Electronic Supplementary Information (ESI) for

A highly crystalline oriented metal–organic framework thin film with an inorganic pillar

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1. Experimental details

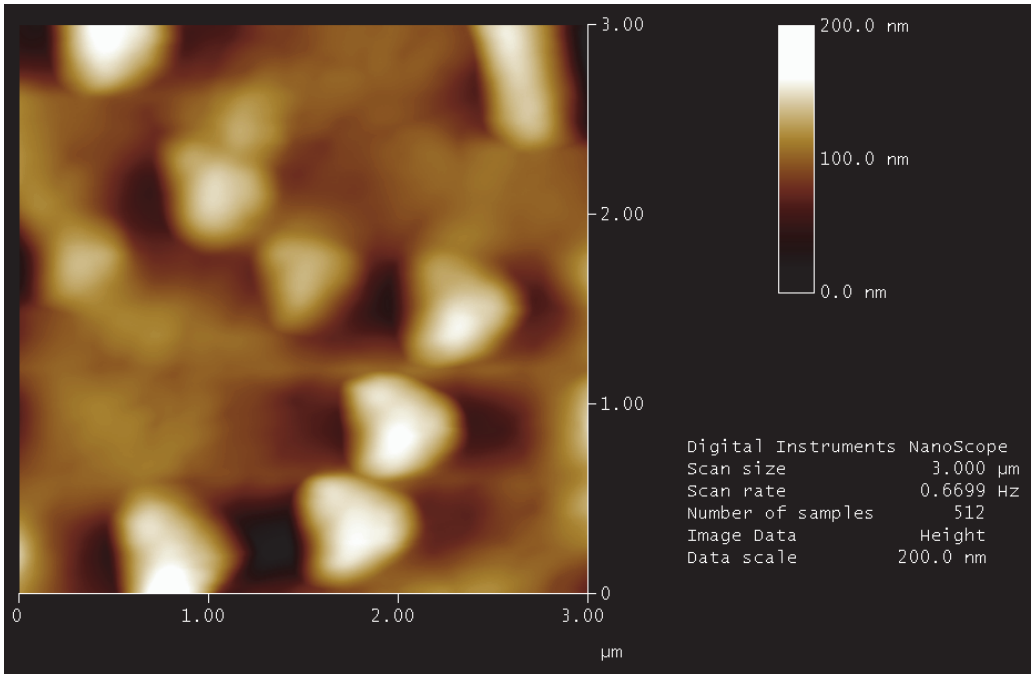
Materials: 4-mercaptopyridine, $Cu(BF_4)_2 \cdot 6H_2O$, 4,4′-bipyridyl (bpy), $(NH_4)_2SiF_6$, ethanol (EtOH) were purchased from Sigma-Aldrich Chemical Co., Tokyo Chemical Industry Co., Ltd., Wako Pure Chemical Industries, Ltd. These materials were used without any purification. The Au substrate was purchased from Geomatec Co., Ltd. It was prepared by evaporating 5 nm of chromium, followed by 100 nm of gold, onto polished silicon wafers (purchased from Nilaco Corp.). The substrate was used after washing with pure EtOH and H_2-annealing treatment.

Fabrication of SIFSIX-1-Cu thin film: First, the Au substrate was immersed in a solution of 4-mercaptopyridine for a day to be functionalized with a self-assembled monolayer (SAM). After a day, the substrate was washed with ethanol and dried with N_2 gas. Next, this substrate was soaked in ethanol solutions of $Cu(BF_4)_2 \cdot xH_2O$ (20 mM) for 10 min, bpy (100 mM) for 5 min and H_2O/ethanol (1/9) solution of $(NH_4)_2SiF_6$ (20 mM) for 10 min in this order at 213 K for 30 cycles. After each immersion process, the substrate was washed with H_2O/ethanol (1/9) solution every immersing.

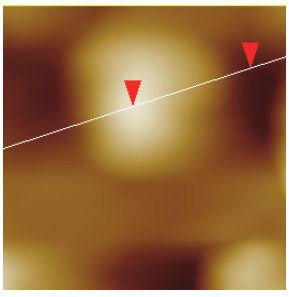
Methods: Synchrotron X-ray diffraction (XRD) measurements were performed on the film using a multi-axis diffractometer (Kohzu-Seiki TDT-17) with a scintillation detector installed on the BL13XU beamline of SPring-8. The incident X-ray was monochromatized to 8 keV (λ = 1.549 Å) with a Si(111) double-crystal monochromator. He gas was supplied during the measurements. Out-of-plane XRD measurement was carried out in a typical θ–2θ scattering geometry. Azimuthal-angle dependence measurements were performed at 001 peak position in the out-of-plane geometry. For the in-plane XRD (grazing-incidence (GI) XRD mode), strong diffraction can be observed on the condition that the X-ray incident angle (α) to the sample is below the critical angle. Therefore, the GIXRD measurement at the 200 peak position was performed before the in-plane XRD measurement, and the diffraction patterns were collected at α = 0.2°. A Soller slit (Huber 3030-I, 0.4°) was located between the sample substrate and the scintillation detector to reduce the effect of scattered background from the diffraction. The XRD pattern fittings in Fig. 3 were performed using the Topas program.[S1] By means of the Mercury software suite, simulated XRD patterns in Fig. 3 were obtained by means of the Mercury Software suite[S2]. Infrared reflection absorption spectra (IRRAS) data were collected using a NEXUS 670 FT-IR apparatus (Thermo Nicolet) and Refractor2™ Grazing Angle Accessory (Harrick Scientific Products). The sorption properties of the film were investigated using quartz crystal microbalance (QCM) measurements with a BELQCM system (MicrotracBEL). Before the measurements, the QCM sensors were activated at 353 K for 1 h under He gas flow inside the QCM chamber. Atomic force microscopy (AFM) images of SIFSIX-1-Cu thin film were obtained in tapping mode with NanoScope IIIa system (Bruker AXS K.K. Ltd.).

