Supporting Information

Linker Competition within a Metal-Organic Framework for Topological Insights

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Table of Contents

I) Materials

All chemicals and solvents were obtained from commercial suppliers and used without further purification. Zirconium(IV) oxynitrate hydrate (99%), formic acid (≥96%), 1,2,4,5-tetrakis(4-carboxyphenyl)benzene (TCPB) (≥98%), p-tolylmagnesium bromide solution (1.0 M in DMF), hexabromobenzene (98%), 1,2,4,5-tetrabromobenzene (97%), bromine (reagent grade), and carbon tetrachloride (99.9%), sulfuric acid-d_2 solution (96-98 wt. % in D_2O, 99.5 atom % D), and dimethyl sulfoxide-d_6 (99.9 atom % D) were purchased from Sigma-Aldrich. *N*,*N*-dimethylformamide (DMF) (99.9%), acetone (99.8%), hydrochloric acid (36.5−38%), nitric acid (67−70%), chloroform (99.8%), and hexane (98.5%) were purchased from Fisher Chemical. Deionized water was used as the water source.

II) Linker Synthesis and characterization

1,2,4,5-tetrakis(4-carboxyphenyl)benzene **L1** and 1,2,4,5-tetrakis(4-carboxyphenyl)- 3,6-dibromobenzene **L2** were synthesized according to literature procedure.[1]

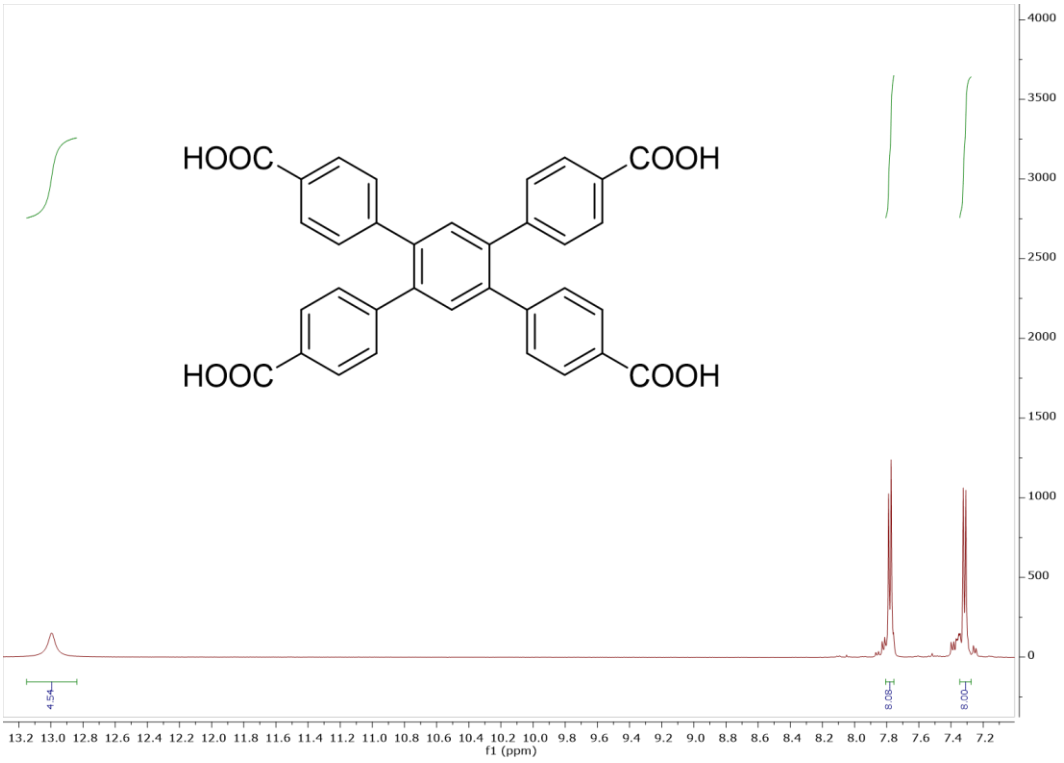

Figure S1: 500 MHz ^{1}H spectrum of **L1** DMSO-d_6.

