Kinetics and mechanism of metal-organic framework thin film growth: Systematic investigation of HKUST-1 deposition on QCM electrodes

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SUPPLEMENTARY INFORMATION

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Experimental Methods

Materials. All starting reagents were reagent grade and obtained from commercial sources. HPLC-grade ethanol was used to prepare copper(II) acetate and trimesic acid solutions.

Preparation of Self-Assembled Monolayers (SAMs) on gold. The QCM electrode surfaces were cleaned using oxygen plasma treatment (Micro RIE, Series 800 Plasma System). The Au-coated QCM crystals were kept for 24 hours in a 1.0 M ethanolic solution of 11-mercaptoundecanoic acid (for COOH-functionalyzed SAMs) or 11-mercaptoundecanol (for OH-terminated SAMs) and rinsed with ethanol before used.

Deposition of $Cu_3(btc)_2$ thin films on QCM crystals. The $Cu_3(btc)_2$ thin films were grown on the surface of the QCM crystals by continously flowing alternating ethanolic solutions of $Cu(OAc)_2$ and H_3btc over the surface for 5 minutes, with 10 minutes ethanol washing steps in between. The injection speed for the three solutions was maintained constant at 0.1 mL/min. 1.0 mM ethanolic solutions of trimesic acid and 0.2 mM solutions of copper(II) acetate were used as stock solutions. After the coating the QCM electrodes were washed with ethanol and dried in a nitrogen stream.

Quartz Crystal Microbalance. Two different Quartz Crystal Microbalances were used in this study: a Q-Sense E4 system (designated QCM-D below) equipped with 4 sensor flow modules (Q-Sense Inc.) and an SRS-200 QCM system with a single module. Both instruments have a fundamental resonance frequency of 5 MHz. The SRS system measures the changes in the first harmonic frequency and the change in resistance, while the QCM-D system runs in pulsed mode and can measure up to seven different harmonics and their corresponding dissipation factors. The isothermal conditions in the Q-Sense system are achieved using Peltier temperature control cells (±0.02 °C), while in the case of the SRS system a water bath is used (±0.1 °C). Temperature-dependent QCM measurements were performed on a LabView-controlled system equipped with peristaltic pumps (Figure S1). The electrodes were formed by evaporating gold onto both sides of AT-cut quartz crystals. The measurements were made in flow cells with one electrode in direct contact with the liquid phase.

Characterization Details. Reflection-absorption infrared (RAIR) measurements were recorded on a Perkin-Elmer FT-IR spectrometer. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy studies were performed on a JEOL 6700 and a Hitachi S4500 electron microscope. Scanning white-light interferometry measurements were performed on a VEECO Instruments Inc. microscope. Atomic Force Microscopy (AFM) was performed using a Digital Instruments Dimension 3000 operating in tapping mode to collect height images. Grazing incidence X-ray diffraction (XRD) measurements were performed on a PANalytical Empyrean system equipped with a PIXcel^{3D} detector using Cu Kα radiation. The samples are placed at an appropriate angle to the source so that the X-rays exhibit grazing incidence with the surface and then the PIXcel detector is physically rotated through an angle of 2θ relative to the sample. The XRD pattern of the bulk HKUST-1 sample (Basolite C300, Sigma-Aldrich) was collected on the same Empyrean system using Bragg-Brentano geometry.

