Supporting Information for:

IRMOF thin films templated by oriented zinc oxide nanowires

Yashar Abdollahian,[†] *Jesse L. Hauser,*[†] *Ian R. Colinas,*[†] *Carolyn Agustin,*[†]

Andrew S. Ichimura[‡] *and Scott R. J. Oliver*[†]*

[†] University of California, Santa Cruz, Department of Chemistry and Biochemistry,

1156 High Street, Santa Cruz, California 95064

[‡] San Francisco State University, Department of Chemistry and Biochemistry,

1600 Holloway Avenue, San Francisco, California 94132

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

CORRESPONDING AUTHOR FOOTNOTE: soliver@ucsc.edu

Synthesis Procedures

ZnO Nanowire Synthesis
An ITO glass substrate (2 cm x 1 cm, Sigma-Aldrich) was first seeded with zinc oxide by annealing with a 5 mM ethanolic solution of zinc acetate dihydrate [$Zn(CH_3CO_2)_2 \cdot 2H_2O$, 98%, Mallinckrodt Chemicals] at 350 °C. The seeded ITO substrate was then immersed in an aqueous solution containing 25 mM zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, 99.5 %, Fisher Scientific] and 25 mM hexamethylenetetramine (HMTA, $C_6H_{12}N_4$, 99.1 %, Fisher Scientific), and allowed to react at 90 °C for 5 h in a sealed scintillation vial. The nanowire coated substrate was removed from the aqueous solution and rinsed with deionized water.

IRMOF-1 Synthesis
The nanowire coated substrate was immersed face down in a dimethylformamide (DMF, C_3H_7NO, 99.8 %, Macron) solution containing 9 mM terephthalic acid ($C_8H_6O_4$, 98+ %, Alfa Aesar), 5 mM HMTA, 12.5 mM zinc nitrate hexahydrate and one drop of concentrated hydrogen peroxide (30 %, Fischer Chemicals). IRMOF-1 growth on the zinc oxide coated substrate proceeded for 20 h at 90 °C in a sealed scintillation vial. The MOF-coated slide was removed from the solution and rinsed with DMF to remove loose precipitate from the slide.

IRMOF-3 Synthesis
A nanowire coated substrate was immersed in a zinc precursor solution containing 13 mM zinc nitrate hexahydrate and one drop of concentrated hydrogen peroxide (30 %) in 12.5 mL of DMF. In a separate container, the organic ligand precursor solution containing 19 mM of 2-aminoterepthalic acid and 13 mM of HMTA in 12 mL of DMF was prepared. After placing the nanowire coated substrate face down in a scintillation vial, the two precursor solutions were mixed and added to the scintillation vial. The reaction proceeded for 24 hours in a 90 °C oven. When removed, the vial was allowed to cool and the MOF-coated slide was rinsed with pure DMF to remove any precipitate present on the slide.

IRMOF-8 Synthesis
A transparent conducting oxide glass slide with pre-synthesized zinc oxide nanowires was placed face down in a 20 mL reaction vial. A zinc precursor solution of 20 mM zinc nitrate hexahydrate and one drop of H_2O_2 in 10 mL DMF was prepared, then mixed with an organic ligand precursor solution containing 20 mM 2,6-naphthalenedicarboxylic acid ($C_{12}H_8O_4$, 98 %, TCI) and 15 mM HMTA in 10 mL DMF. The reaction mixture was subsequently added to the 20 mL vial containing the zinc oxide nanowire substrate and was heated at 90 °C for 20 h. The slide was carefully removed with forceps and both sides were rinsed with DMF.

IRMOF-9 Synthesis
A transparent conducting oxide glass slide with pre-synthesized zinc oxide nanowires was placed face down in a 20 mL reaction vial. A zinc precursor solution of 20 mM zinc nitrate hexahydrate and one drop of H_2O_2 in 10 mL DMF was prepared and mixed with an organic ligand precursor solution containing 20 mM 4,4'-biphenyldicarboxylic acid ($C_{14}H_{10}O_4$, 98 %, Acros Organics) and 10 mM HMTA in 10 mL DMF. The reaction mixture was subsequently added to the 20 mL vial containing the zinc oxide nanowire substrate and was heated at 90 °C for 20 h. The slide was carefully removed with forceps and both sides were rinsed with DMF.

