Supplementary Information

Improved optical quality of heteroepitaxially grown metal–organic framework thin films by modulating the crystal growth

Yuka Koseki,[a] Kenji Okada,[*a] Shotaro Hashimoto,[b] Shun Hirouchi, [b] Arisa Fukatsu [a] and Masahide Takahashi [*a]

[a] *Department of Materials Science, Graduate School of Engineering, Osaka Metropolitan University, Sakai, Osaka, 599–8531, Japan.* [b] *Department of Materials Science, Graduate School of Engineering, Osaka Prefecture University, Sakai, Osaka, 599–8531, Japan.*

Synthesis of the $Cu_2(bdc)_2$dabco thin film with a three times-thicker $Cu(OH)_2$-oriented thin film

A three times thicker $Cu(OH)_2$-oriented film on a Si wafer (~15 mm × 20 mm) was prepared by three-times repeated transfer process of $Cu(OH)_2$. H_2bdc (4 mM) and dabco (256 mM) were dissolved in methanol (50 mL) at 40 ºC in advance. A $Cu(OH)_2$-oriented film was immersed in 50 mL of the solution and left for an hour at 60 ºC. Subsequently, the film was removed from the solution, washed with ethanol, and dried.

Synthesis of the $Cu_2(bdc)_2$dabco thin film at 40 ºC

H_2bdc (4 mM) and dabco (256 mM) were dissolved in methanol (50 mL) at 40 ºC in advance. A $Cu(OH)_2$-oriented film on a Si wafer was immersed in 50 mL of the solution and left for an hour at 40 ºC. Subsequently, the film was removed from the solution, washed with ethanol, and dried.

Synthesis of the $Cu_2(bdc)_2$dabco thin film at 80 ºC

H_2bdc (4 mM) and dabco (256 mM) were dissolved in methanol (50 mL) at 40 ºC in advance. The solution (50 mL) was transferred to an autoclave. A $Cu(OH)_2$-oriented film on a Si wafer was immersed in the solution in an autoclave and left for an hour at 80 ºC. After an hour, the autoclave was cooled to room temperature. Subsequently, the film was removed from the solution, washed with ethanol, and dried.

Synthesis of oriented $Cu_2(bdc)_2$ thin films with modulator

$Cu_2(bdc)_2$ thin films on Si wafer (~15 mm × 15 mm) were fabricated by a reported method[1]. Saturated ligand solutions (2.86 mL of water and 7.14 mL of ethanol mixture containing 1 mg of H_2bdc) were prepared. Diluted acetic acid (1742 mM) and sodium acetate (molar ratio 1:9) were added to the saturated ligand solution at predefined concentration up to 10 mM and dissolved with sonication. $Cu(OH)_2$ oriented films on Si wafers were immersed in the solution and left for 10 min at room temperature. After 10 min, the films were removed from the solution, washed with ethanol, and dried by an air gun.

Synthesis of $Cu_2(2,6\text{-ndc})_2$dabco oriented thin films with modulator

$Cu_2(2,6\text{-ndc})_2$dabco thin films on Si wafer (~15 mm × 20 mm) were fabricated by a modified reported method[2]. 2,6-H_2ndc (1 mM) and dabco (64 mM) were dissolved in methanol at room temperature. Diluted acetic acid (1742 mM) and sodium acetate (molar ratio 9:1) were added to the methanol solution at predefined concentration up to 20 mM and dissolved with sonication. $Cu(OH)_2$ oriented films on Si wafers were immersed in 30 mL of the solution and left for 2 hours at 60ºC. After 2 hours, the films were removed from the solution, washed with ethanol, and dried by an air gun.

Synthesis of a random $Cu_2(bdc)_2$dabco thin film on a silica glass

A random assembly film of $Cu(OH)_2$ nanobelts on a silica glass (~20 mm × 20 mm)was fabricated by drop cast of dispersed solution[3] of $Cu(OH)_2$. H_2bdc (4 mM) and dabco (256 mM) were dissolved in methanol at 40ºC. Diluted acetic acid (1742 mM) and sodium acetate were added to the methanol solution as the modulator (30 mM) where the molar ratio of acetic acid and sodium acetate was fixed at 9:1 and dissolved with sonication. A random $Cu(OH)_2$ thin film was immersed in 10 mL of the reaction solution in a teflon container and left for an hour at 60 ºC. Subsequently, the films were removed from the solution, washed with ethanol, and dried by an air gun. Thickness of the obtained random $Cu_2(bdc)_2$dabco thin film was 384 nm.