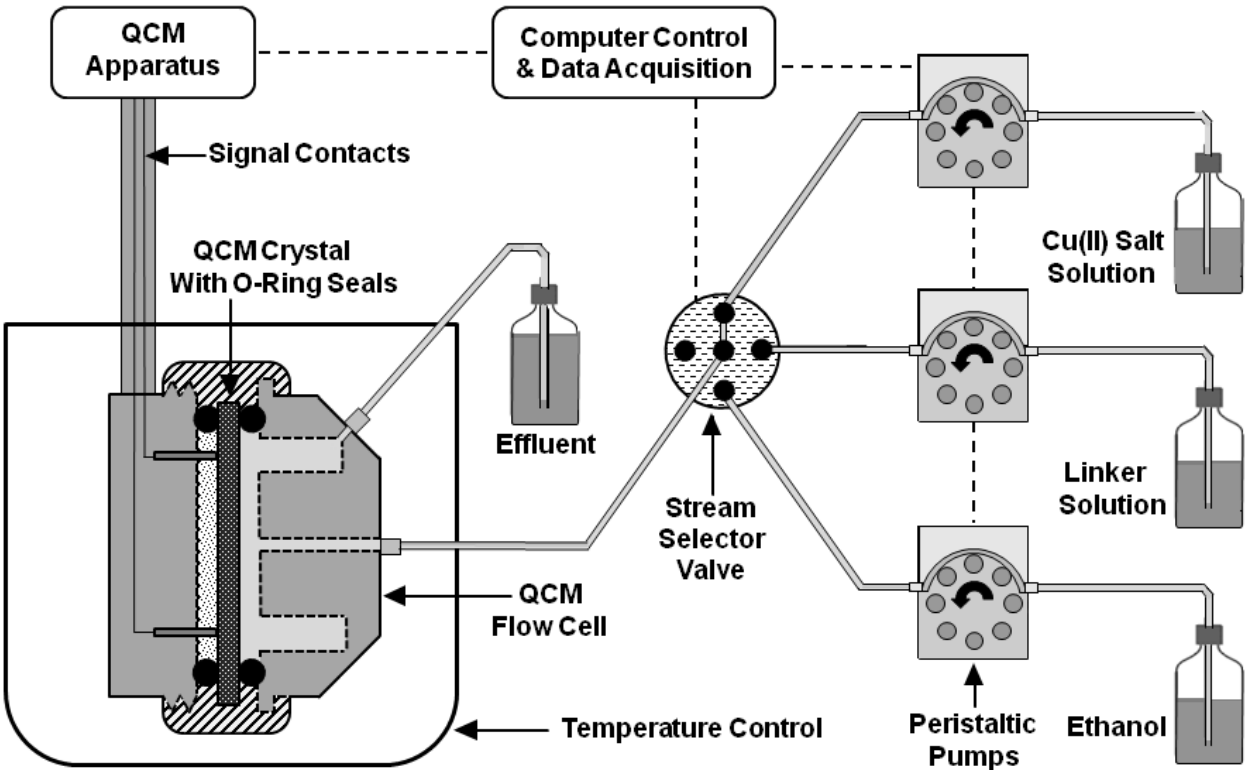

Figure S1. A schematic representation of the QCM experimental setup.

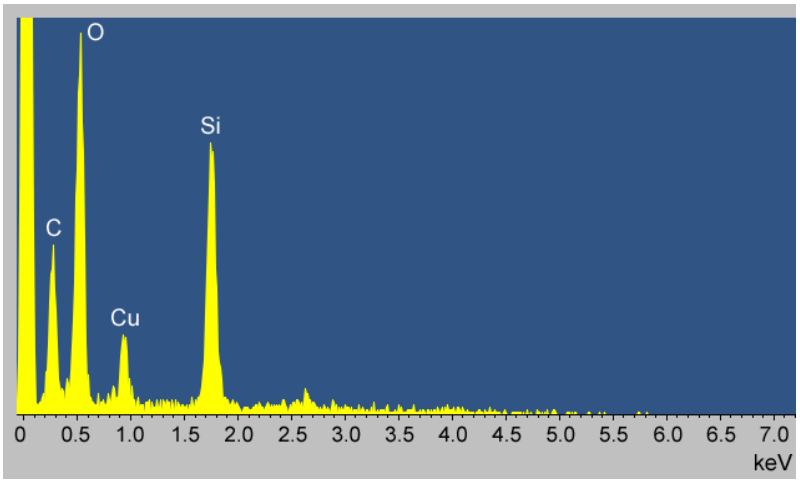

Figure S2. EDS of the $Cu_3(btc)_2$@SiO_2 film obtained after five cycles of $Cu_2(OAc)_4$ + H_3btc step-by-step deposition showing the presence of copper on the surface.

