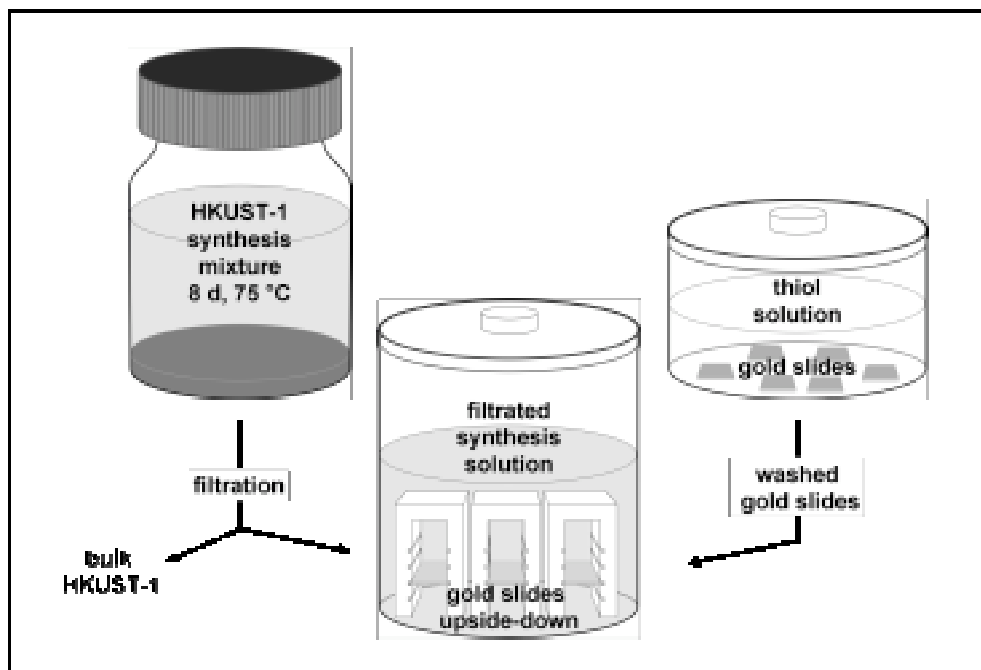


## Supporting Information - JA0701208

# **Oriented Growth of HKUST-1 Thin Films on Gold Substrate Controlled by Functionalized Self-Assembled Monolayers.**

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**Scheme S1.** Illustration of the HKUST-1 films preparation procedure.

## Self-assembled monolayer on gold:

The gold-coated slides (glass slides (76 x 26 mm<sup>2</sup>) coated with 10 nm Ti / 100 nm Au by electron-beam evaporation, Advantix AG) were cut in smaller pieces (10 x 13 mm<sup>2</sup>) cleaned in a piranha solution (H<sub>2</sub>SO<sub>4</sub>(95-98%) : H<sub>2</sub>O<sub>2</sub>(30%) - 3:1), and then treated 20 min in an oxygen-plasma. The cleaned gold slides were immersed in a 1 mmol ethanolic solution (6 pieces in 30 ml) of the desired thiol, and left at RT for 48 h. The SAM-functionalized gold slides were repeatedly washed with ethanol, and stored in fresh

absolute ethanol till needed. The alkanethiols employed in this work: 11-Mercapto-1-undecanol (97 %, Aldrich), 11-Mercaptoundecanoic acid (95 %, Aldrich) and 1-Mercaptoundecan (98 %, Aldrich).

