diffraction measurement

Synchrotron X-ray single-crystal diffraction measurement was carried out at Synchrotron Radiation Facility (SPring-8, beam line: BL40XU, Harima, Hyogo, Japan). The synchrotron X-ray beam was 0.78202 Å of wavelength and 3.39×10^8 photon/sec of photon flux (with attenuator). The X-ray beam was focused by zone plate. The micro-beam size at the sample position was 1.44 μm (V) × 3.66 μm (H). The diffraction data were corrected on a RIGAKU CCD camera Saturn 724 in steps of 1 ° over the total ω range of 270 °. A needle-like crystal ($95 \times 11 \times 8\ \mu m^3$) was selected from the sample and was fixed using epoxy glue onto the sharpened tip of glass capillary.

Crystal data for $C_{32}H_{16}O_{16}Zn_3 \cdot 5H_2O \cdot 2H_3O$: colorless needle, $95 \times 11 \times 8\ \mu m^3$, orthorhombic, $Pna2_1$, $a = 19.4674(4)$, $b = 5.92693(11)$, $c = 31.1266(7)$, $V = 3591.45(12)$ Å^3, $Z = 4$, $T = 223$ K, $2\theta_{min} = 2.716$ °, $2\theta_{max} = 28.105$ °, synchrotron X-ray beam radiation, $\lambda = 0.78202$ Å, $R_1 = 0.0287$, $wR_2 = 0.0682$. CCDC–1422942 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

As the minor component, small amount of Zn atom, Zn4, connects with one ortho-phthalate and four water molecules (Figure S5). The sum of occupancy factor of Zn atoms was constrained by

SUMP command. Because the occupancy factor of Zn4 is 7.8%, the frame of MOF fiber are mainly formed by Zn1, Zn2 and Zn3 in Figure 4.

2.9 Electrical conductivity measurement

The electrical conductivity of the Zn-MOF fiber and the calcined sample was measured by using a DC two-prove method with voltage sweep mode (Semiconductor Parameter Analyzer 4156A, Hewlett-Packard). Prior to the measurements, chromium electrode with a 20-μm gap and 50-nm thickness was deposited on a glass substrate by a DC magnetron sputtering. On the patterned gap electrode, the Zn-MOF fiber was prepared by the drop-casting method in the same manner (as mentioned above). After vaporizing DMF under wet air, the Zn-MOF fiber bridged the gap electrode. The current-voltage characteristics were examined before and after calcination of Zn-MOF fiber at 500 ºC for 30 min in the air.