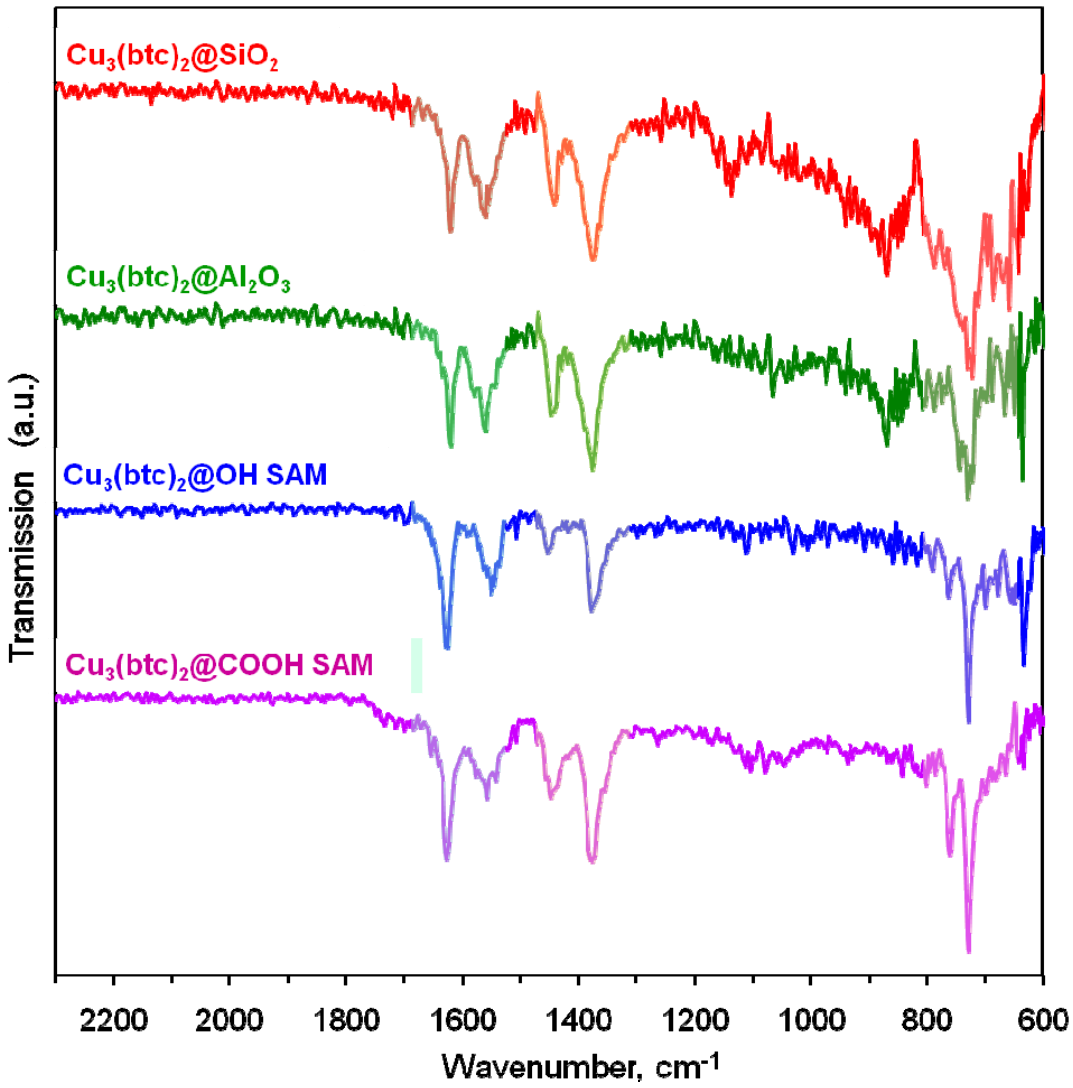

Figure S3. Reflection-Absorption Infrared (RAIR) spectra of $Cu_3(btc)_2$ coatings on various QCM electrodes deposited for 20 cycles at 32 °C.