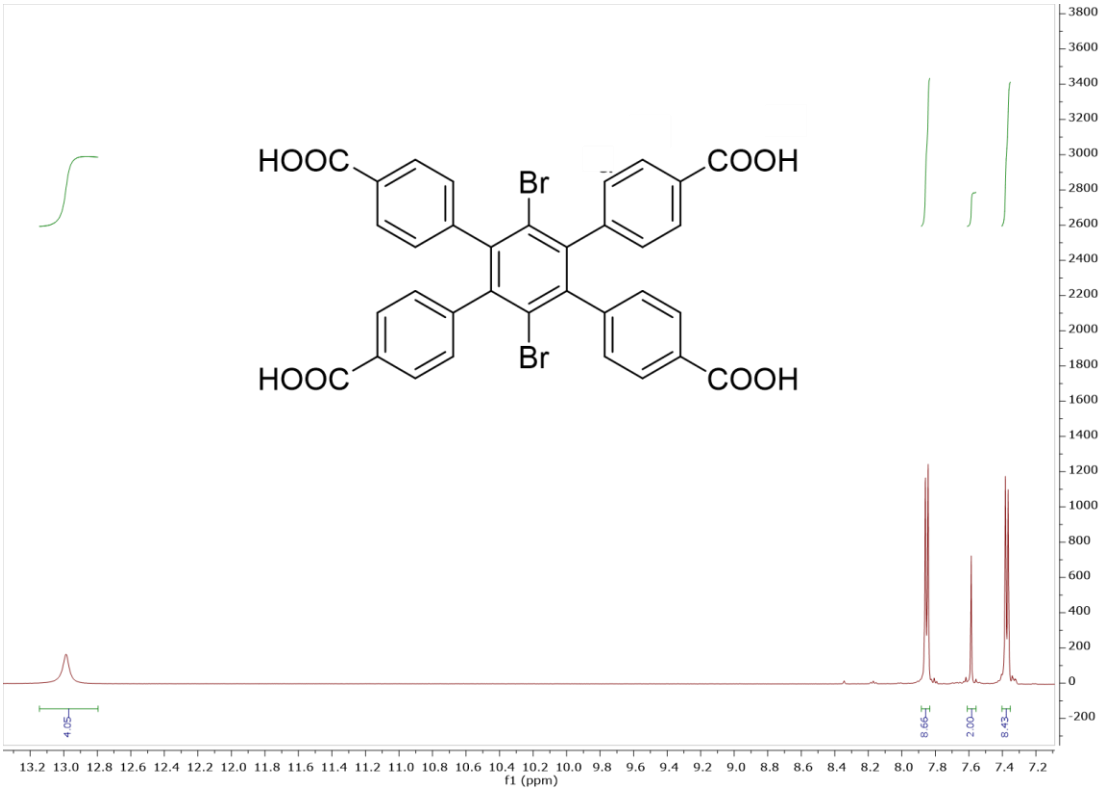

Figure S2: 500 MHz ^{1}H spectrum of **L1** DMSO-d_6.

III) MOF Synthesis Protocols

Competition Reaction for Simultaneous Nucleation of **L1** and **L2**

Zirconium oxynitrate hydrate (79.7 mg, 0.345 mmol) was placed in a 2-dram vial. 1 mL of *N*,*N*-dimethylformamide was added and the solution was sonicated until solubility was achieved. 1 mL of formic acid was added to the vial, which turned clear shortly thereafter. The Zr_6 node solution was sonicated if any remaining particles were not yet soluble. The vial was placed in an 80 °C oven for 1 hour. A **L1** solution was prepared by adding 14.9 mg (0.0267 mmol) of **L1** to 1 mL of *N*,*N*- dimethylformamide and was sonicated until soluble. A **L2** solution was prepared by adding 19.1 mg (0.0267 mmol) of **L2** to 1 mL of *N*,*N*- dimethylformamide and sonicated to ensure solubility. After the Zr_6 node solution was removed from the oven and cooled to room temperature, 200 µL aliquots of the solution were placed in nine separate 0.5 dram vials. The following amounts of **L1** and **L2** (in µL) were added to each of the nine vials: 20, 180; 40, 160; 60, 140; 80, 120; 100, 100; 120, 80; 140, 60; 160, 40; 180, 20. The vials were then placed in a 100 °C oven for 16 hours. Solutions were removed from the oven and cooled to room temperature. The mixtures were placed in 1.5 mL centrifuge tubes and centrifuged for five minutes to remove the supernatant. Then, the resultant white powder was washed with *N*,*N*-dimethylformamide (1.5 mL×2) and acetone (1.5 mL×2). The material was then dried in a vacuum oven at 80 °C for 1 hour.