Measurement of degree of in-plane orientation

The degrees of in-plane orientation were determined using the full width at half maximum (FWHM) of the peaks of the azimuthal angle profiles (φ scan profiles) in the same method as our previous work[4]. The equation (1) was used to calculate the degrees of in-plane orientation (F_{XRD}).

$$F_{XRD} = \frac{180° - FWHM}{180°} \#(1)$$

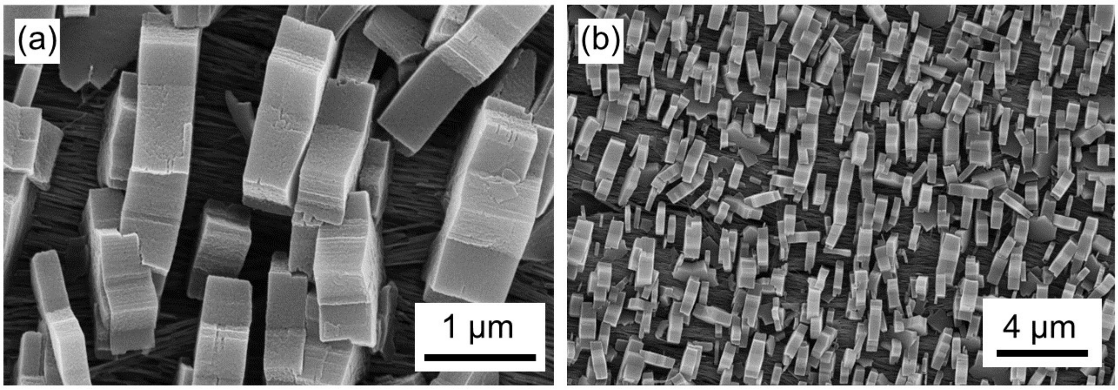

Fig. S1 (a, b) SEM images of $Cu_2(bdc)_2$dabco thin films fabricated without a modulator. Direction of *a*- and *c*- axis is vertical direction and horizonal direction of images, respectively. The $Cu_2(bdc)_2$dabco thin films was prepared according to our previous study[2]. The films were fabricated using methanol solution (50 mL) including H_2bdc (4 mM) and dabco (256 mM) at 60 ºC for an hour.

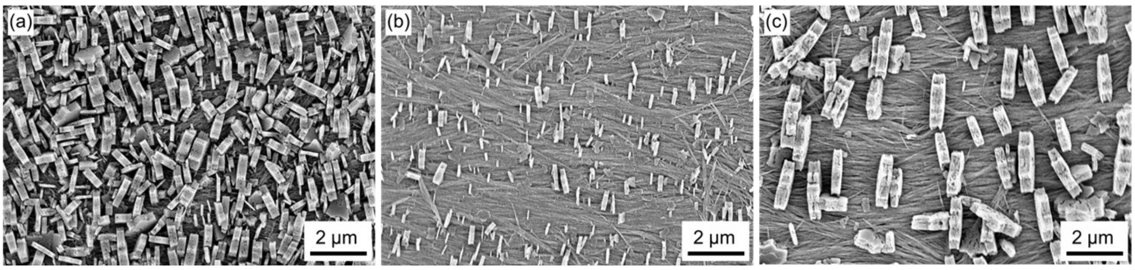

Fig. S2 (a) An SEM image of the $Cu_2(bdc)_2$dabco thin film fabricated from a three-times thicker $Cu(OH)_2$ thin film. SEM images of $Cu_2(bdc)_2$dabco thin films fabricated at (b) 40 ºC and (c) 80 ºC.

The effect of amount of Cu source and reaction temperature on the crystal morphologies was investigated. Although number of crystals per area and size of crystals changed slightly in both cases, morphologies (aspect ratio) and orientation of crystals little change. Therefore, these conditions were not dominant factors for controlling the morphologies of the MOF crystals in order to fabricate high-quality $Cu_2(bdc)_2$dabco thin films.

