Physical Vapor Deposition of an Oriented Metal–Organic Framework HKUST-1 Thin Film on an Insulating Substrate

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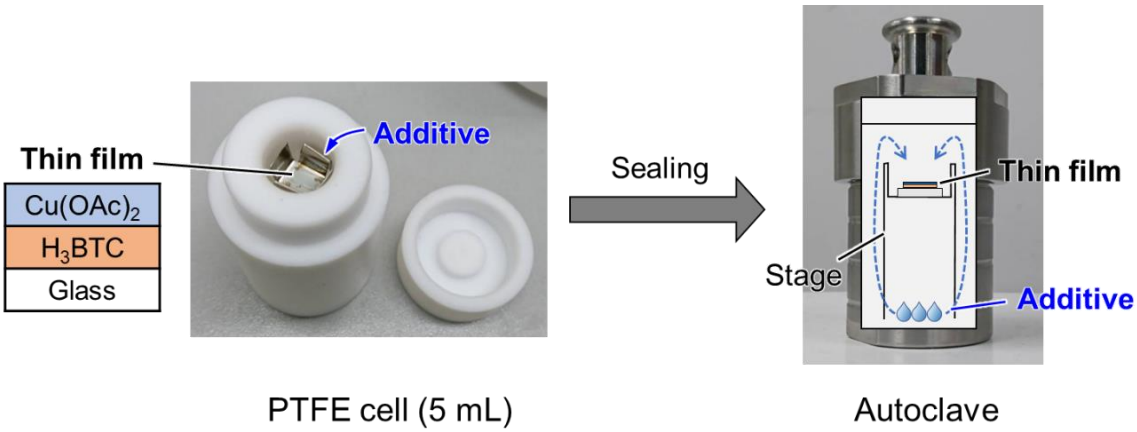

Fig. S1. Setup for the annealing of thin films with solvent vapor.

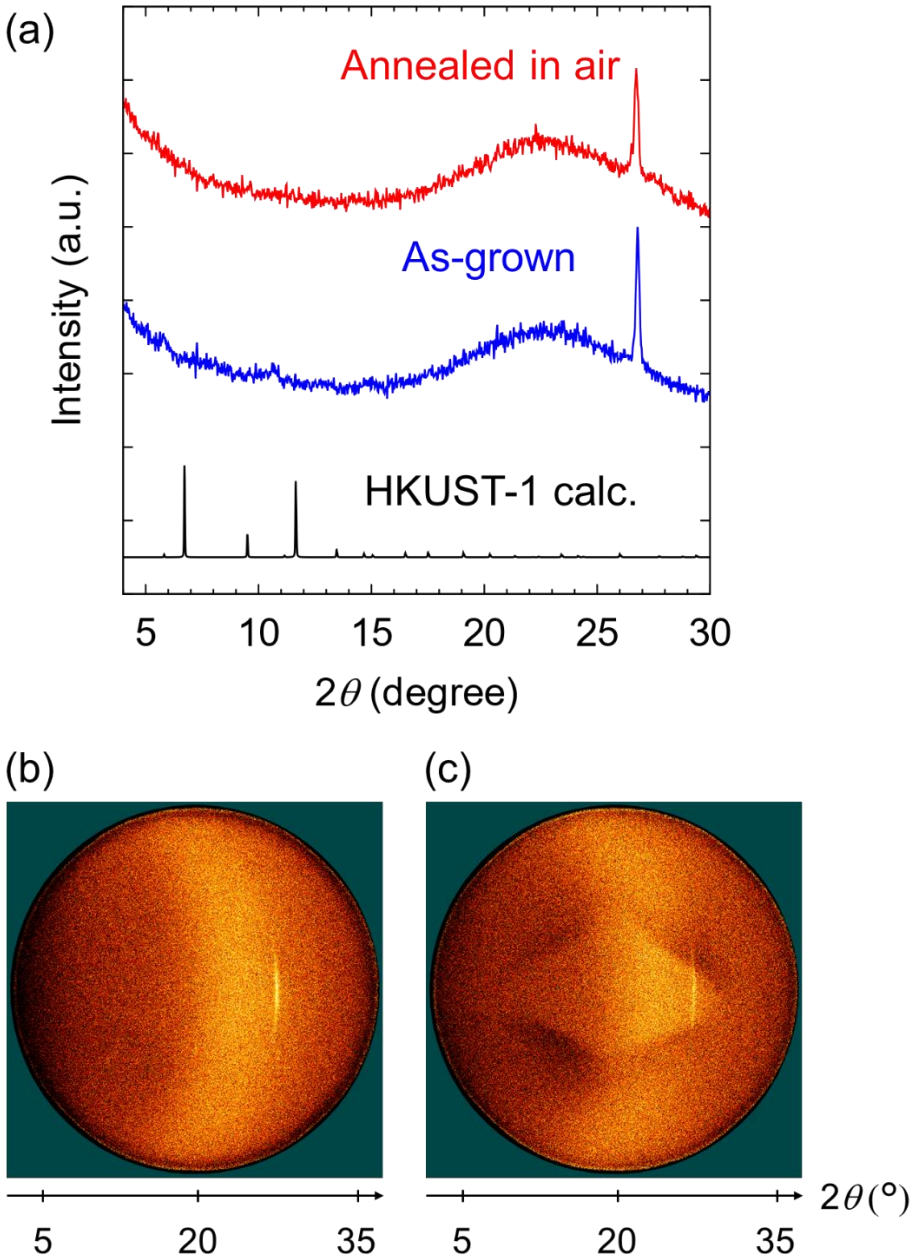

Fig. S2. (a) Out-of-plane X-ray diffraction patterns of the as-grown thin film and thin film annealed in air. Two-dimensional X-ray diffraction patterns of the (b) as-grown thin film and (c) thin film annealed in air.

