Supporting Information

Orientation control of $Cu_3(HHTP)_2$ MOF films using a dual working electrode electrochemical synthesis method

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Supplementary figures

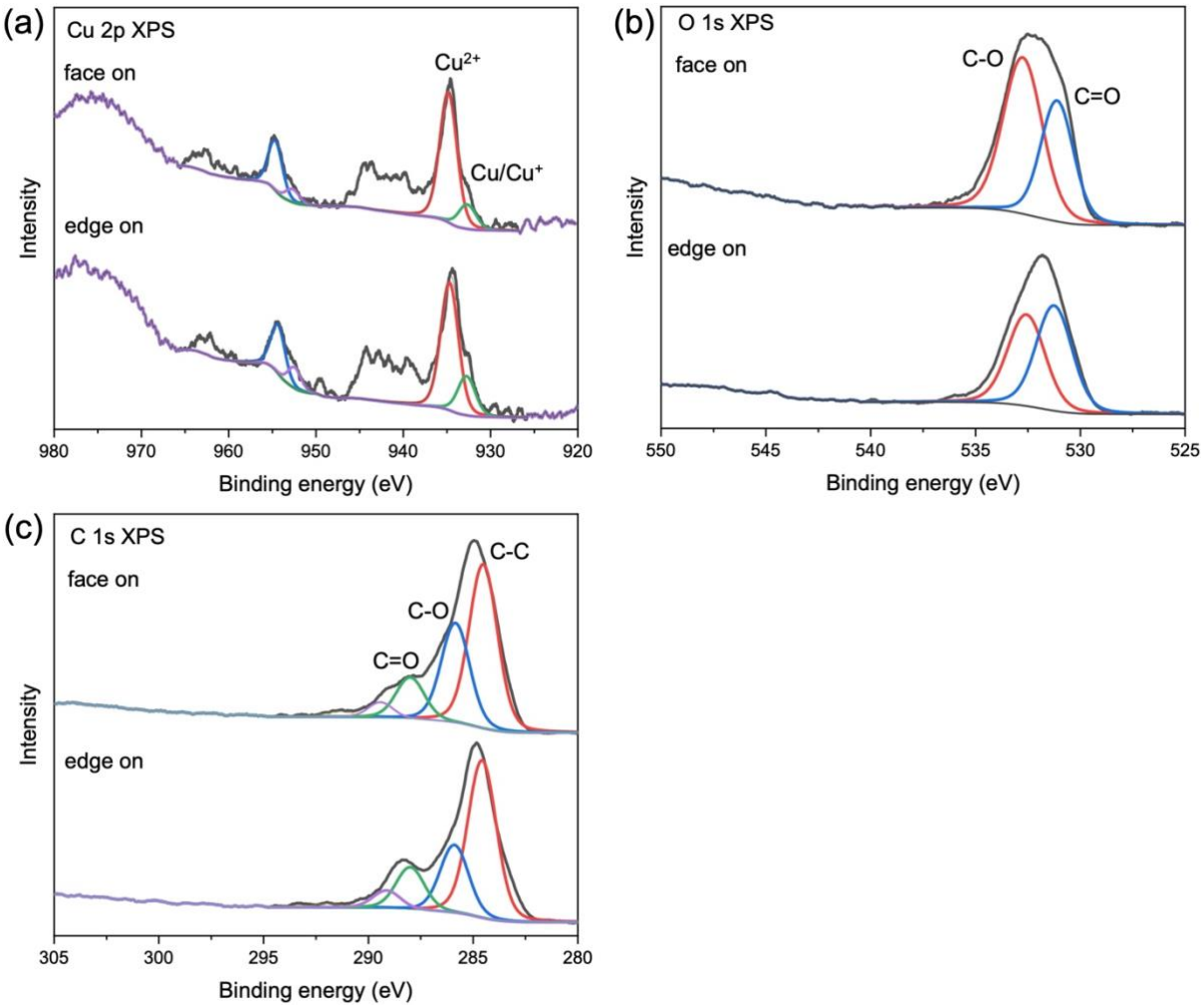

Fig. S1 XPS spectra of face-on (upper scans) and edge-on (lower scans) $Cu_3(HHTP)_2$ films on ITO substrates. (a) The Cu 2p peaks are shown with the main Cu^{2+} $2p_{3/2}$ peak in red at 934.8 eV and the weaker Cu/Cu+ in green at 932.5 eV. The Cu^{2+} $2p_{1/2}$ peak is shown in blue at 954.9 eV. (b) The O 1s peaks for C-O bonding and C=O bonding are shown in red (left) and blue (right). (c) The C 1s peaks showing C=O, C-O, and C-C bonding in green, blue, and red, respectively.