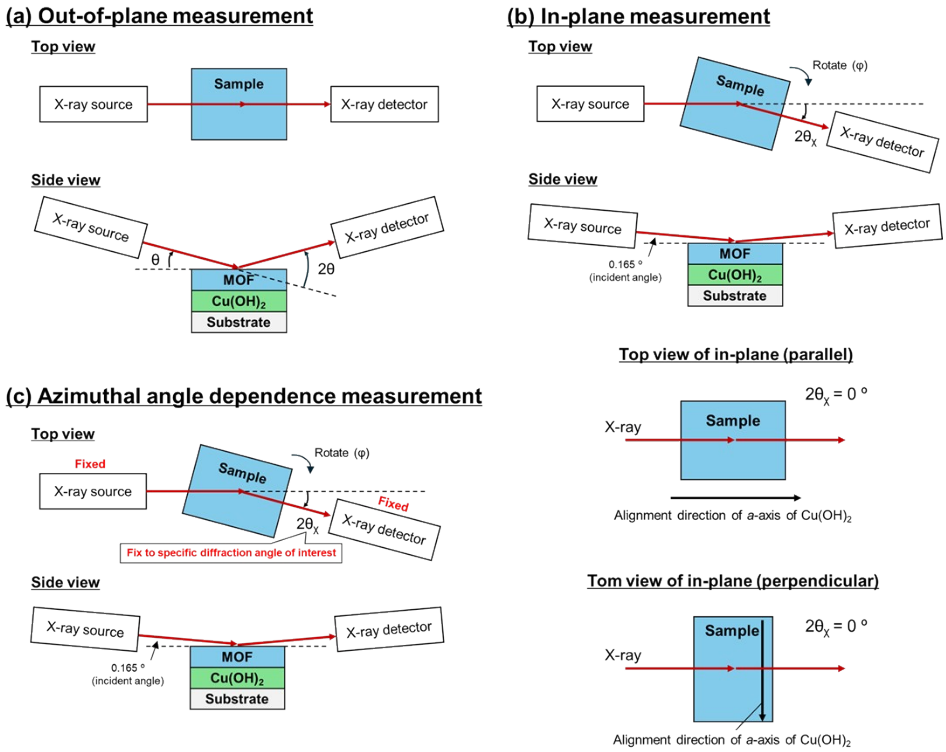

Fig. S3 Schematic illustration of the experimental setups characterize the MOF thin films for (a) out-of-plane, (b) in-plane and (c) azimuthal angle dependence measurements.

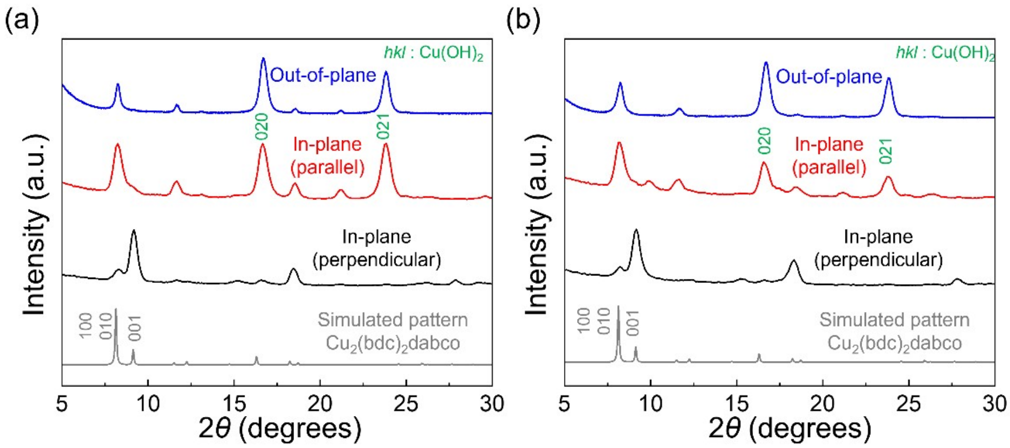

Fig. S4 XRD patterns of oriented $Cu_2(bdc)_2$dabco thin films fabricated (a) without and (b) with a modulator (30 mM).