#### HKUST-1 Synthesis Mixture:

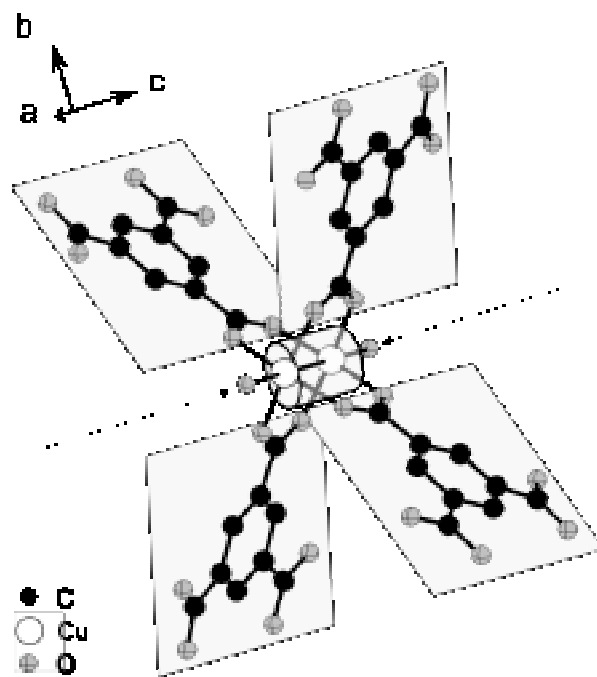
A water solution (12 ml) of 0.837 g (3.6 mmol)  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (98%, Aldrich) was added to an absolute ethanol solution (12 ml) of 0.42 g (2.0 mmol) of 1,3,5-benzentricarboxylic acid (% , Fluka) in a sealed-glass reactor, and left for 8 days in a preheated oven at 75 °C.

#### Synthesis Solution:

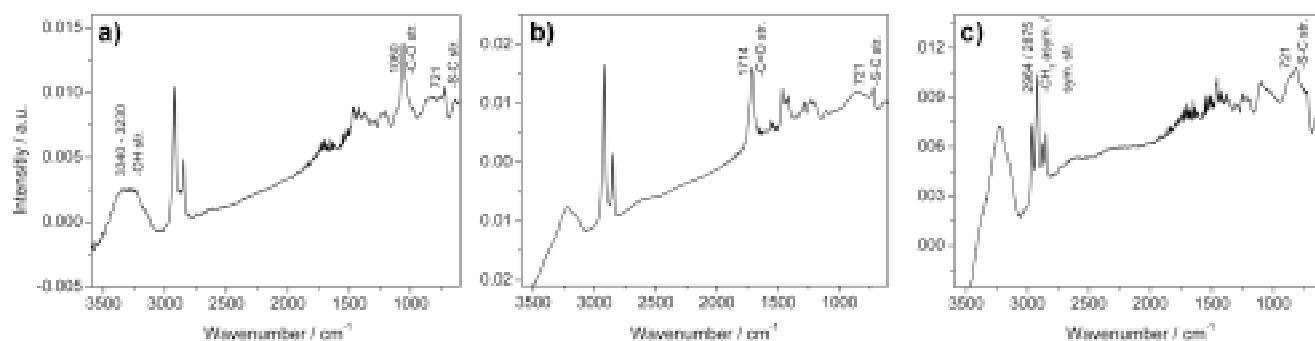
After cooling the HKUST-1 synthesis mixture in a water/ice bath, the crystalline product was filtrated and stored for further characterization. The filtrated solution was used as crystallization sol for growing the films. All reagents were used as received.

#### Thin-films growth:

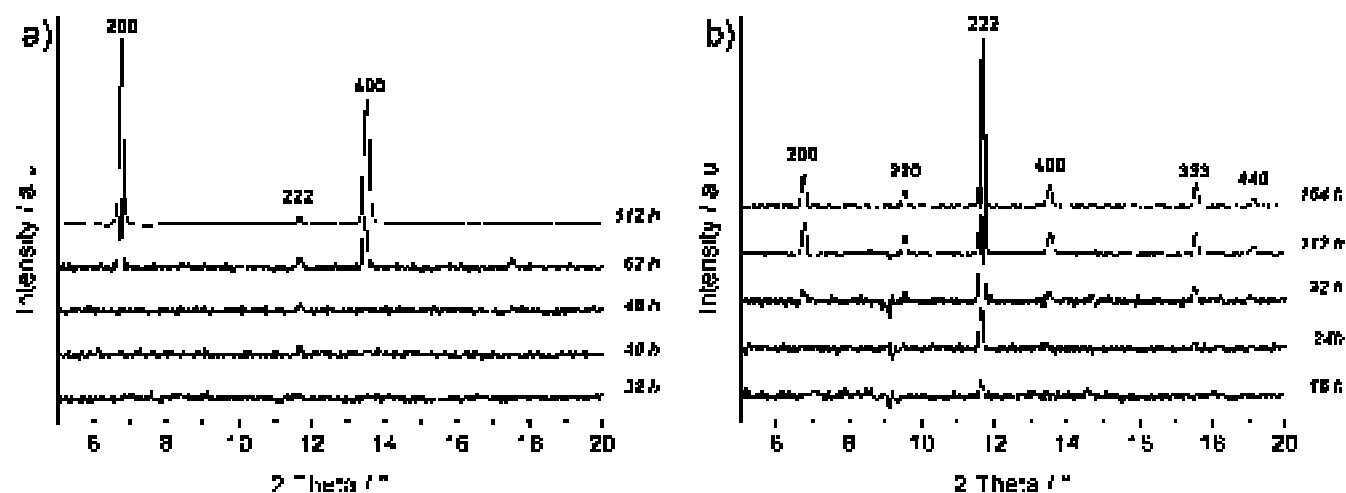
The SAM-functionalized gold-slides were placed upside-down on Teflon<sup>®</sup>-supports in a clear HKUST-1 crystallization solution (3 pieces in 20 ml). The growth step take place at RT in a glass closed reactor. For the kinetic investigation the slides were removed after various immersion times (8-210 h).