4. Supporting Figures

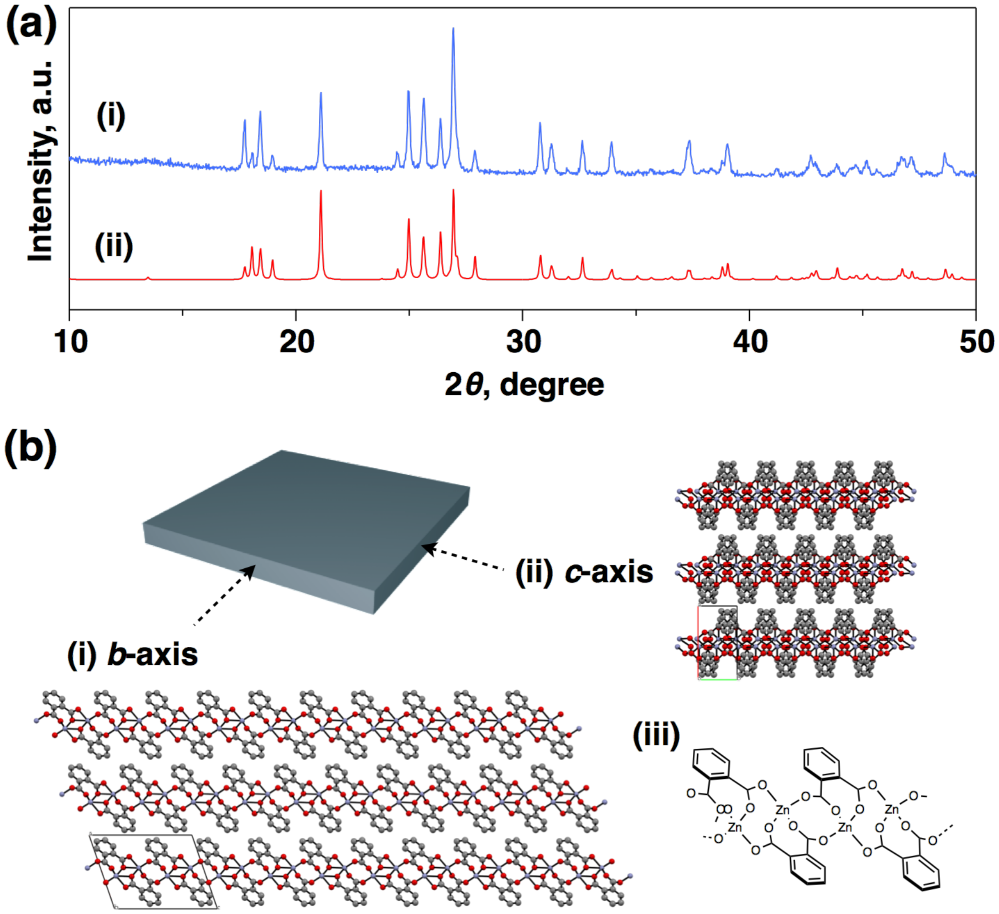

Fig. S1 (a) Comparison of XRD diffraction patterns: (i) as-prepared MOF powder in this study and (ii) calculated XRD pattern from the cif file (CCDC-908149; ref. 13). (b) representative crystal structure from (i) *b*-axis, (ii) *c*-axis, and (iii) chemical structure drawing of repeating unit.

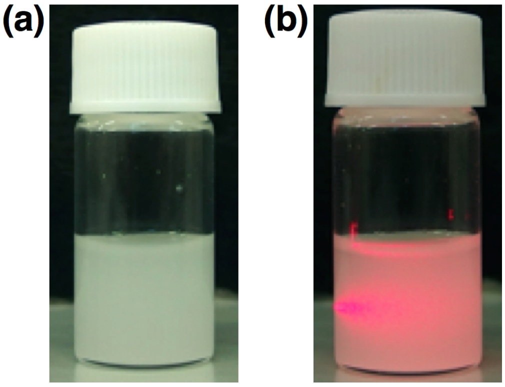

Fig. S2 Photographs of the DMF dispersion of as-prepared Zn-MOF powder (a, under room lighting; b, with red laser irradiation). The concentration of Zn-MOF sample in DMF is 2 mg/mL.

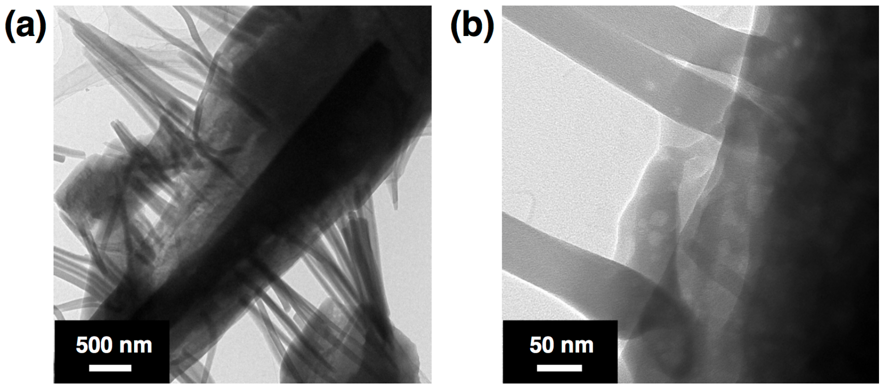

Fig. S3 TEM images of the MOF crystal surface in the process of the fiber growing, taken at (a) moderate and (b) high magnification.