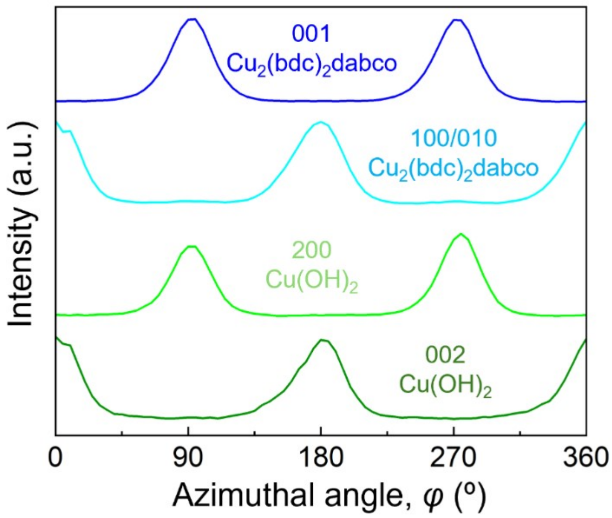

Fig. S5 φ scan profiles for the 001 and 100/010 reflection of $Cu_2(bdc)_2$dabco and the 200 and 002 reflection of $Cu(OH)_2$ in oriented $Cu_2(bdc)_2$dabco thin films fabricated with a modulator (30 mM). The X-ray incident angle is perpendicular to the longitudinal direction of the nanobelts at φ= 0°. The in-plane orientation of $Cu(OH)_2$ and $Cu_2(bdc)_2$dabco in the film was calculated to be 82% and 81% from the full width at half maximum.

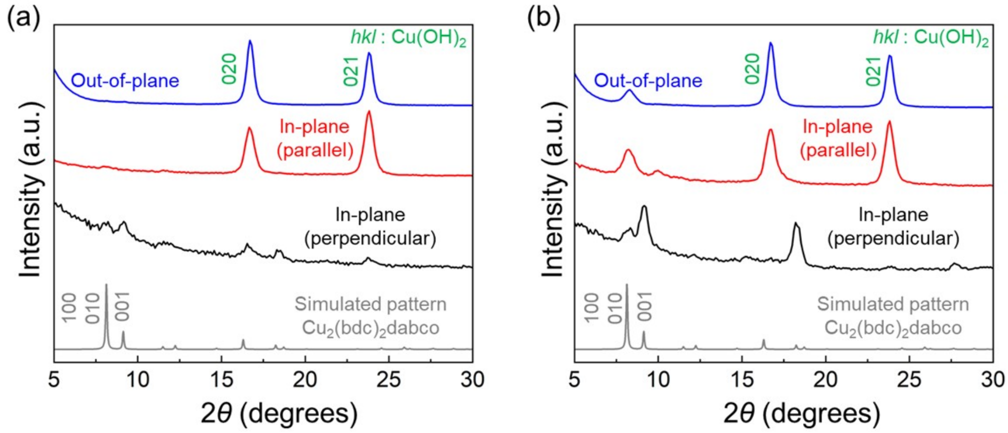

Fig. S6 XRD patterns of the $Cu_2(bdc)_2$dabco thin films (reaction time: 2.5 min) fabricated (a) without and (b) with a modulator (30 mM).

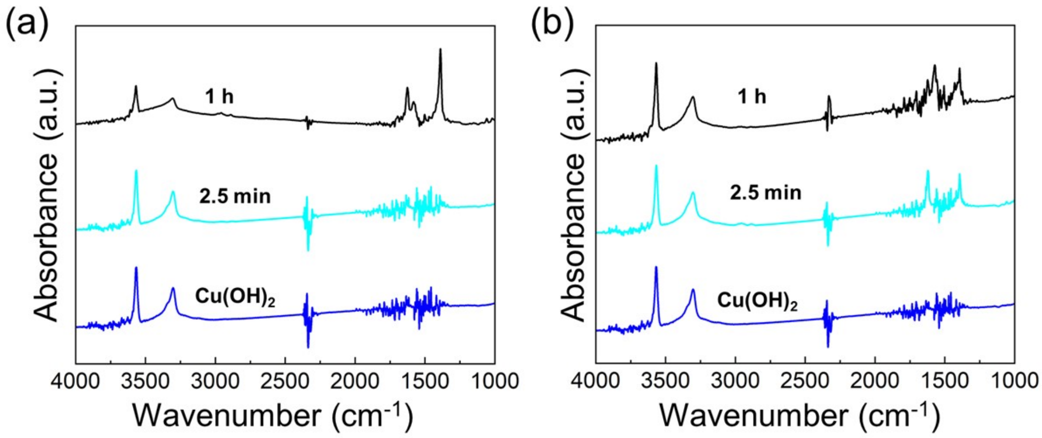

Fig. S7 FT-IR spectra of the $Cu(OH)_2$ oriented thin films and $Cu_2(bdc)_2$dabco thin films fabricated (a) without a modulator and (b) with 30 mM of a modulator in varied reaction times.