To obtain adequate material for N_2 isotherm measurement of a specific ratio, the above procedure was repeated using the specific **L1**: **L2** ratio of interest on the same scale but repeated 10 times. The reacted solutions were then combined into a 15 mL centrifuge tube and washed with DMF (5

mL x 3) and acetone (5 mL x 3). The material soaked in acetone overnight, followed by washing with acetone (5 mL x 3). The material was then dried in the vacuum oven for 1 hour at 80 °C. The material was then activated by heating at 120 ˚C for overnight under high vacuum on a Micromeritics Smart Vacprep.

Competition Reaction for Prior Seeding of **L1**

Zirconium oxynitrate hydrate (79.7 mg, 0.345 mmol) was placed in a 2-dram vial. 1 mL of *N*,*N*-dimethylformamide was added and the solution was sonicated until solubility was achieved. 1 mL of formic acid was added to the vial, which turned clear shortly thereafter. The Zr_6 node solution was sonicated if any remaining particles were not yet soluble. The vial was placed in an 80 °C oven for 1 hour. A **L1** solution was prepared by adding 14.9 mg (0.0267 mmol) of **L1** to 1 mL of *N*,*N*- dimethylformamide and was sonicated until soluble. After the Zr_6 node solution was removed from the oven and cooled to room temperature, 200 µL aliquots of the solution were placed in nine separate 0.5 dram vials. The following amounts of **L1** (in µL) were added to each of the nine vials: 20, 40, 60, 80, 100, 120, 140, 160, and 180. The vials were then placed in a 100 °C oven for 30 minutes. The vials were removed from the oven and cooled to room temperature. A **L2** solution was prepared by adding 19.1 mg (0.0267 mmol) of **L2** to 1 mL of *N*,*N*- dimethylformamide and sonicated to ensure solubility. The **L1** nucleated systems were removed from the oven and cooled to room temperature. Then, aliquots of **L2** (in µL) were added in the following order to the vials containing the above specific amounts of **L1** in solution: 180, 160, 140, 120, 100, 80, 60, 40, and 20. The vials were then placed in a 100 °C oven for 16 hours to react. Upon reaction completion, the vials were removed from the oven and cooled to room temperature. The mixtures were placed in 1.5 mL centrifuge tubes and centrifuged for five minutes to remove the supernatant. Then, the resultant white powder was washed with *N*,*N*-dimethylformamide (1.5 mL×2) and acetone (1.5 mL×2). The material was then dried in a vacuum oven at 80 °C for 1 hour.

To obtain adequate material for N_2 isotherm measurement of a specific ratio, the above procedure was repeated using the specific **L1**: **L2** ratio of interest on the same scale but repeated 10 times. The reacted solutions were then combined into a 15 mL centrifuge tube and washed with DMF (5 mL x 3) and acetone (5 mL x 3). The material soaked in acetone overnight, followed by washing with acetone (5 mL x 3). The material was then dried in the vacuum oven for 1 hour at 80 °C. The material was then activated by heating at 120 ˚C for overnight under high vacuum on a Micromeritics Smart Vacprep.