Figure S2(a) shows the out-of-plane XRD patterns of the as-grown and annealed-in-air films. The XRD patterns do not show the diffraction peaks of HKUST-1. The peak at 2θ

= 26.8° observed for both films does not correspond with the precursors or HKUST-1 powder. The spot-like diffraction at 2θ = 26.8° indicates that the unidentified product is oriented out-of-plane (Figs. S2(b) and (c)). The peak at 2θ = 26.8° will be identified in future work because it disappears after annealing with solvent vapor.

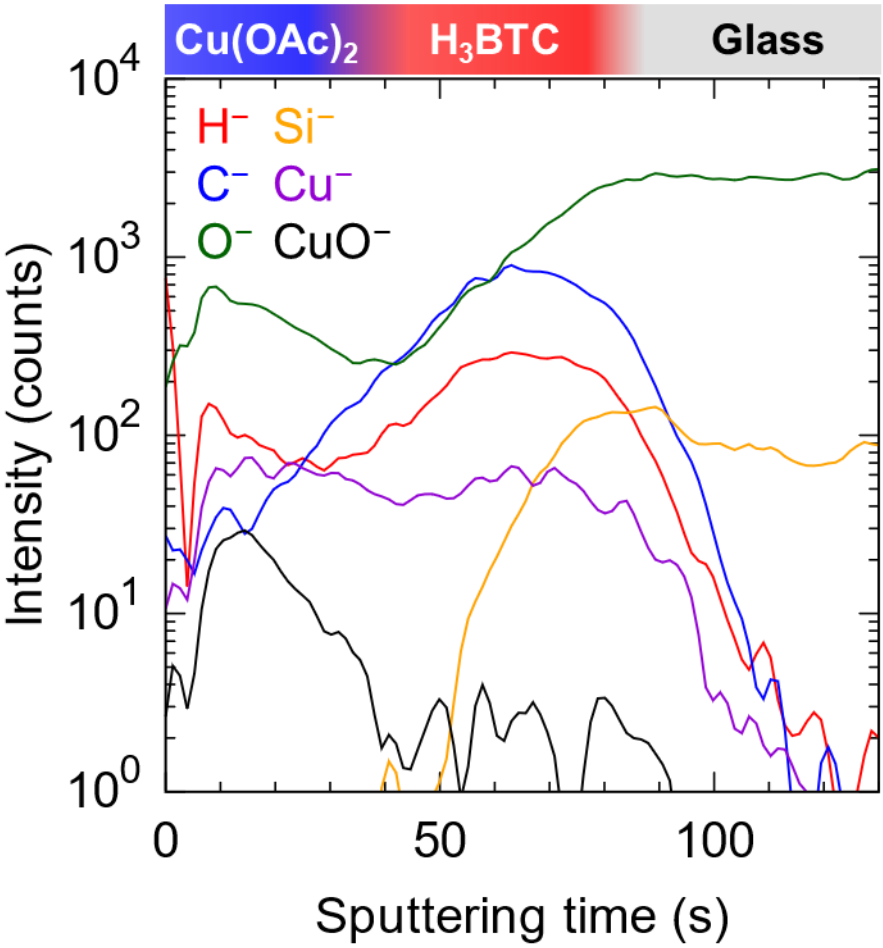

Fig. S3. Depth profiles of the chemical components of the as-grown thin film obtained by secondary ion mass spectroscopy.

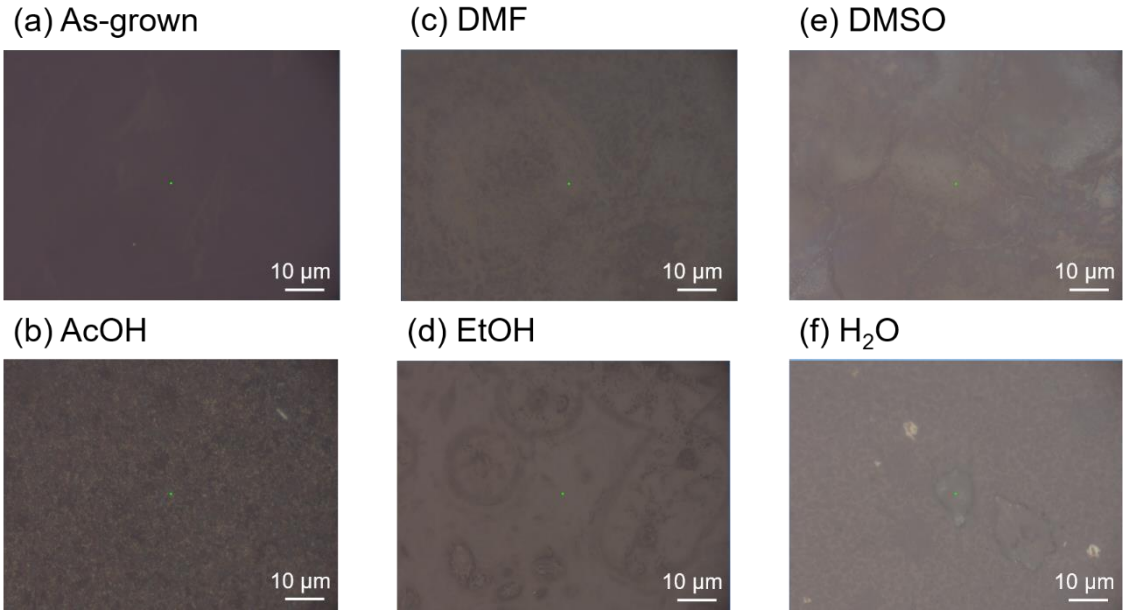

Fig. S4 Optical microscopy image of the thin films of (a) As-grown (before annealing) and annealed with (b) acetic acid (AcOH), (c) *N*,*N*-dimethylformamide (DMF), (d) ethanol (EtOH), (e) dimethyl sulfoxide (DMSO), and (f) water (H_2O)