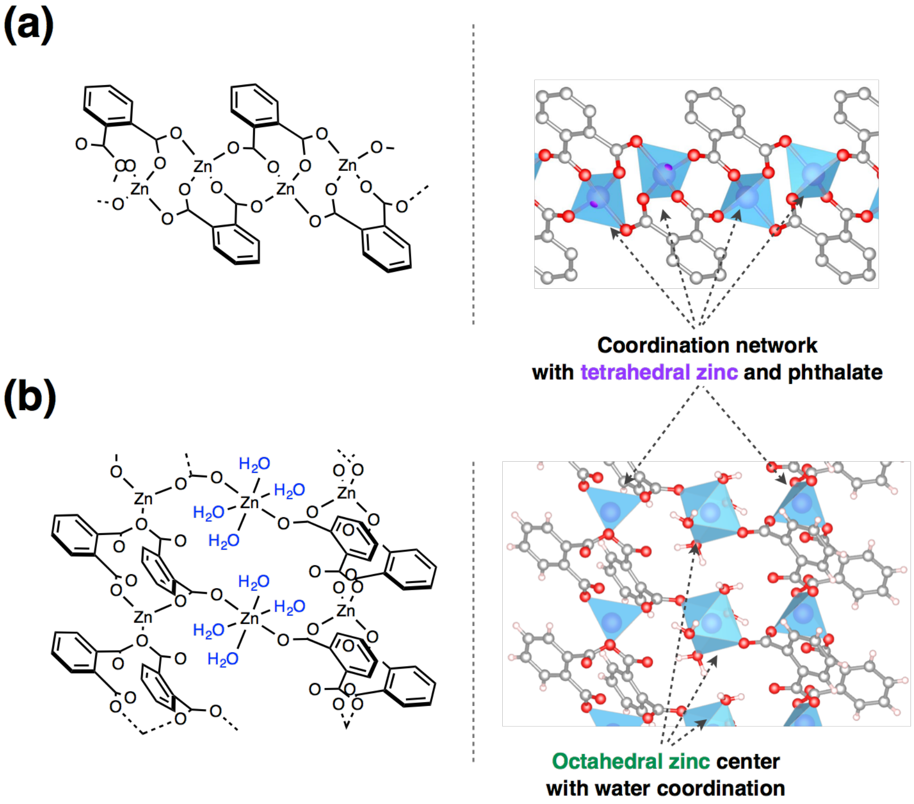

Fig. S4 Comparison of coordination network structure of (a) MOF sheet and (b) MOF fiber.

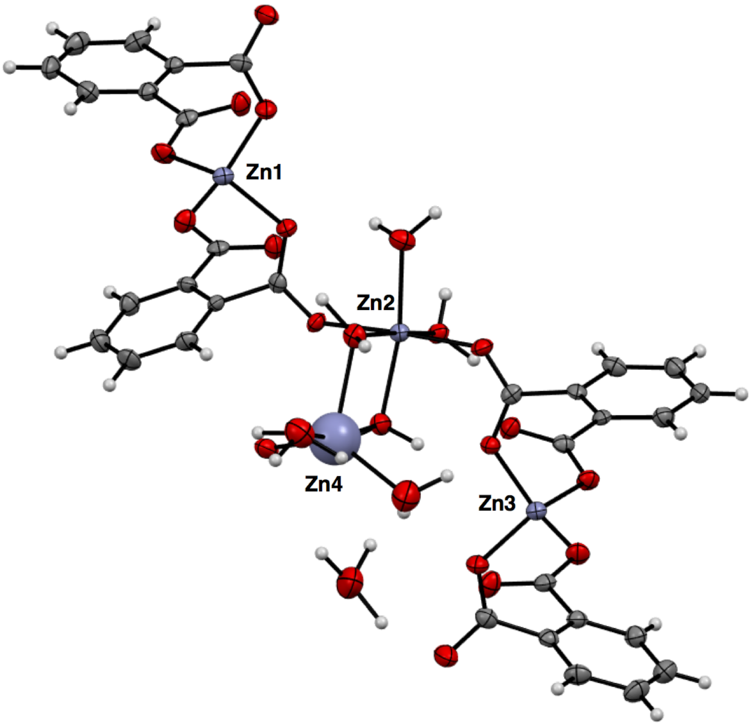

Fig. S5 An ORTEP drawing of the monomeric unit structure including Zn4 with a low occupancy factor (7.4%).