Microwave Synthesis of IRMOF-1
Vertically oriented ZnO nanowire substrates were submerged face down at a 45 degree angle in individual Teflon test tubes containing 10 mL of a DMF solution consisting of 1.563 mM zinc nitrate hexahydrate and 1.125 mM terephthalic acid. The test tubes were sealed and heated in a microwave for 10 minutes continuously at 150 W. A maximum solution temperature of 95 °C was reached at the end of 10 minutes. Once cooled to ambient temperature, the slides were rinsed with pure DMF

several times and then characterized by GIXRD and SEM.

Instrumental
GIXRD data was collected on a Rigaku SmartLab X-ray diffractometer equipped with a copper X-ray tube [λ (Cu-Kα) = 1.54056 Å, tube energy 44 mA / 40 kV]. The sample was analyzed using parallel beam optics with the incident angle held at 0.3 ° to eliminate substrate peaks. Scan rate was conducted at 3.0 °/min with a step size of 0.01 °. SEM data was collected with a Carl Zeiss Ultra 55 Field Emission Scanning Electron Microscope operating at 5 kV and ~5 pA. Samples were sputter coated with a 10 nm layer of platinum to increase conductivity. Microwave synthesis of the IRMOF films were performed in an Anton Paar Multiwave 3000 rotary microwave.

Characterization of IRMOF Films

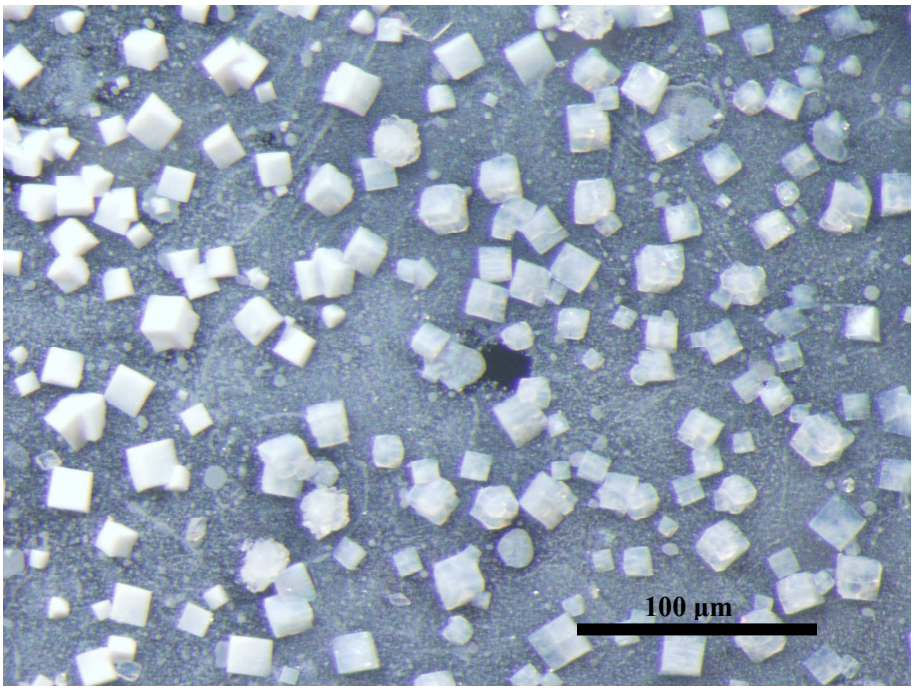

Figure S1. Optical micrograph of IRMOF-1 film taken after 5 hours of exposure to the MOF precursor solution.