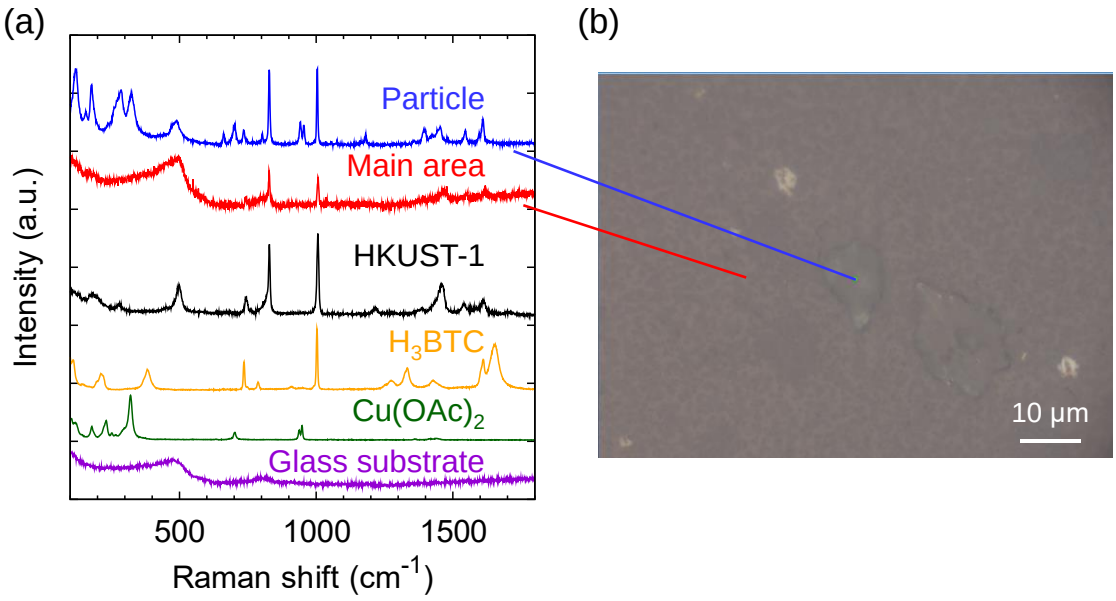

Fig. S5 (a) Raman spectra and (b) optical microscopy image of the film annealed with water vapor