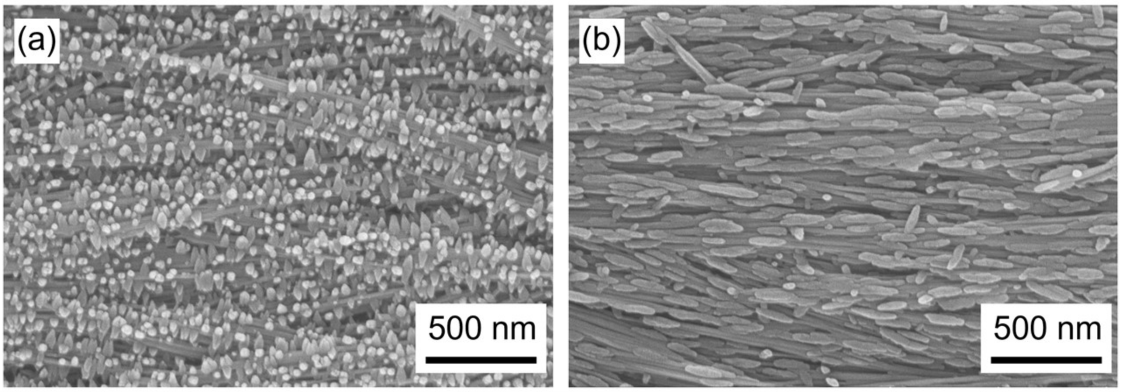

Fig. S8 SEM images of $Cu_2(bdc)_2$ thin films fabricated (a) without and (b) with a modulator (10 mM).

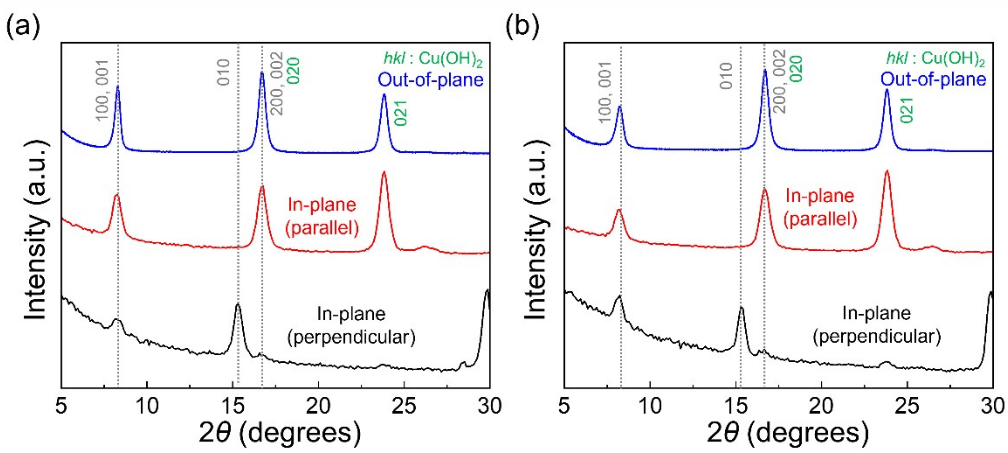

Fig. S9 XRD patterns of $Cu_2(bdc)_2$ thin films fabricated (a) without and (b) with a modulator (10 mM).

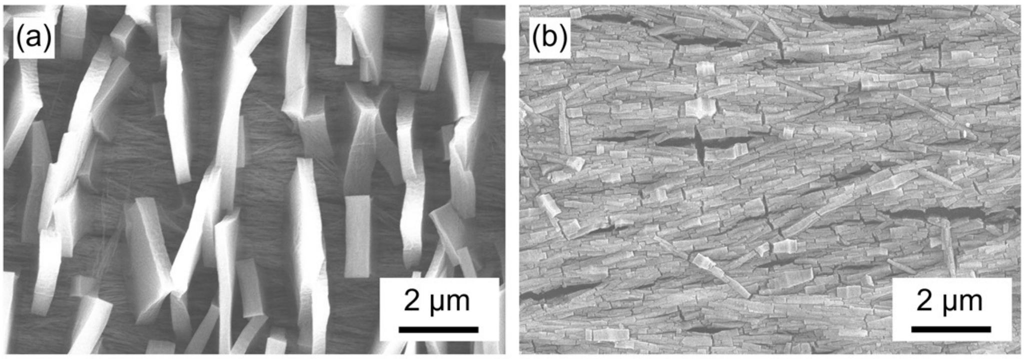

Fig. S10 SEM images of Cu_2(2,6-ndc)$_2$dabco thin films fabricated (a) without and (b) with a modulator (20 mM). Direction of *a*- and *c*- axis is vertical direction and horizonal direction of images, respectively.