Competition Reaction for Prior Seeding of **L2**

Zirconium oxynitrate hydrate (79.7 mg, 0.345 mmol) was placed in a 2-dram vial. 1 mL of *N*,*N*-dimethylformamide was added and the solution was sonicated until solubility was achieved. 1 mL of formic acid was added to the vial, which turned clear shortly thereafter. The Zr_6 node solution was sonicated if any remaining particles were not yet soluble. The vial was placed in an 80 °C oven for 1 hour. A **L2** solution was prepared by adding 19.1 mg (0.0267 mmol) of **L2** to 1 mL of *N*,*N*- dimethylformamide and was sonicated until soluble. After the Zr_6 node solution was removed from the oven and cooled to room temperature, 200 µL aliquots of the solution were placed in nine separate 0.5 dram vials. The following amounts of **L2** (in µL) were added to each of the nine vials:

20, 40, 60, 80, 100, 120, 140, 160, and 180. The vials were then placed in a 100 °C oven for 30 minutes. The vials were removed from the oven and cooled to room temperature. A **L1** solution was prepared by adding 19.1 mg (0.0267 mmol) of **L1** to 1 mL of *N*,*N*- dimethylformamide and sonicated to ensure solubility. The **L2** nucleated systems were removed from the oven and cooled to room temperature. Then, aliquots of **L1** (in µL) were added in the following order to the vials containing the above specific amounts of **L2** in solution: 180, 160, 140, 120, 100, 80, 60, 40, and 20. The vials were then placed in a 100 °C oven for 16 hours to react. Upon reaction completion, the vials were removed from the oven and cooled to room temperature. The mixtures were placed in 1.5 mL centrifuge tubes and centrifuged for five minutes to remove the supernatant. Then, the resultant white powder was washed with *N*,*N*-dimethylformamide (1.5 mL×2) and acetone (1.5 mL×2). The material was then dried in a vacuum oven at 80 °C for 1 hour.

To obtain adequate material for N_2 isotherm measurement of a specific ratio, the above procedure was repeated using the specific **L1**: **L2** ratio of interest on the same scale but repeated 10 times. The reacted solutions were then combined into a 15 mL centrifuge tube and washed with DMF (5 mL x 3) and acetone (5 mL x 3). The material soaked in acetone overnight, followed by washing with acetone (5 mL x 3). The material was then dried in the vacuum oven for 1 hour at 80 °C. The material was then activated by heating at 120 ˚C for overnight under high vacuum on a Micromeritics Smart Vacprep.

NU-903 and NU-1008 Syntheses

The pure phase synthesis of NU-903 and NU-1008 were preformed following published procedure.[1]

IV) Methods for Material Characterization

Powder X-ray Diffraction Analysis

Powder X-ray diffraction (PXRD) patterns of the samples were measured by a STOE-STADI MP powder diffractometer operating at 40 kV voltage and 40 mA current with Cu-Kα1 X-ray radiation (λ = 0.154056 nm) in transmission geometry.

N_2 Sorption Isotherm Measurements

N_2 adsorption and desorption isotherms on activated materials were measured on a Micromeritics Tristar (Micromeritics, Norcross, GA) instrument at 77 K. Around 20 mg of sample was used in each measurement and the specific surface areas were determined using the Brunauer−Emmett−Teller model from the N_2 sorption data in the region P/P_0 = 0.005–0.05. Pore size distributions were obtained using DFT calculations using a carbon slit-pore model with a N_2 kernel.

^{1}H NMR

MOF samples (1 mg) were digested with 8 drops of D_2SO_4. After sonication for 20 min, 600 µL of DMSO-d_6 was added into the mixture. Proton NMR spectra were collected on a Bruker Avance III 500 MHz system equipped with DCH CryoProbe and automated with a BACS-60 autosampler.

Transmission Electron Imaging

Transmission electron microscopy (TEM) images were collected at Northwestern University's EPIC /NUANCE facility using a Hitachi HD2300 STEM using a standard copper mesh sample holder at 200 kV.

Scanning Electron Microscope Imaging

Prior to observation, the samples were coated with OsO_4 (~9 nm) in a Denton Desk III TSC Sputter Coater. Scanning electron microscopy (SEM) images were acquired from a Hitachi SU8030 scanning electron microscope.