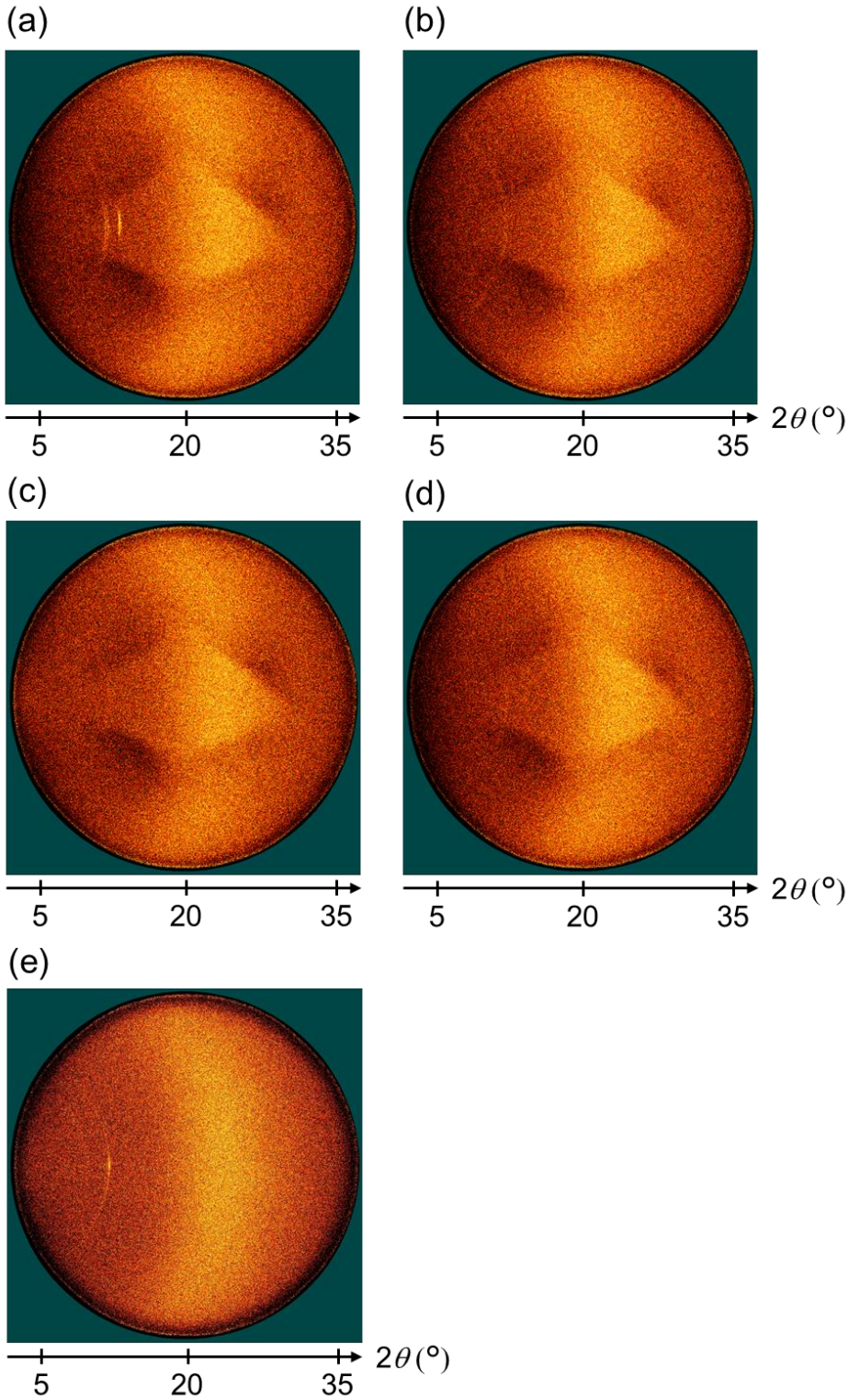

Fig. S6. Two-dimensional X-ray diffraction patterns of (a) water, (b) dimethyl sulfoxide, (c) *N*,*N*-dimethylformamide, (d) ethanol, and (e) acetic acid.

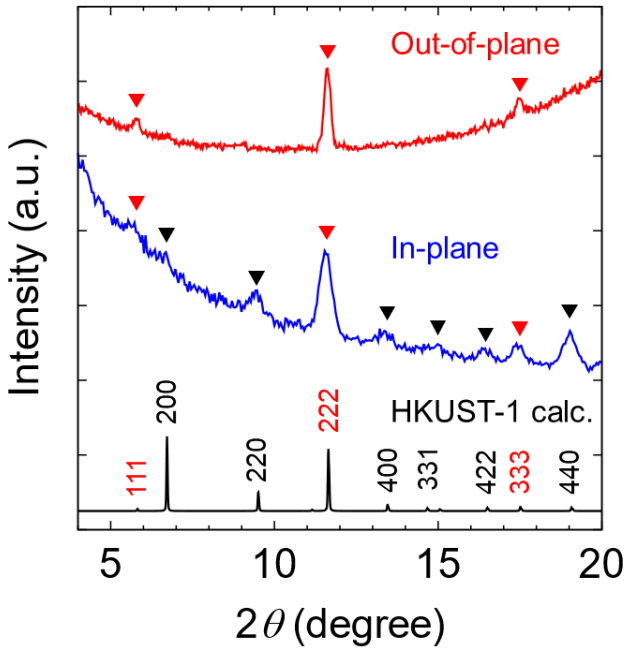

Fig. S7. Out-of-plane and in-plane XRD patterns of HKUST-1 thin film

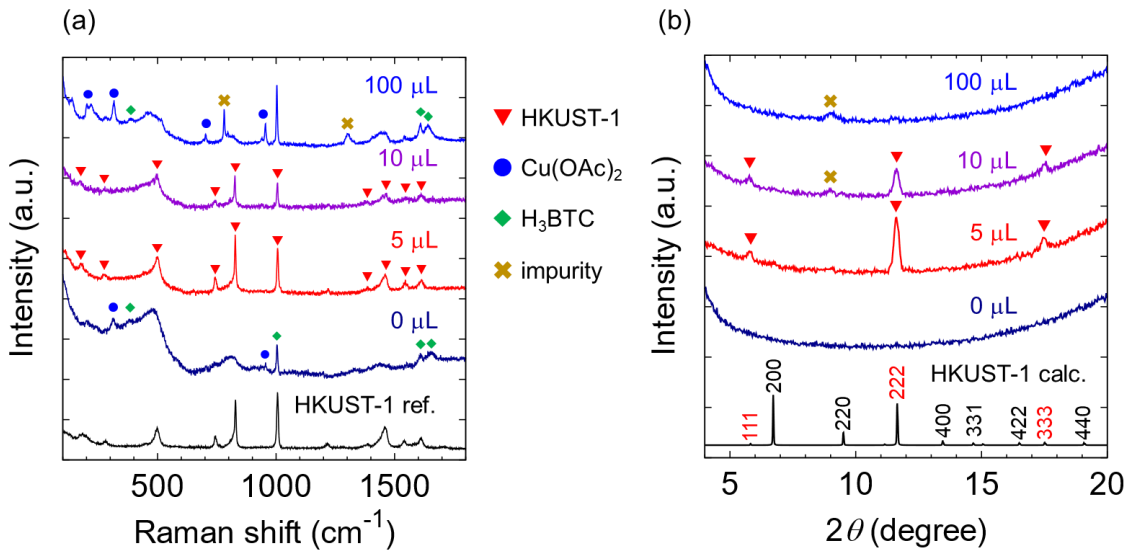

Fig. S8. (a) Raman spectra and (b) out-of-plane X-ray diffraction patterns of films annealed using different volumes of acetic acid.