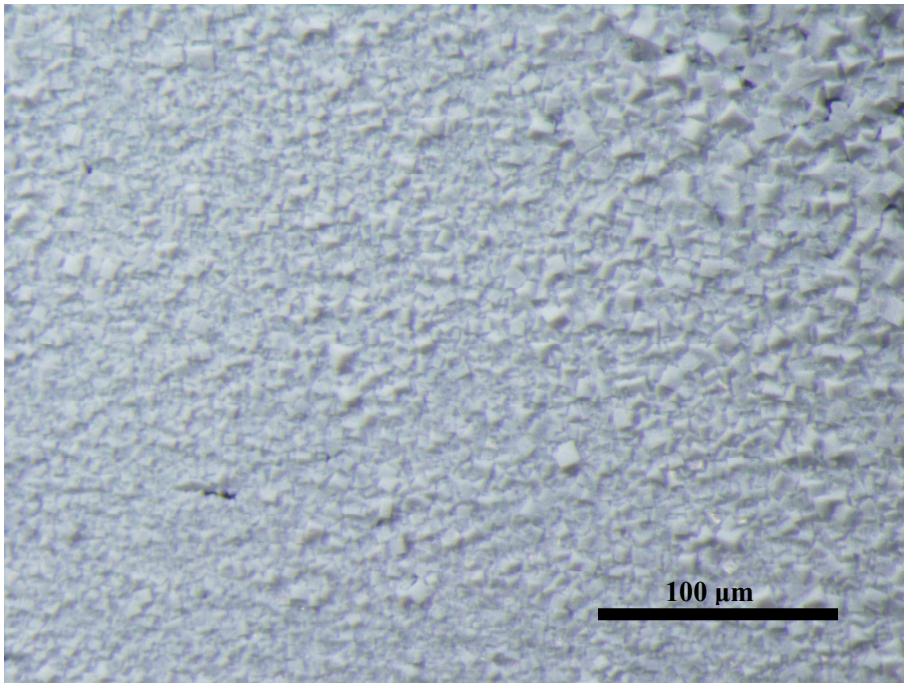

Figure S2. Optical micrograph of IRMOF-1 film taken after 20 hours of exposure to the MOF precursor solution.

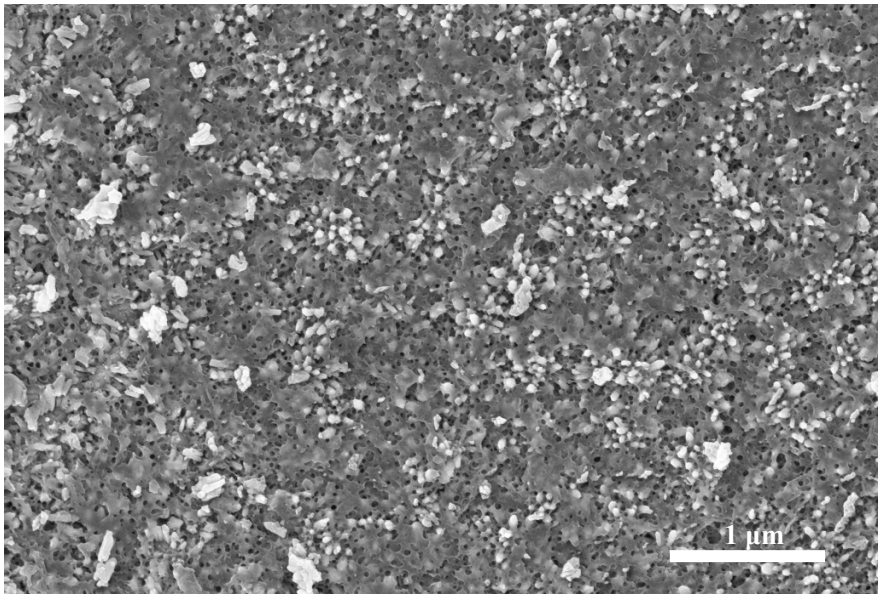

Figure S3. Top-down view of the IRMOF-1 crystalline layer after dislodging crystals from the nanowire substrate. Small clusters of nanowires can be seen protruding through the crystalline layer.