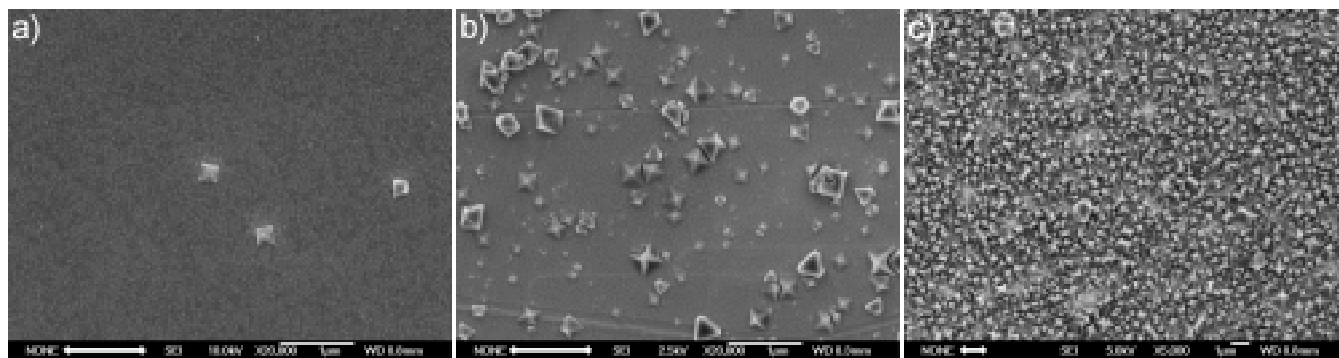
**Figure S1.** “Paddle-wheel” bimetallic cluster of HKUST-1. The structure presents a residual coordination site, collocated on the axial-direction, which is occupied by a weakly bound water molecule, easily removable.



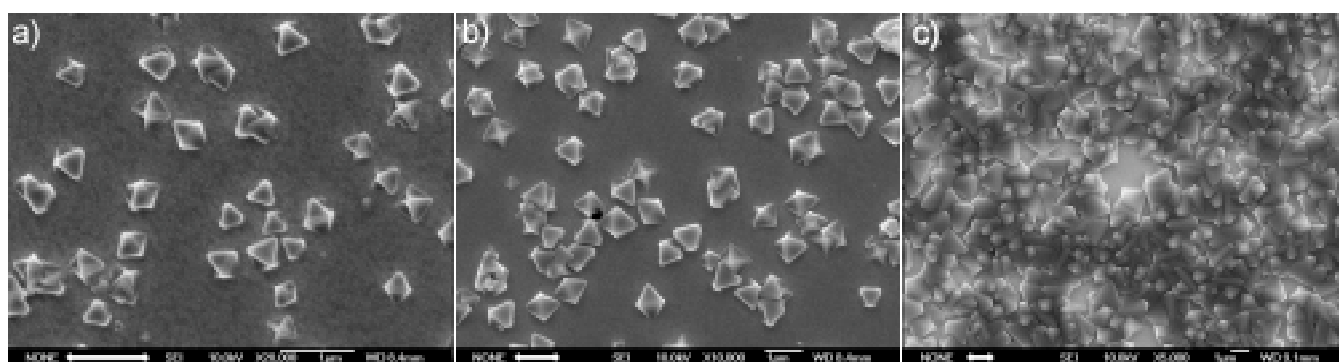
**Figure S2.** RAIIR-spectra of alkanethiol self-assembled monolayers on gold substrate: (a) 11-Mercapto-1-undecanol-SAM, (b) 11-Mercaptoundecanoic acid-SAM, and (c) 1-Mercaptoundecan-SAM. The measurements were performed on a IFS 66v/S-Spectrometer (BrukerOptics) with an incident angle of  $83^\circ$ .