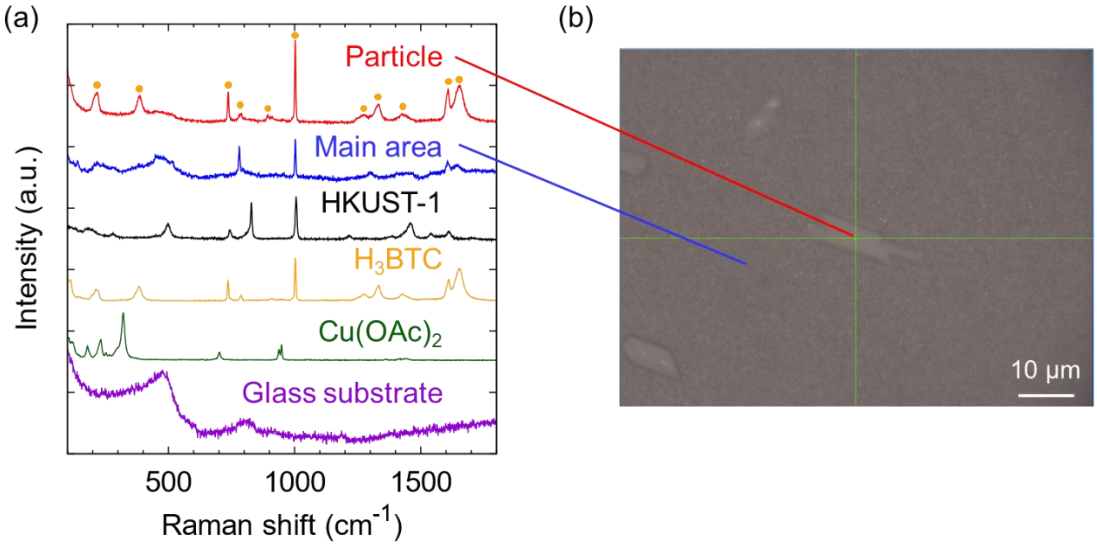

Fig. S9. (a) Raman spectra and (b) optical microscopy image of the film synthesized using a Cu:1,3,5-benzenetricarboxylate (BTC) stoichiometric ratio of 2:2.

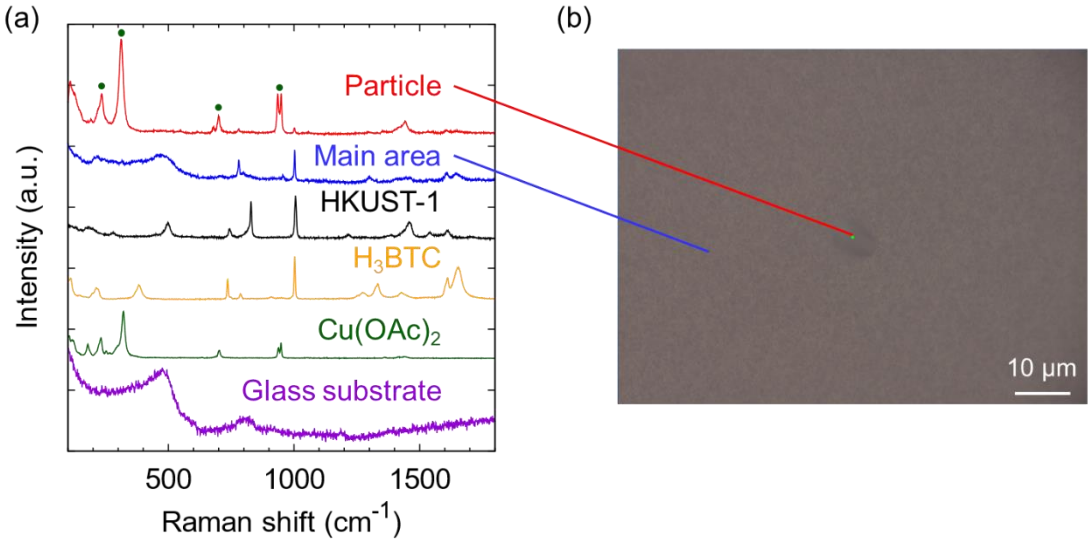

Fig. S10. (a) Raman spectra and (b) optical microscopy image of the film synthesized using a Cu:1,3,5-benzenetricarboxylate (BTC) stoichiometric ratio of 4:2.

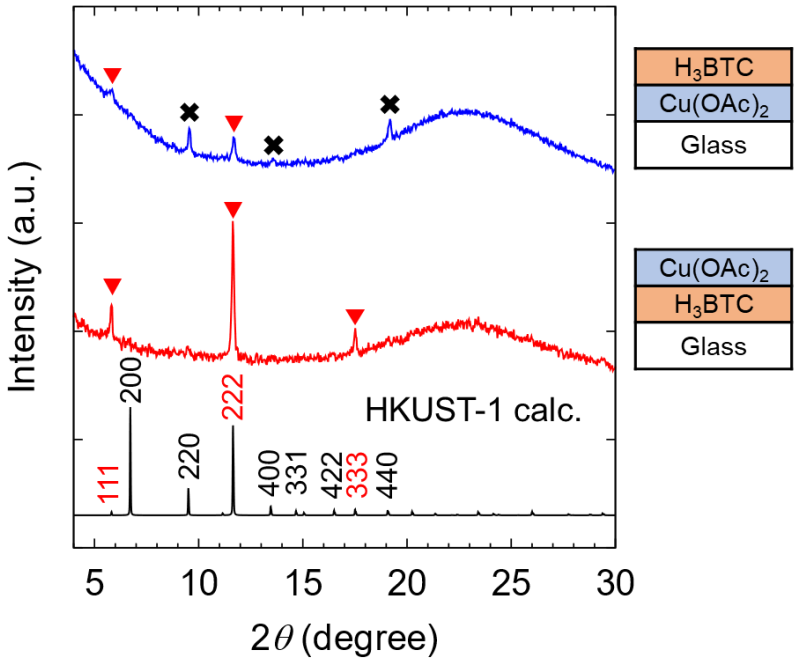

Fig. S11. out-of-plane X-ray diffraction pattern of thin films with different deposition sequence.

