Supplementary Material (ESI) for Chemical Communications

Supporting Information

Single Layer Growth of Sub-micron Metal-Organic Framework Crystals Observed by In Situ Atomic Force Microscopy

Neena S. John, Camilla Scherb, Maryiam Shöâeè, Michael W. Anderson, Martin P. Attfield,* and Thomas Bein*

I Film Synthesis

Self-assembled monolayer on gold

The gold-coated slides (glass slides (76 x 26 mm^2) coated with 10 nm Ti / 100 nm Au by electron-beam evaporation, Advalytix AG) were cut into smaller pieces (10 x 13 mm^2) and cleaned in pure ethanol and methanol. The cleaned gold slides were immersed into a 1 mmol ethanolic solution (6 pieces in 30 ml) of 16-mercapto-1-hexadecanol at RT for 48 h. The SAM-functionalized gold slides were repeatedly washed with ethanol, and stored in fresh absolute ethanol until needed.

HKUST-1 synthesis mixture

A solution (12 ml) of 0.837 g (3.6 mmol) $Cu(NO_3)_2 \cdot 2.5H_2O$ (98%, Aldrich) in water was added to a solution (12 ml) of 0.42 g (2.0 mmol) of 1,3,5-benzentricarboxylic acid (97%, Fluka) in absolute ethanol. The mixture was filled into a sealed-glass reactor and left for 8 days in a preheated oven at 75 °C.

Thin-film growth

After cooling the HKUST-1 synthesis mixture in a water/ice bath, the crystalline product was filtrated and stored for further characterization. The filtrated solution was used for the surface crystal growth on SAMs.

The SAM-functionalized gold-slides were placed upside-down on Teflon®-supports in the clear HKUST-1 crystallization solution (3 pieces in 20 ml). The surface crystal growth takes place at room temperature in a closed glass reactor. For the in situ AFM studies, the samples were immersed in the HKUST-1 crystallisation solution for 8 days.

II Preparation of crystallisation solution for in situ AFM

The following growth solution was used in the in-situ AFM experiment:

A solution of 0.139 g (0.6 mmol) $Cu(NO_3)_2 \cdot 2.5H_2O$ (98%, Aldrich) in 6 ml water was added to a solution of 0.070 g (0.334 mmol) of 1,3,5-benzentricarboxylic acid (97%, Fluka) in 6 ml absolute ethanol, resulting in a $[Cu^{2+}]$ concentration of 0.05 mmol/ml that was injected directly into the AFM liquid cell.

III In situ AFM measurements

The gold-coated glass slide supporting the crystals was fixed on to a cover glass using a Bi: Sn alloy (58:42 wt % - Alfa Aesar) and sealed in the liquid cell of a Nanowizard II, JPK Instruments A.G. AFM used to collect all the micrographs. Ex situ scanning was initially performed to image the topography of crystals and then 0.5 mL of the above growth solution (see II) was injected directly into the AFM liquid cell. The laser intensity of the AFM was re-adjusted and the scanning continued under ambient conditions. The time at which the solution was injected was taken as time zero. The solution within the liquid cell was static and hence the supersaturation dropped as the growth proceeded. Stable scans of the growing crystal were possible once the supersaturation was sufficiently low. Imaging was done in contact mode using commercial silicon nitride cantilevers with a low spring constant of 0.06 N/m and a scan rate of 2.5 or 3.5 Hz. Height analysis was performed using the JPK software.

IV Computational Analyses of AFM Scans

Height analysis was performed using the JPK software. Plane fitting was done with respect to a flat terrace prior to height measurements. Approximately ten measurements were taken on every step to determine the precision of the step heights. The advancement of points at the vertex of the triangular growth step in the [11-2] direction and the [2-1-1] step were tracked in consecutive images in relation to the opposite crystal edge, with the latter assumed to be constant throughout the growth. The time for the points to advance between consecutive images was calculated from the pixel values of the particular point in the images and the scan rate. The distance measurements were repeated several times to provide mean deviations for each value plotted in Fig. 2e. The velocities were determined from the gradients of the linear fits to the data.