V) N_2 Sorption Experiments

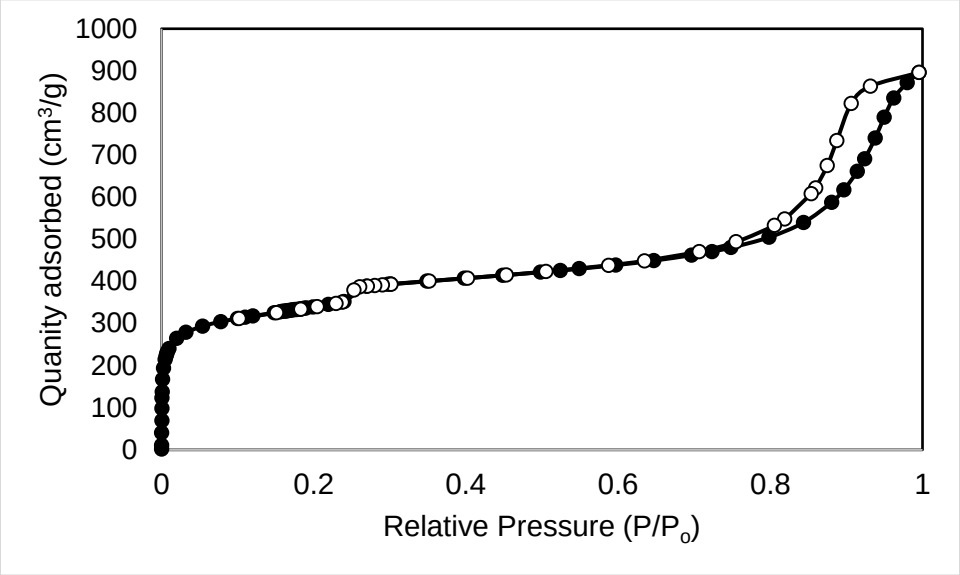

Figure S3: N_2 Isotherm of 30% **L2** prior nucleation followed by 70% **L1**. Reported BET surface area of 1245 m^2/g

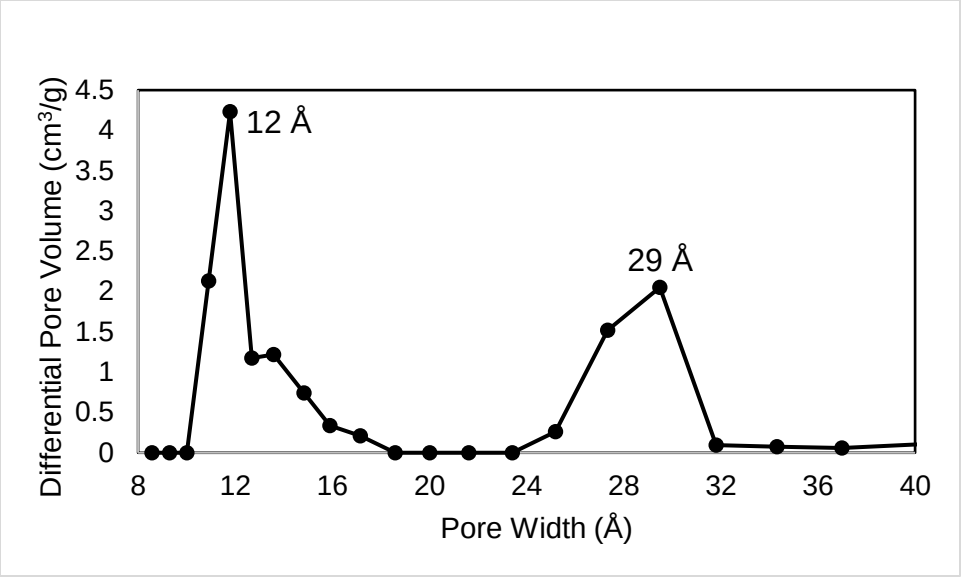

Figure S4: Pore Size Distribution of 30% **L2** prior nucleation followed by 70% **L1.**