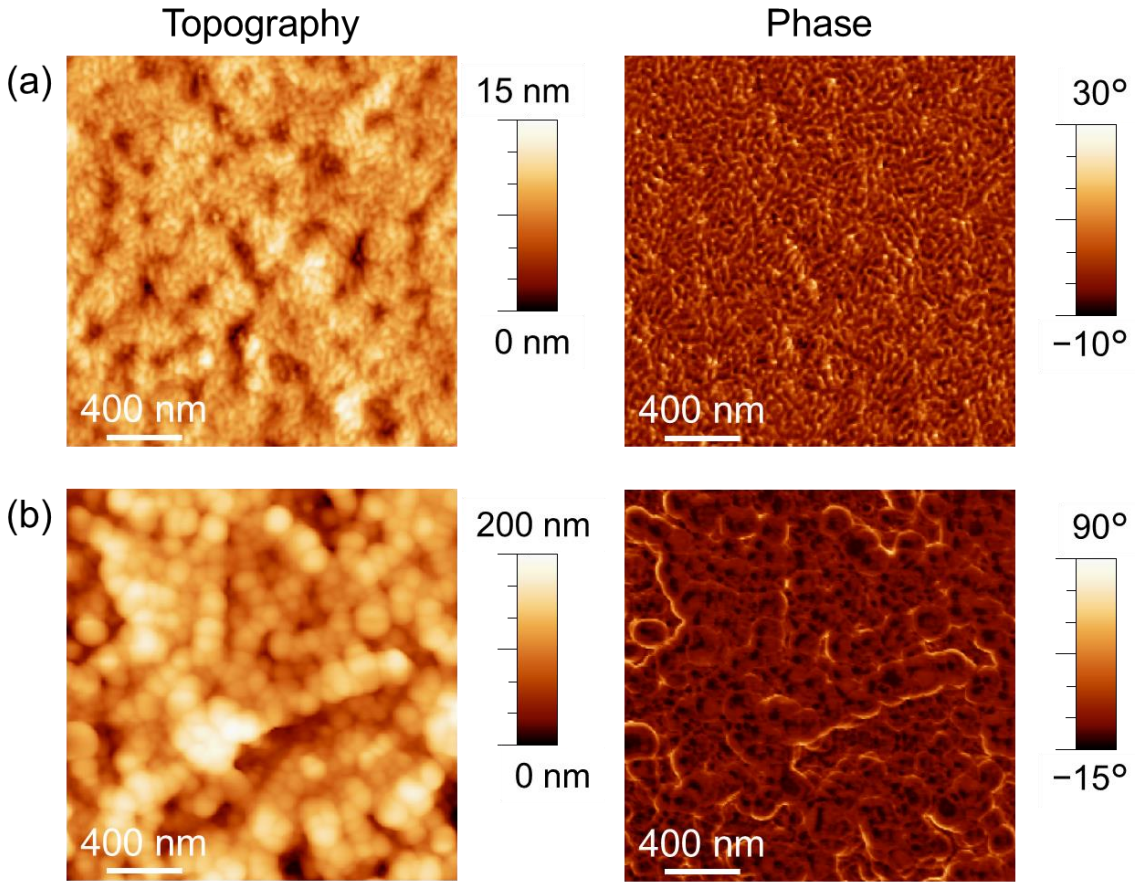

Fig. S12. Atomic force microscopy images of the (a) as-grown and (b) (111)-oriented HKUST-1 films.

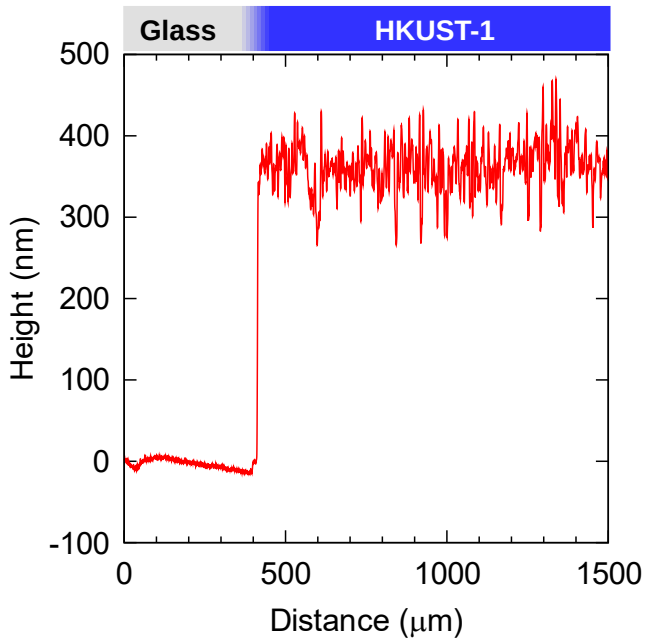

Fig. S13. Surface profile of (111)-oriented HKUST-1 thin film

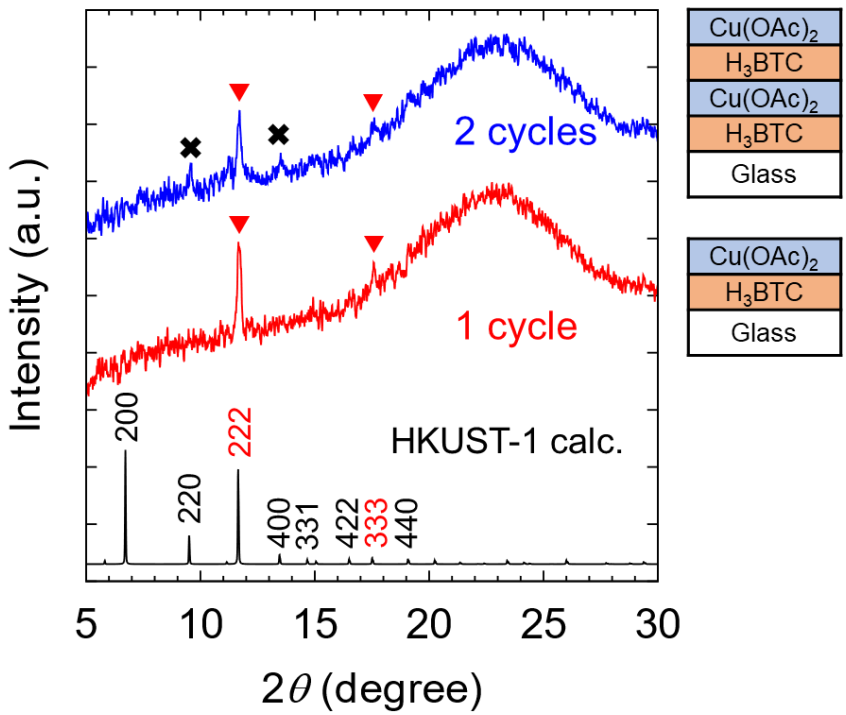

Fig. S14. out-of-plane X-ray diffraction pattern of thin films with different deposition sequence.