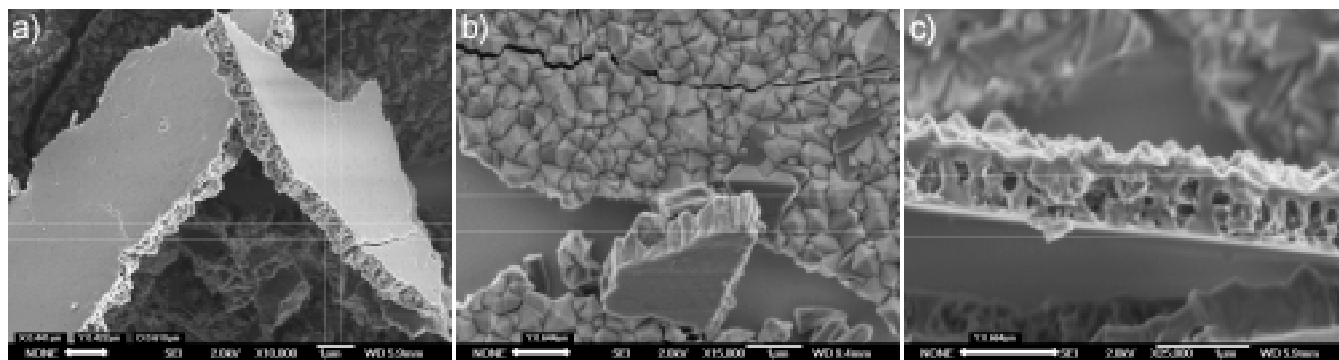
**Figure S3.** X-Ray diffraction patterns of HKUST-1 grown crystals collected after various immersion times in the crystallization solution: a) sample-set relative to the gold-slides modified with the COOH-SAM, b) measurements of thin films grown on methyl-functionalized gold surfaces. The diffraction patterns were collected between  $5$  and  $20^\circ 2\theta$ , on a XDS-2000 diffractometer (Scintag Inc.) using  $\text{Cu } K_{\alpha}$  radiation ( $\lambda = 154.18 \text{ pm}$ ). The measurements were performed in theta/theta mode, with a step-size of  $0.02$  degree, and a scan-rate of  $0.004^\circ 2\theta \text{ s}^{-1}$ .



**Figure S4.** Scanning electron micrographs of [100]-oriented HKUST-1 grown crystals on COOH-SAM modified gold-slides. The measurements were performed on different samples after immersion times of a) 32 h, b) 40 h and c) 112 h. The SEM-pictures were collected using a JEOL JSM-6500F scanning electron microscope. The scale-bar on each image represents 1  $\mu\text{m}$ .



**Figure S5.** SEM-pictures of HKUST-1 crystals grown on  $\text{CH}_3$ -SAM. No unique orientation can be observed. a) represent a sample immersed for 16 h, while b) show a gold-slide after 24 h crystallization time, and (c) 112 h. The SEM-pictures were collected using a JEOL JSM-6500F scanning electron microscope. The scale-bar on each image represents 1  $\mu\text{m}$ .



**Figure S6.** SEM-pictures of HKUST-1 thin films on 11-Mercapto-1-undecanol-SAM (a), 11-Mercaptoundecanoic acid-SAM (b), and 1-Mercaptoundecan-SAM (c). All samples were measured after equal immersion time (112 h). The thickness was measured directly on the images, and is similar for all the sample (ca. 600 nm). The orientation of the crystals at this stage is difficult to recognize, thus the films are composed of a monolayer of closed packed intergrown crystals. Therefore the kinetic-study was needed to characterize the evolution of the films. The scale-bar on each image represents 1  $\mu\text{m}$ .