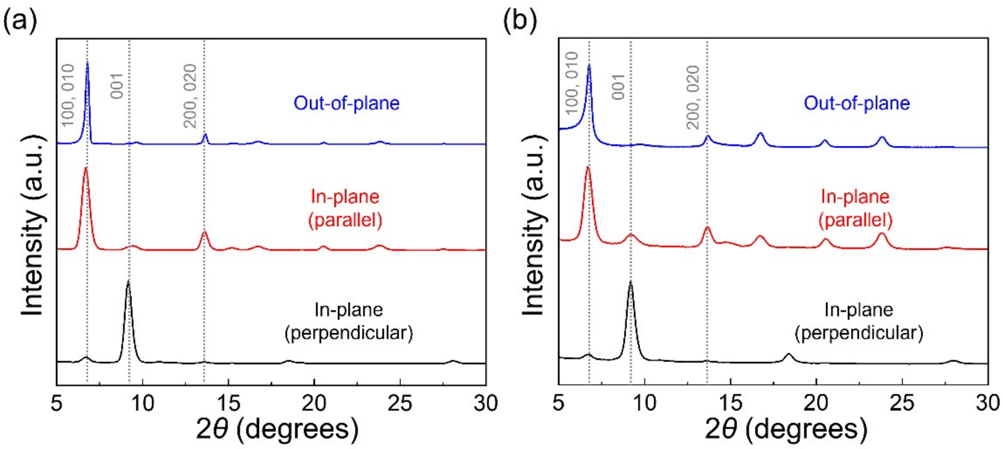

Fig. S11 XRD patterns of Cu_2(2,6-ndc)$_2$dabco thin films fabricated (a) without modulator and (b) with a modulator (20 mM).

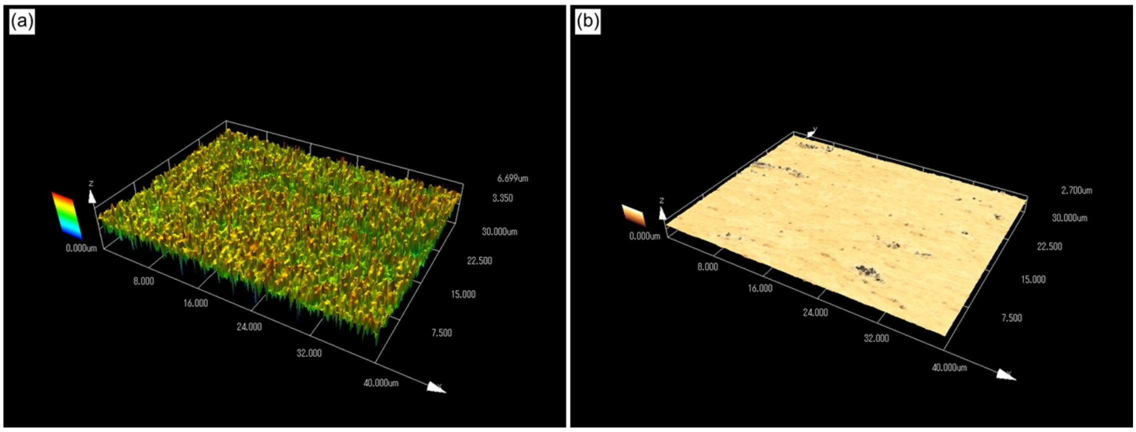

Fig. S12 Images of three-dimensional morphologies of surface of $Cu_2(bdc)_2$dabco fabricated (a) without and (b) with a modulator (30 mM) measured by CLSM.