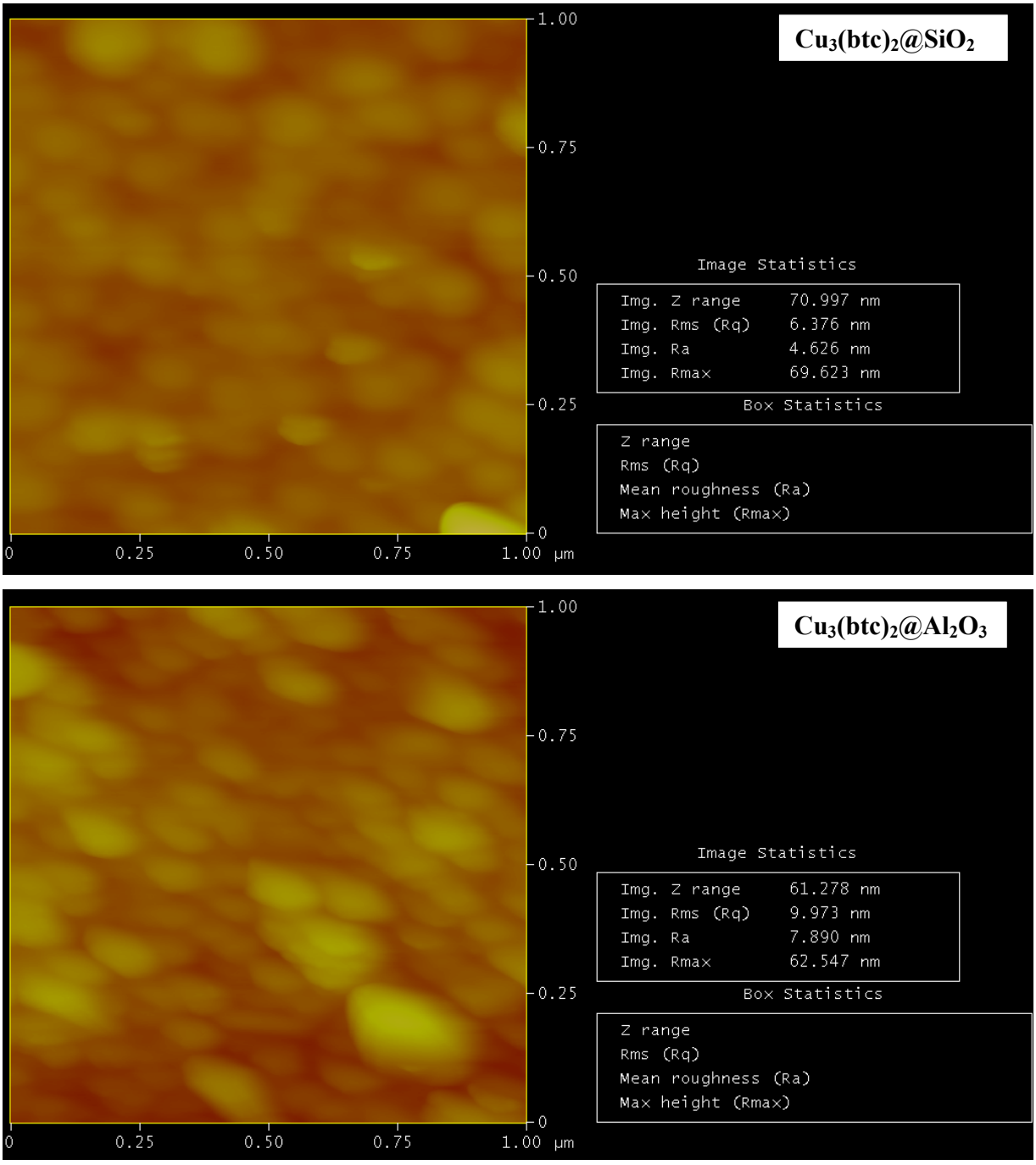

Figure S4. Comparison of root-mean-square (RMS) roughness between $Cu_3(btc)_2@SiO_2$ and $Cu_3(btc)_2@Al_2O_3$ films grown on QCM electrodes for 20 cycles at 32 °C.

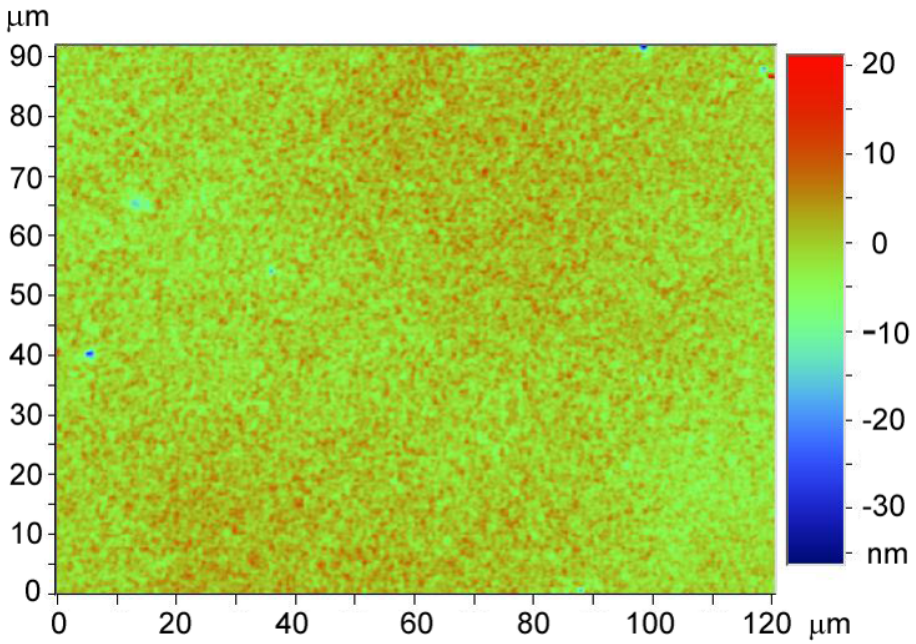

Figure S5. A representative interferometry scan on a large area (121 × 92 µm) of the $Cu_3(btc)_2$@SiO_2 coating obtained after 20 cycles of $Cu_2(OAc)_4$ + H_3btc step-by-step deposition.