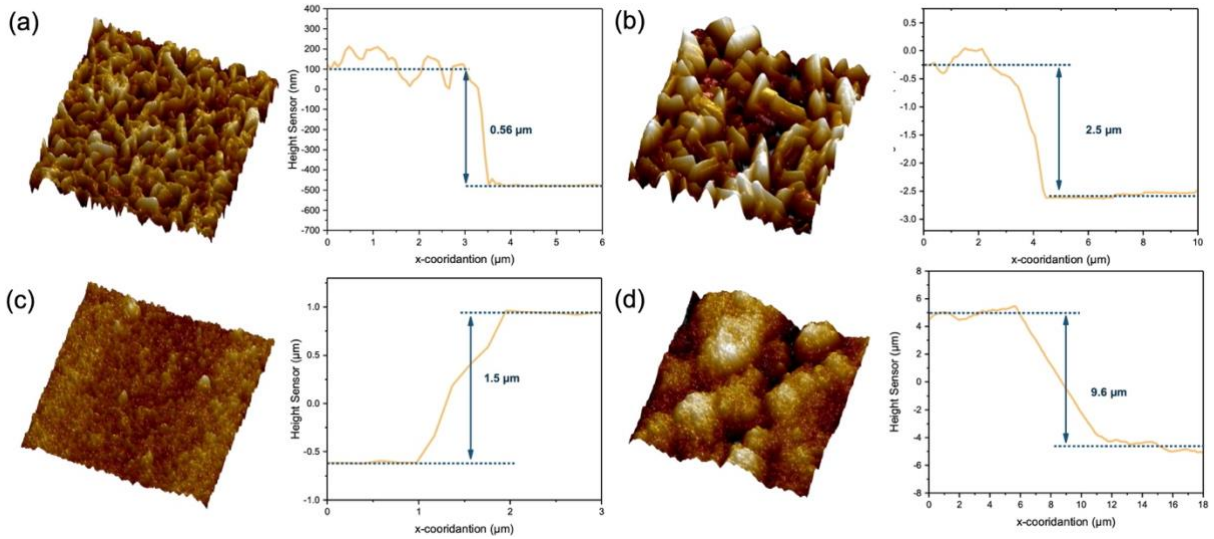

Fig. S2 3D rendering of AFM images of the edge-on and face-on $Cu_3(HHTP)_2$ film synthesized for two durations, and the corresponding thickness measurements. The height differences are between the MOF grown in solution and the exposed ITO substrate that was not immersed in the solution. All AFM images have scan sizes of 5 μm × 5 μm with a height range of 0 – 400 nm. (a) Edge-on film synthesized for 2 hours, showing a thickness of 0.56 μm. (b) Edge-on film synthesized for 10 hours, with a thickness of 2.5 μm. (c) Face-on film synthesized for 2 hours, with a thickness of 1.5 μm. (d) Face-on film synthesized for 10 hours, with a thickness of 9.6 μm.