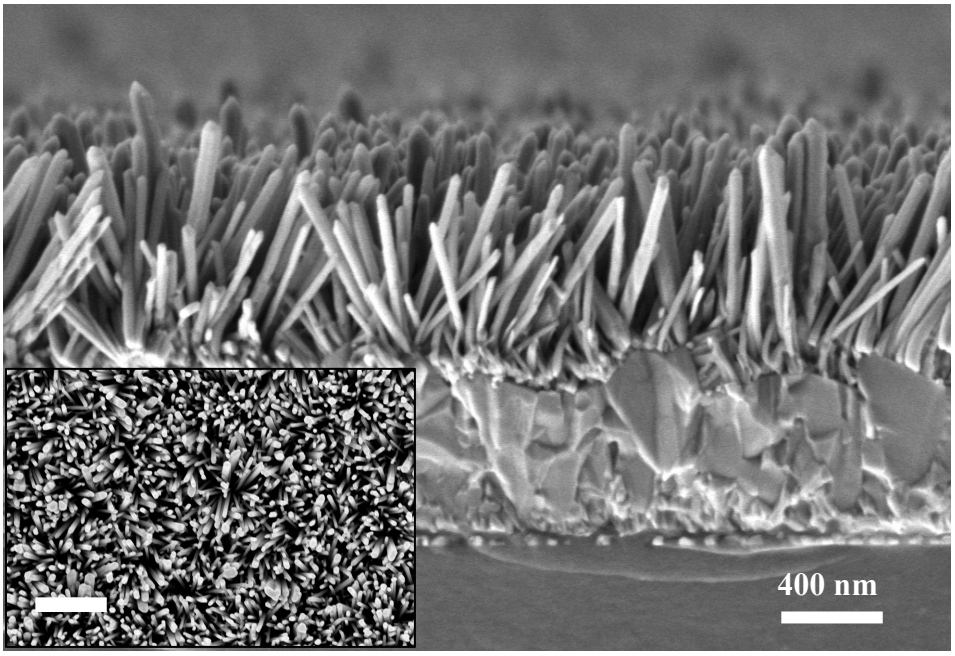

Figure S4. Cross-sectional SEM of ZnO nanowires grown on FTO glass. The inset on the bottom left shows the top-down image of the nanowire film (inset scale bar: 1 μm).

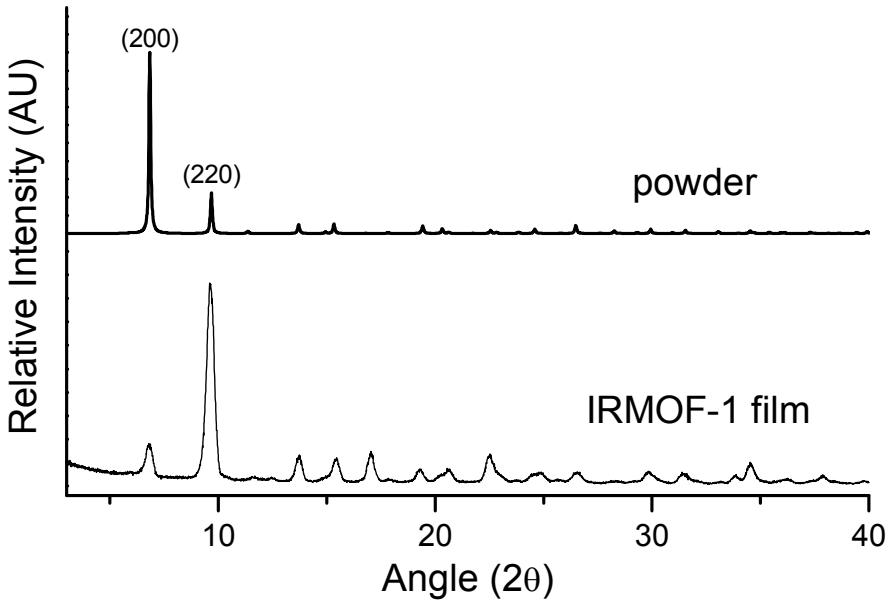

Figure S5. GIXRD pattern of IRMOF-1 film (bottom) and corresponding powder pattern of the bulk solid (top). The *hkl*-indices are denoted for the peaks used in the CPO index calculation.