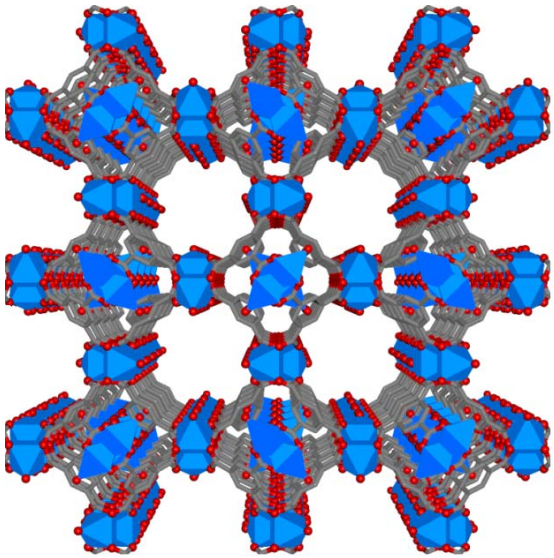

Fig. S1: The structure of HKUST-1 viewed along the [100] direction. Key: blue octahedra - Cu; red - oxygen; grey – carbon.

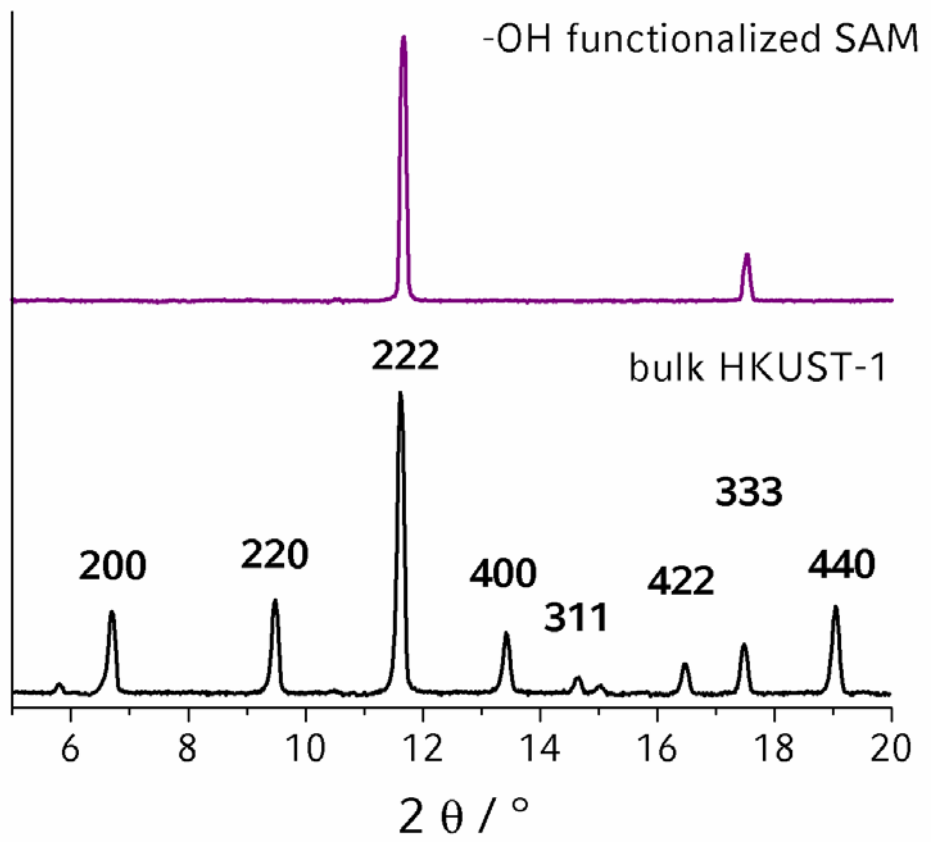

Fig. S2: X-ray diffraction data of the crystals attached to the substrate compared to bulk HKUST-1, demonstrating the perfect [111] orientation.