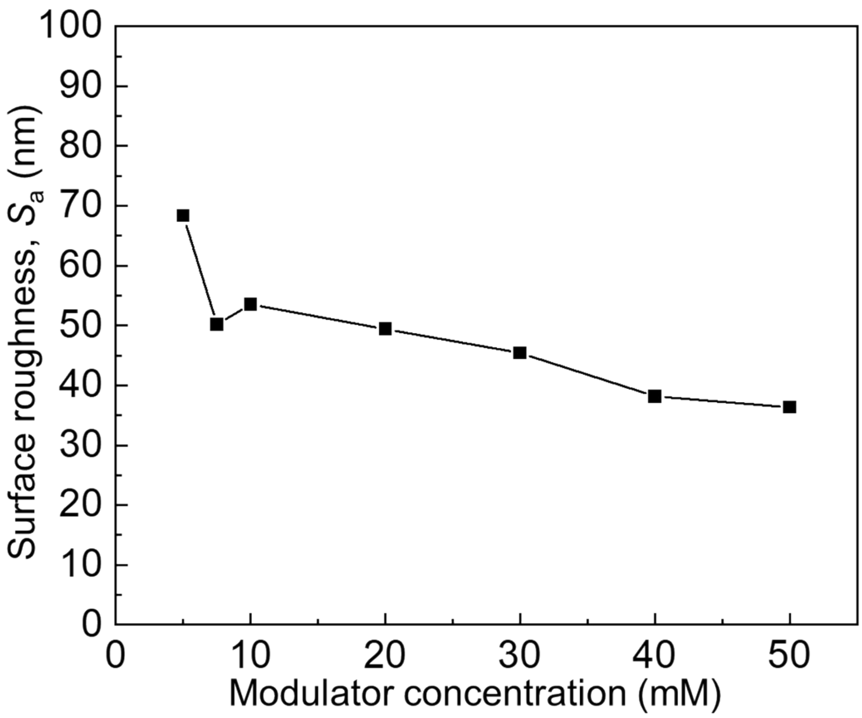

Fig. S13 Surface roughness measured by AFM of $Cu_2(bdc)_2$dabco thin films fabricated with each concentration of the modulator.

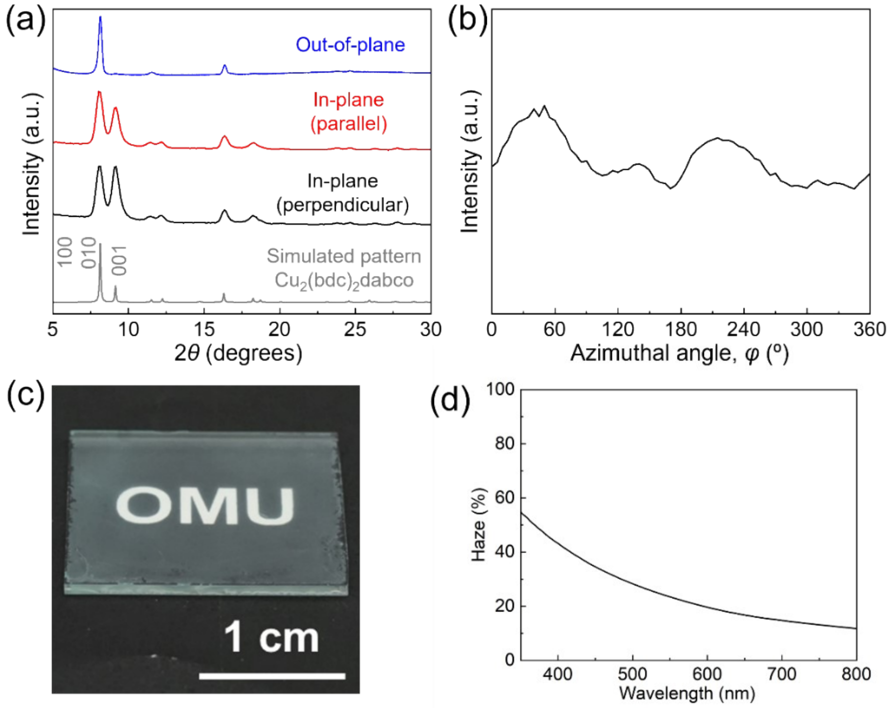

Fig. S14 (a) XRD patterns , (b) φ scan profiles for the 001 reflection of $Cu_2(bdc)_2$dabco, (c) a photo image and (d) haze spectrum of the random $Cu_2(bdc)_2$dabco thin film fabricated with a modulator (30 mM).

Reference

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2. K. Okada, M. Nakanishi, K. Ikigaki, Y. Tokudome, P. Falcaro, C. J. Doonan and M. Takahashi, *Chem. Sci*., 2020, **11**, 8005–8012.
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4. B. Baumgartner, K. Ikigaki, K. Okada and M. Takahashi, *Chem. Sci*., 2021, **12**, 9298-9308