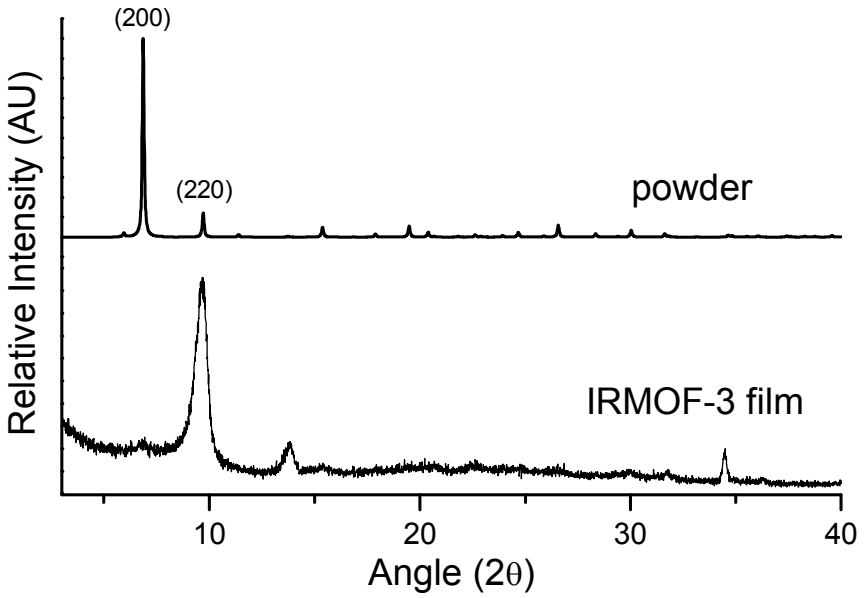

Figure S6. GIXRD pattern of IRMOF-3 film (bottom) and corresponding powder pattern of the bulk solid (top). The *hkl*-indices are denoted for the peaks used in the CPO index calculation.

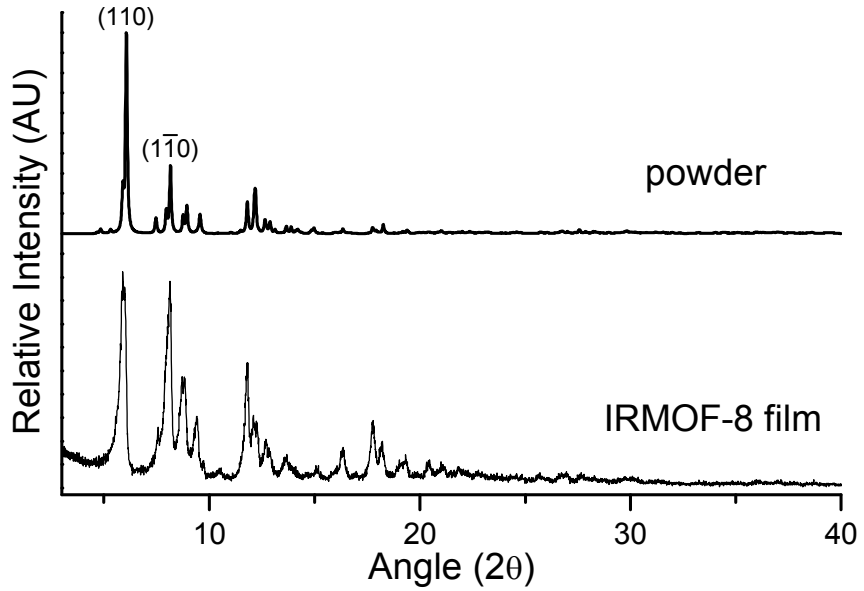

Figure S7. GIXRD pattern of IRMOF-8 film (bottom) and corresponding powder pattern of the bulk solid (top). The *hkl*-indices are denoted for the peaks used in the CPO index calculation.