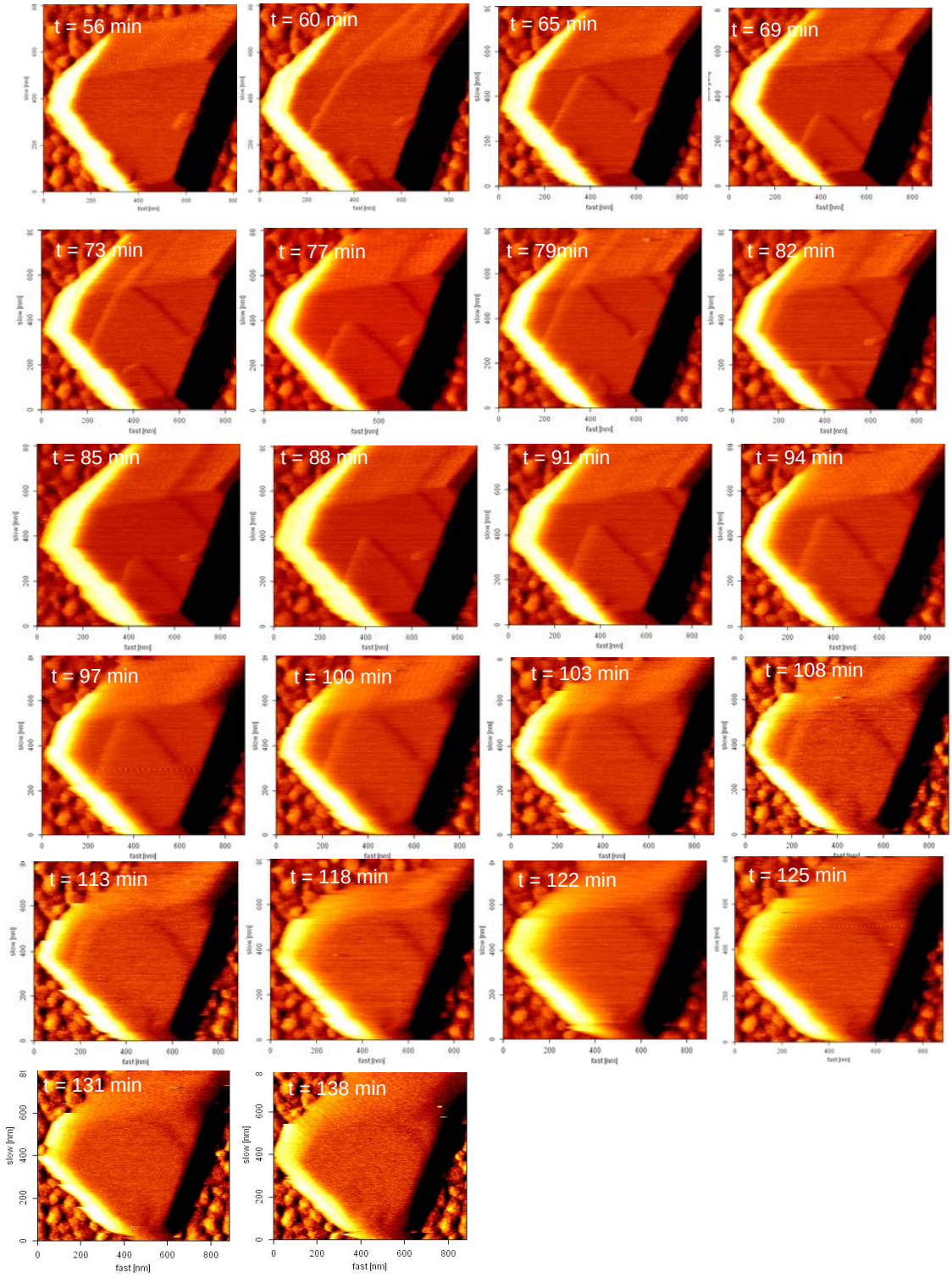

Fig. S3: AFM deflection images of a {111} facet of a *ca.* 600 nm HKUST-1 crystal in the growth medium (starting concentration of Cu^{2+} = 0.05 M) as a function of time (time is indicated in each image). Image size is 885 × 800 nm^2. It should be noted that the interaction of the AFM tip with the growing crystal, combined with the rather weak

surface-attachment of the crystal, appears to cause some movement of the crystal after about 108 min after injection of the solution.