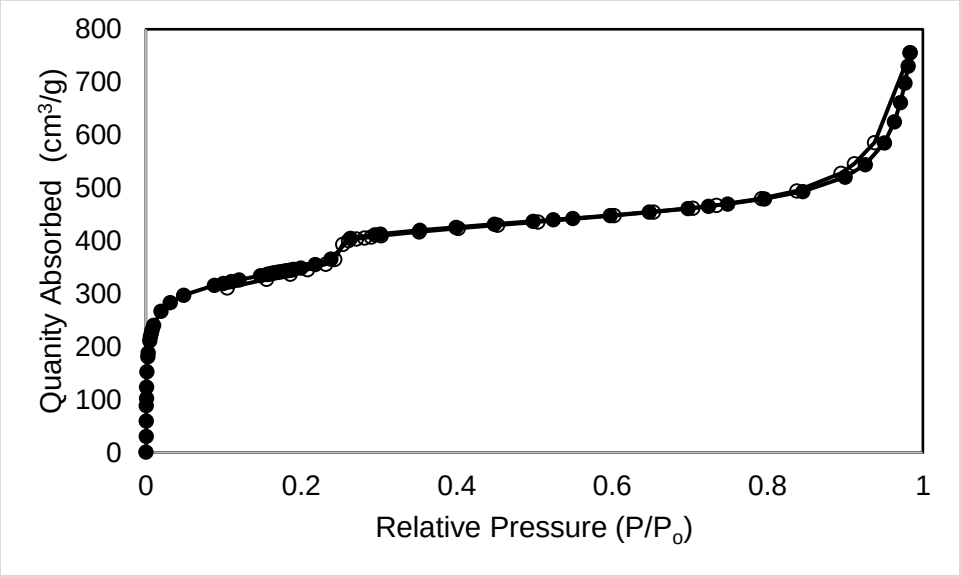

Figure S5: N_2 Isotherm of 30% **L1** prior nucleation followed by 70% **L2**. Reported BET surface area of 1280 m^2/g

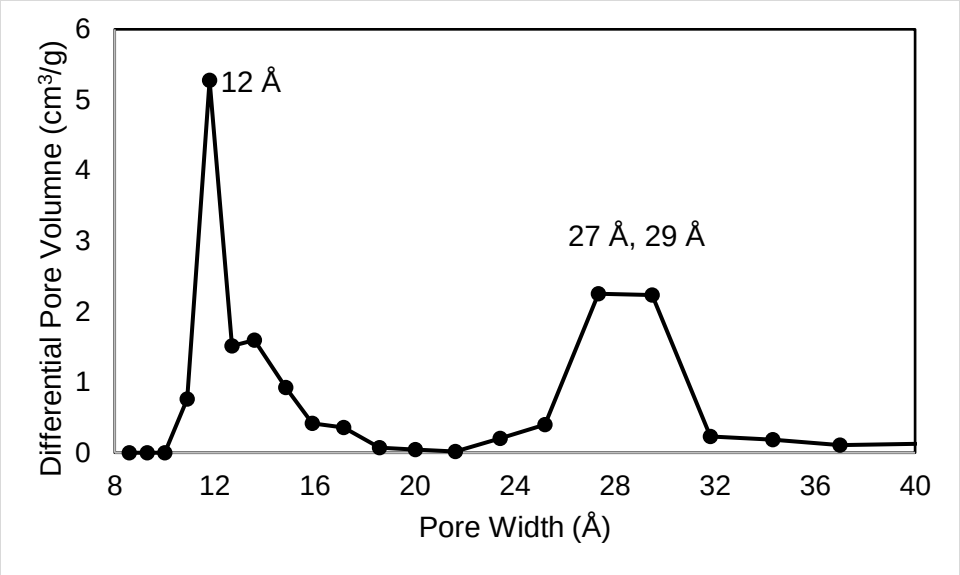

Figure S6: Pore Size Distribution of 30% **L1** prior nucleation followed by 70% **L2.**