2. AFM image of thin film

(a)



(b)



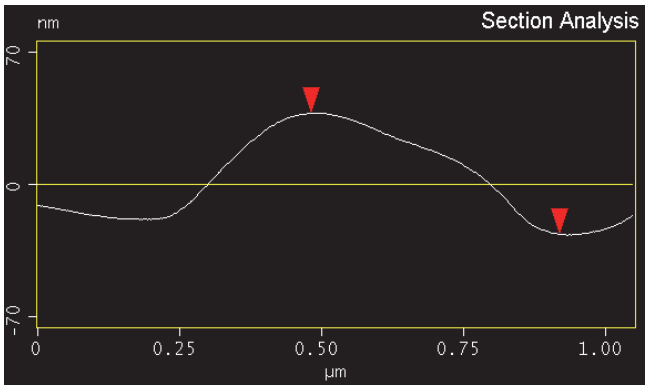
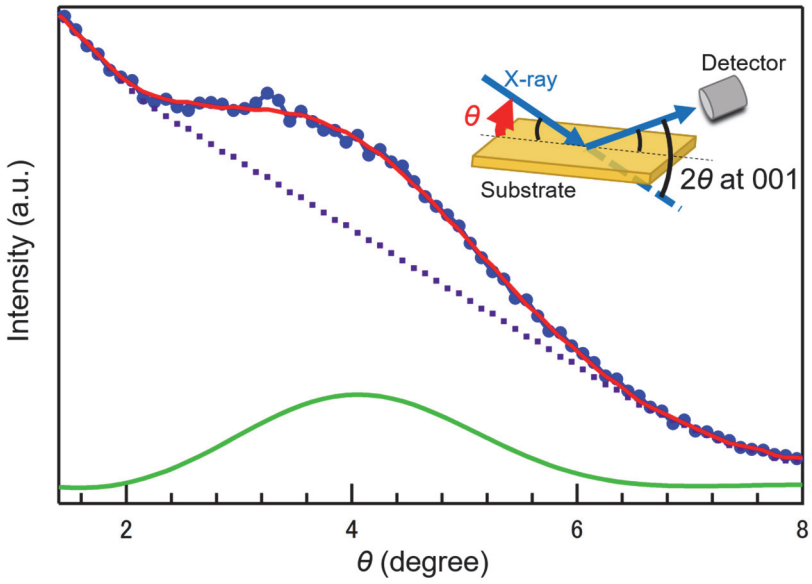


Fig. S1 AFM image of the SIFSIX-1-Cu thin film at RT. (a) Height mode in a large range (b, left) height mode in a small range and (b, right) section analysis.

3. Rocking curve and azimuthal angle scans

(a)



(b)

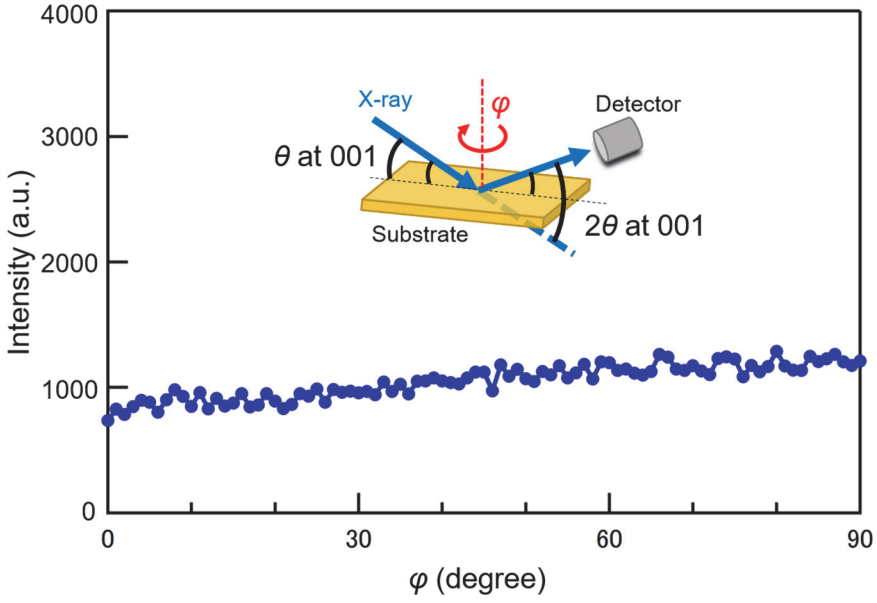


Fig. S2 (a) Rocking curve scan and (b) azimuthal-angle scan at the 001 position for SIFSIX-1-Cu. The absence of peak intensity dependence on the azimuthal angle means that the film is uniformly fabricated on the substrate.

4. References

S1. Bruker AXS, TOPAS V3: General profile and structure analysis software for powder diffraction data, Bruker AXS, Karlsruhe, Germany, 2005.

S2. Mercury: visualization and analysis of crystal structures, C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.*, 2006, **39**, 453–457.