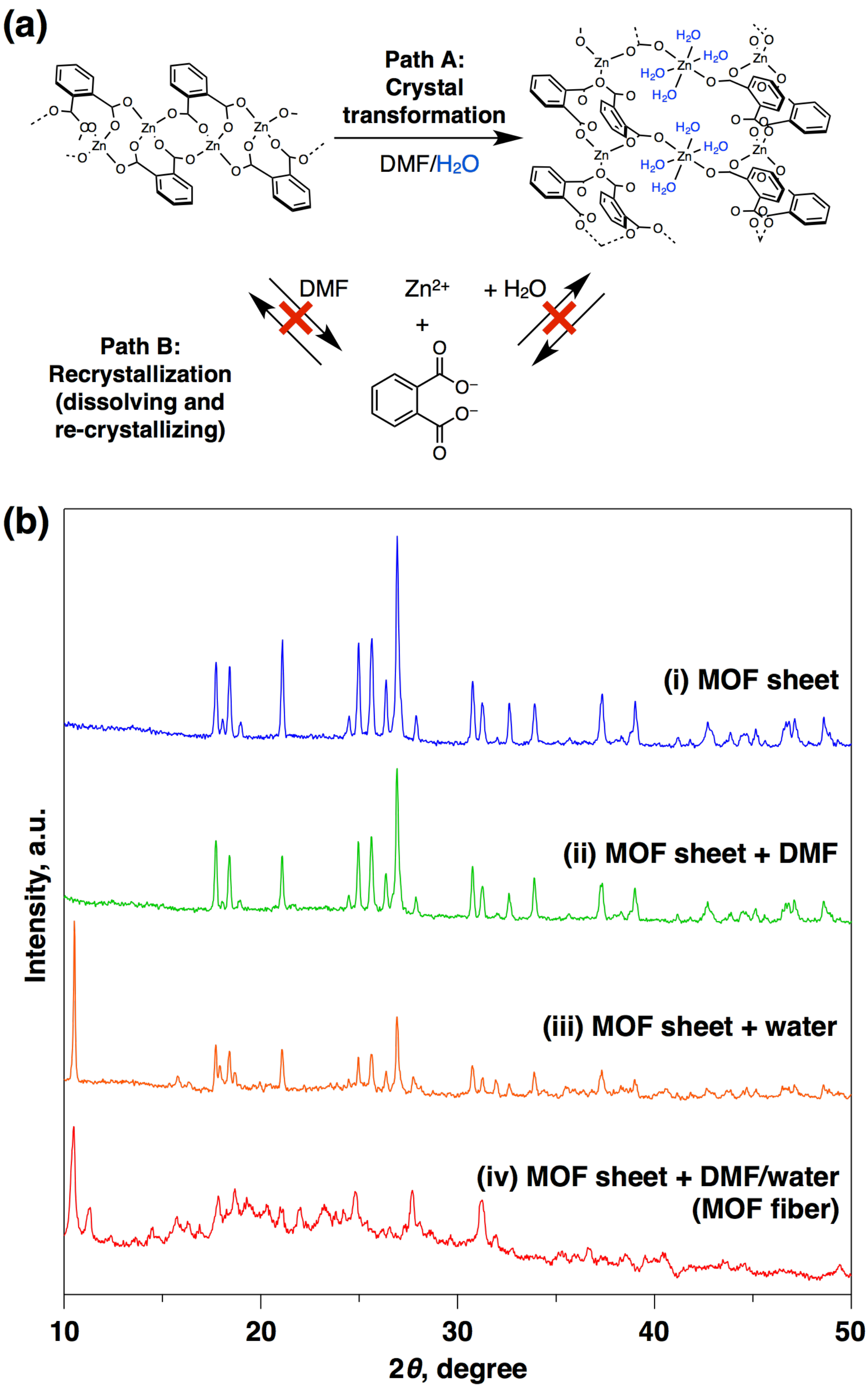

Fig. S6 (a) Possible pathway for structural change from a MOF sheet to a MOF fiber: (Path A) direct crystal transformation and (Path B) recrystallization including dissolving and recrystallizing processes. (b) Comparison of XRD diffraction patterns: (i) as-prepared MOF sheet, (ii) MOF sheet exposed to DMF, (iii) MOF sheet exposed to DMF, and (iv) MOF sheet exposed to DMF with humid environment (MOF fiber).

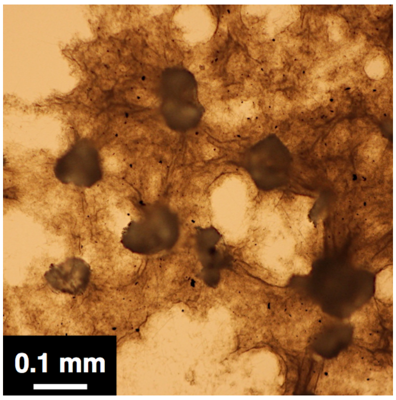

Fig. S7 An optical microscope image of the MOF sheet powder exposed to water, corresponding to Figure S6b-iii.