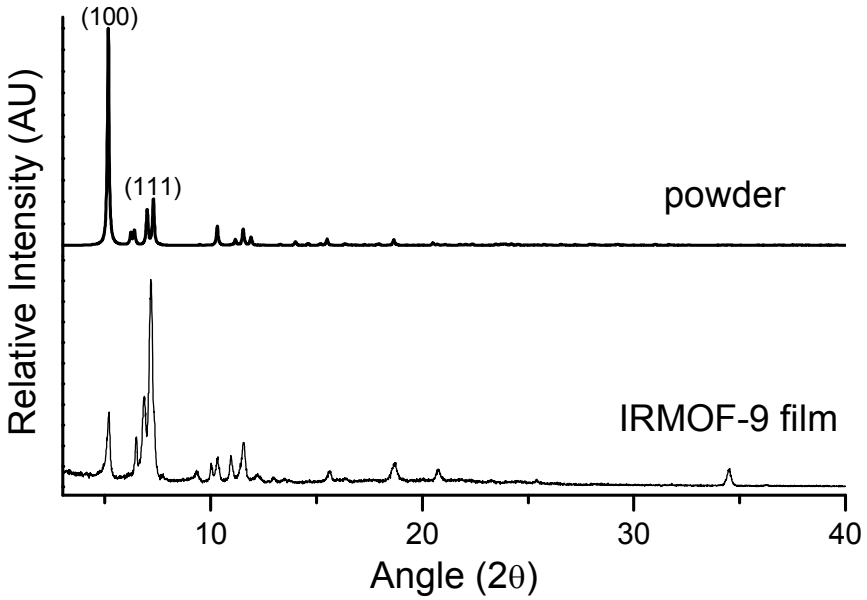

Figure S8. GIXRD pattern of IRMOF-9 film (bottom) and corresponding powder pattern of the bulk solid (top). The *hkl*-indices are denoted for the peaks used in the CPO index calculation.

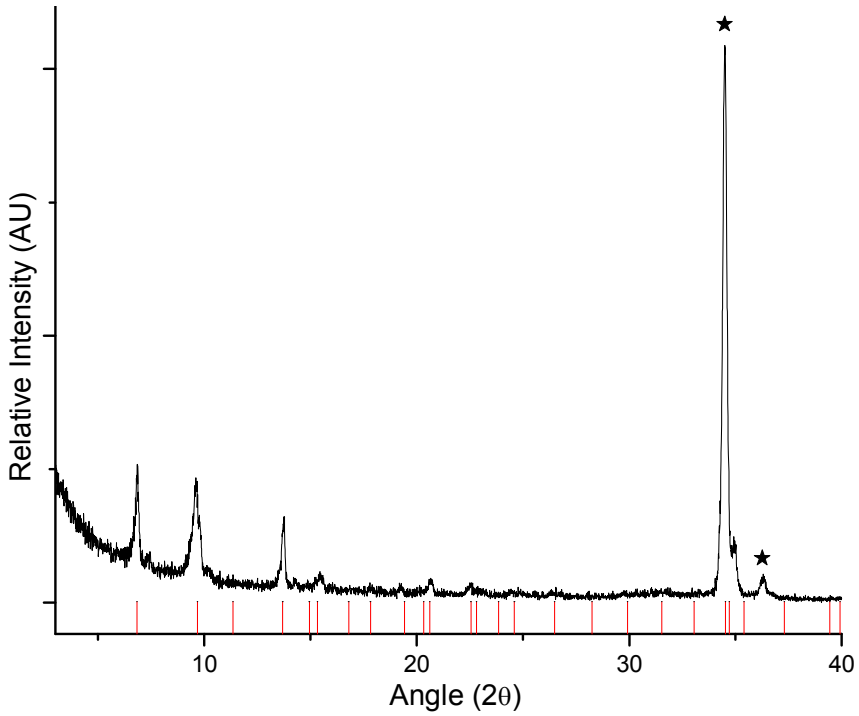

Figure S9. GIXRD spectrum of the microwave synthesized IRMOF-1 film on zinc oxide nanowires. Asterisks correspond to oriented zinc oxide nanowires. Bars at the bottom indicate the theoretical pattern for IRMOF-1.

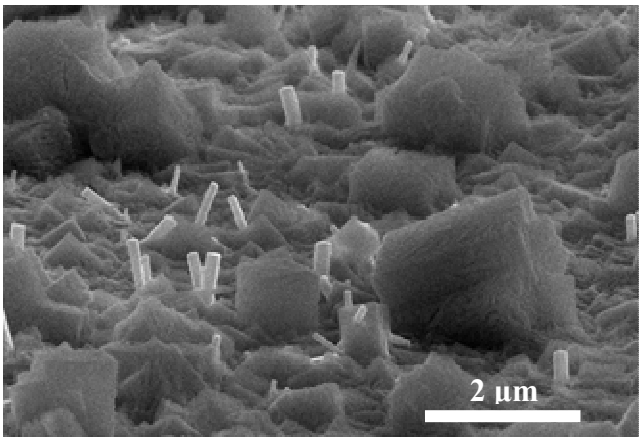

Figure S10. Side-view SEM image of microwave-synthesized IRMOF-1 film on ZnO nanowires.