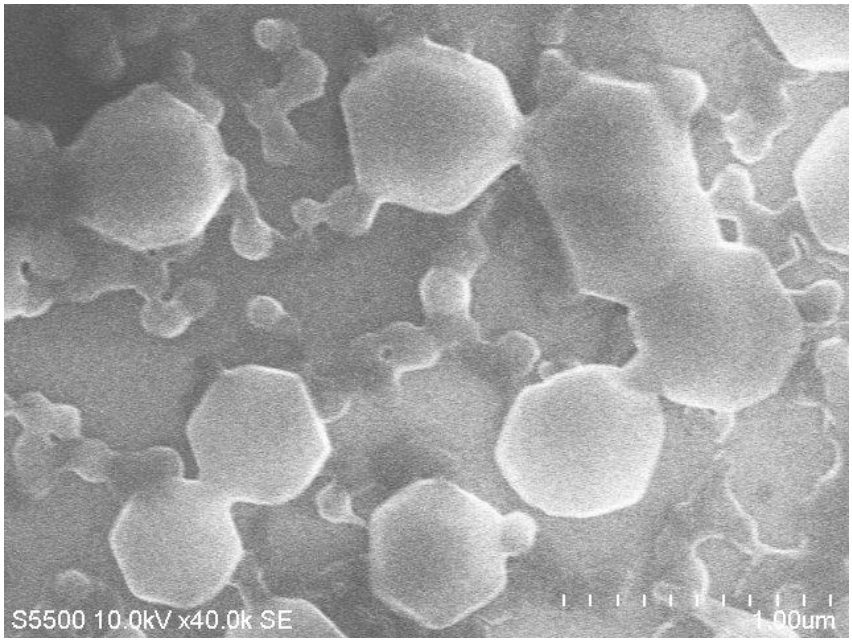

Fig. S15. Enlarged SEM image of (111)-oriented HKUST-1 thin film

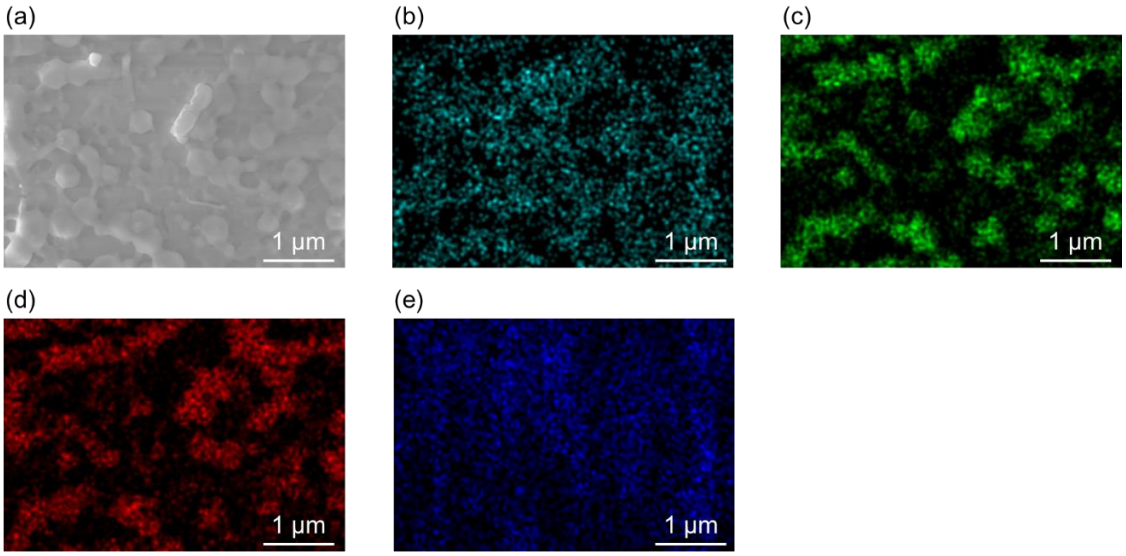

Fig. S16. (a) Scanning electron microscopy image and energy-dispersive X-ray spectroscopy mapping of (b) Si, (c) C, (d) Cu, and (e) O in the (111)-oriented HKUST-1 film.