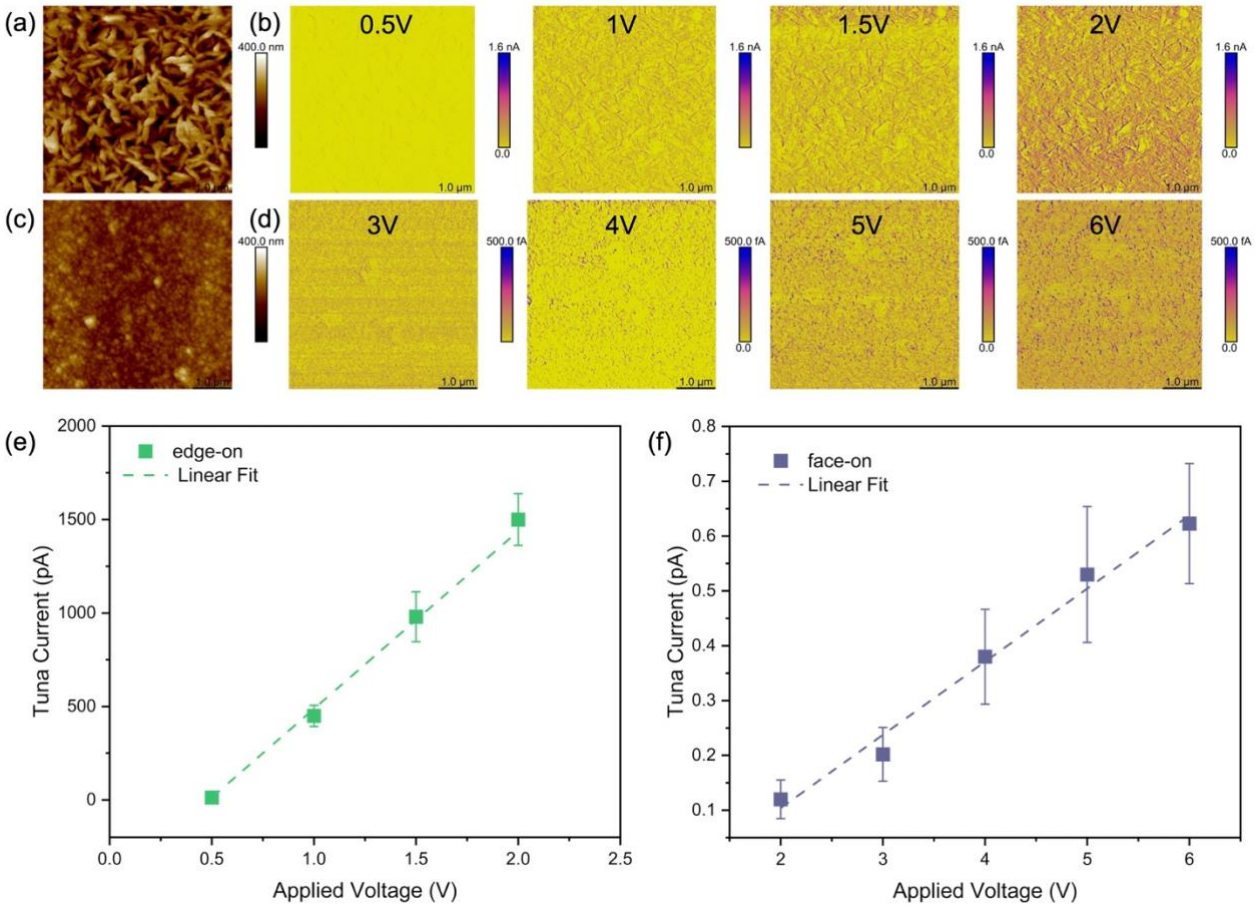

Fig. S3 (a) AFM image of an edge-on Cu-HHTP film (5 μm × 5 μm). (b) Local current maps of the edge-on film under applied voltages from 0.5 V to 2 V. (c) AFM image of a face-on Cu-HHTP film (5 μm × 5 μm). (d) Local current maps of the face-on Cu-HHTP film under applied voltages from 3 V to 6 V. (e) Through a fit of the mapping data the conductivity of the edge-on film is determined to be $(6.78 \pm 0.45)\times10^{-2}$ S cm^{-1}. (f) For the face-on film the conductivity is significantly lower at $(2.56 \pm 0.97)\times10^{-5}$ S cm^{-1}.