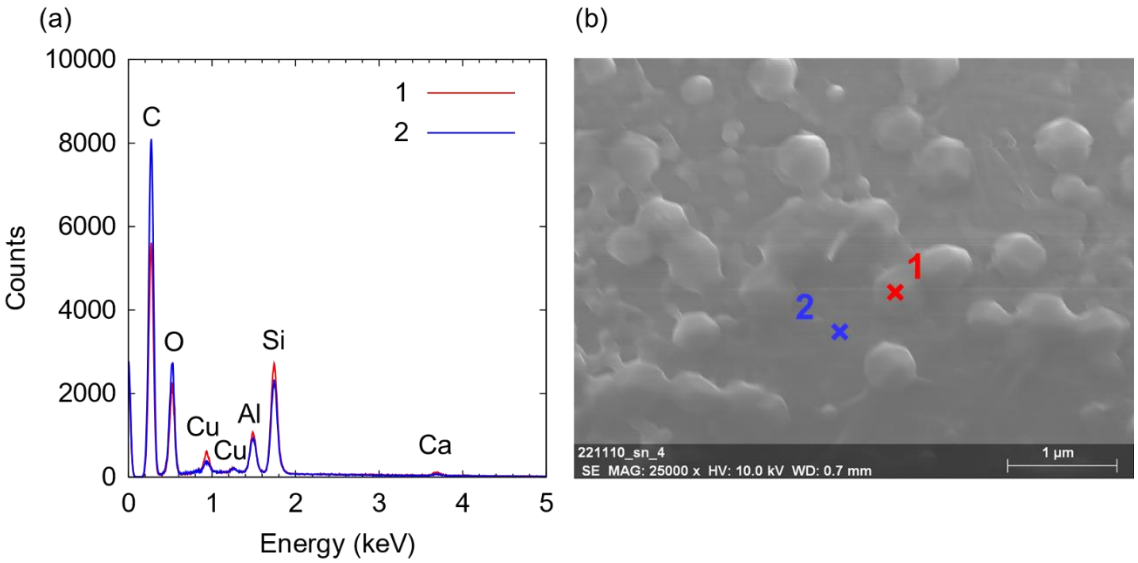

Fig. S17. (a) Point analysis of the energy-dispersive X-ray spectroscopy spectra and (b) corresponding sampling points in the scanning electron microscopy image of the (111)-oriented HKUST-1 film.

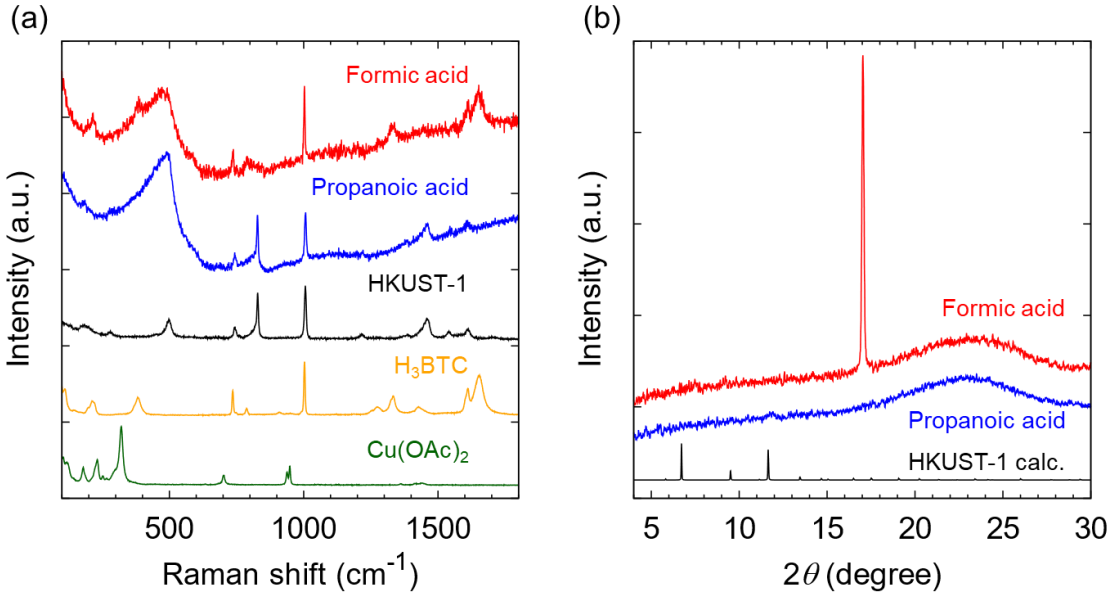

Fig. S18. (a) Raman spectra and (b) X-ray diffraction patterns of films annealed with different monocarboxylic acids.

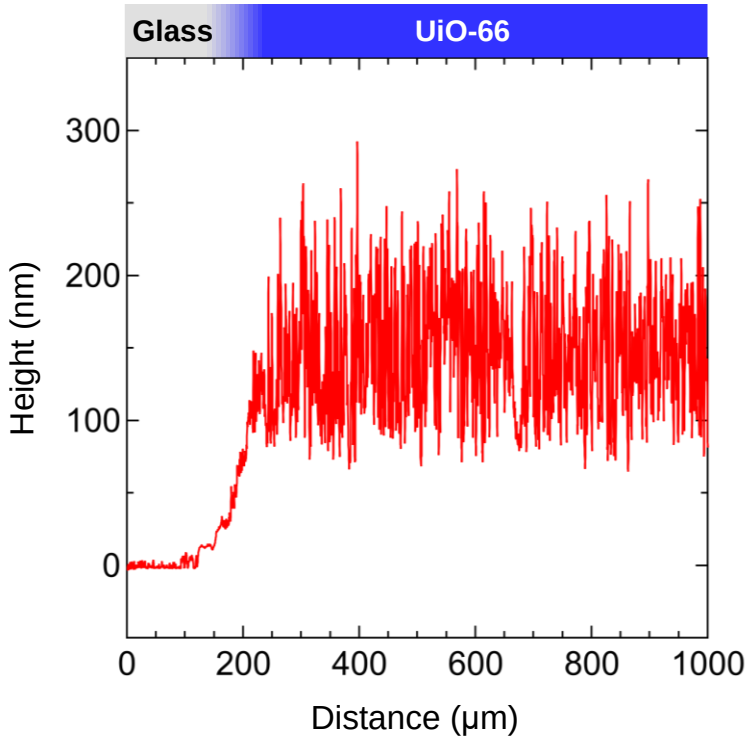

Fig. S19. Surface profile of UiO-66 thin film on a glass substrate