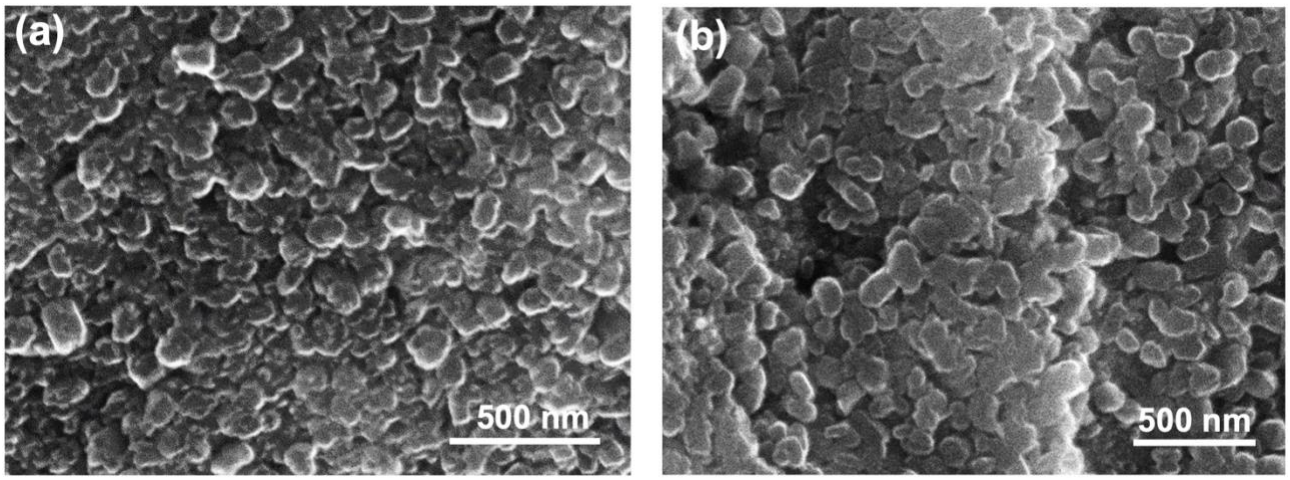

Fig. S4 SEM images of the Cu tape following MOF growth with (a) high ligand concentration, and (b) low ligand concentration.

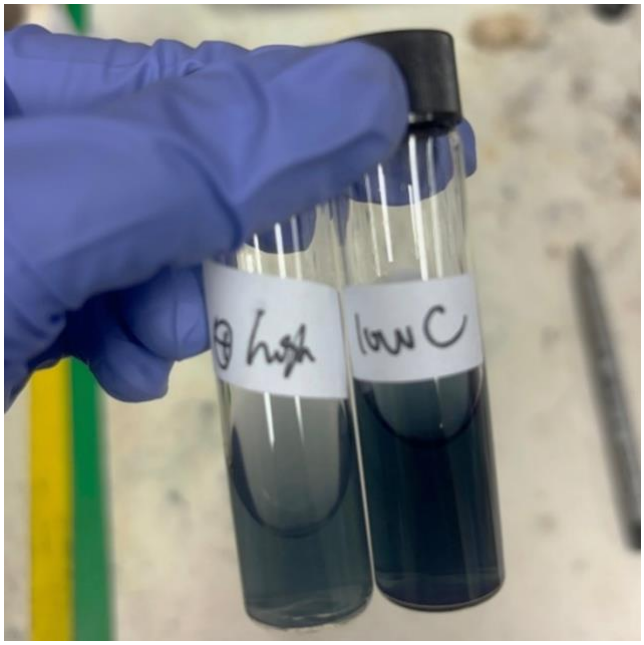

Fig. S5 Solutions collected during electrochemical synthesis of $Cu_3(HHTP)_2$ with the high ligand concentration on the left (light blue) and the low ligand concentration on the right (dark blue).