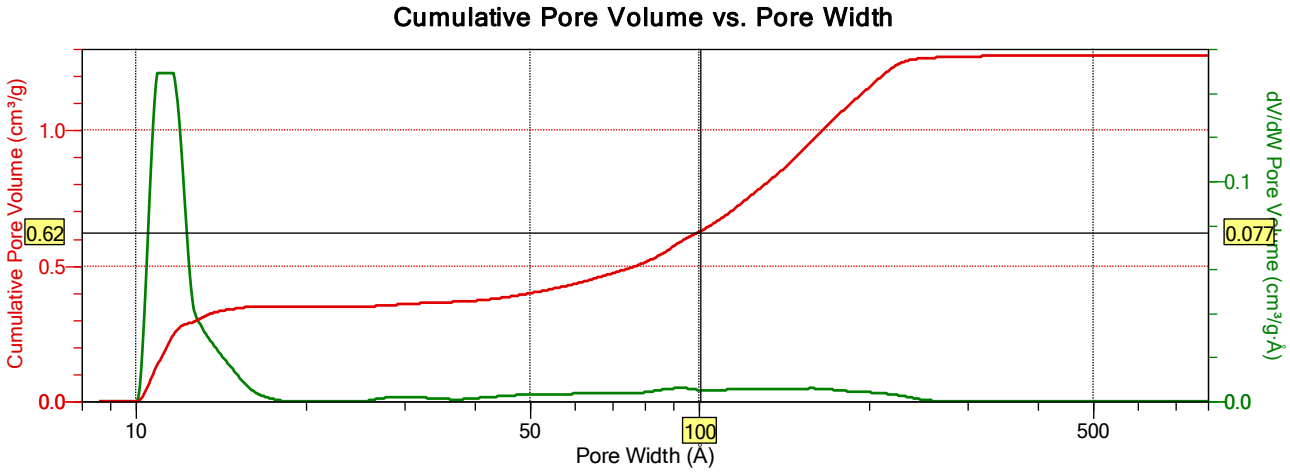

Figure S7: Cumulative pore volume and differential pore volume vs. pore width for simultaneous nucleation of 70% **L1**: 30% **L2**.

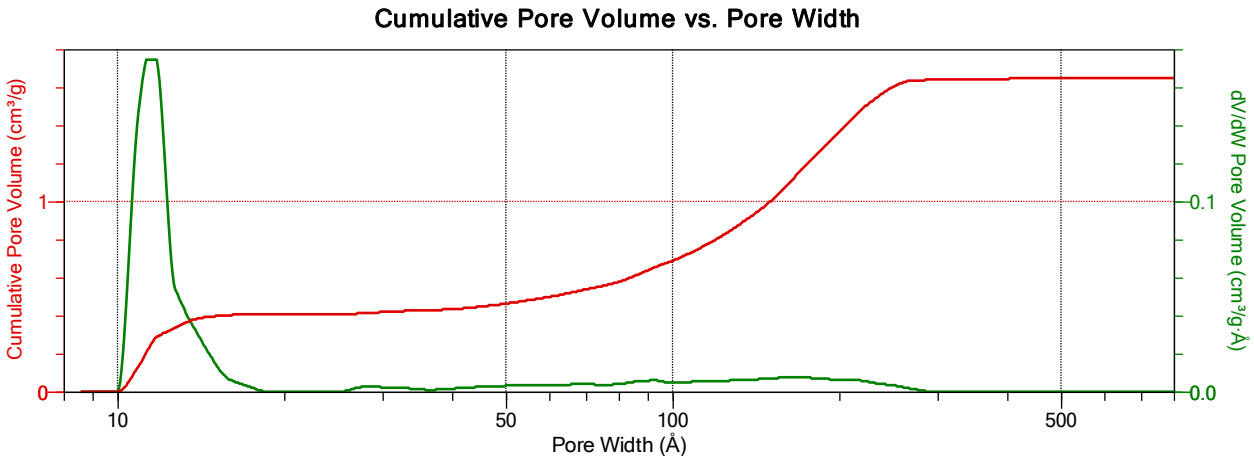

Figure S8: Cumulative pore volume and differential pore volume vs. pore width for simultaneous nucleation of 50% **L1**: 50% **L2**.

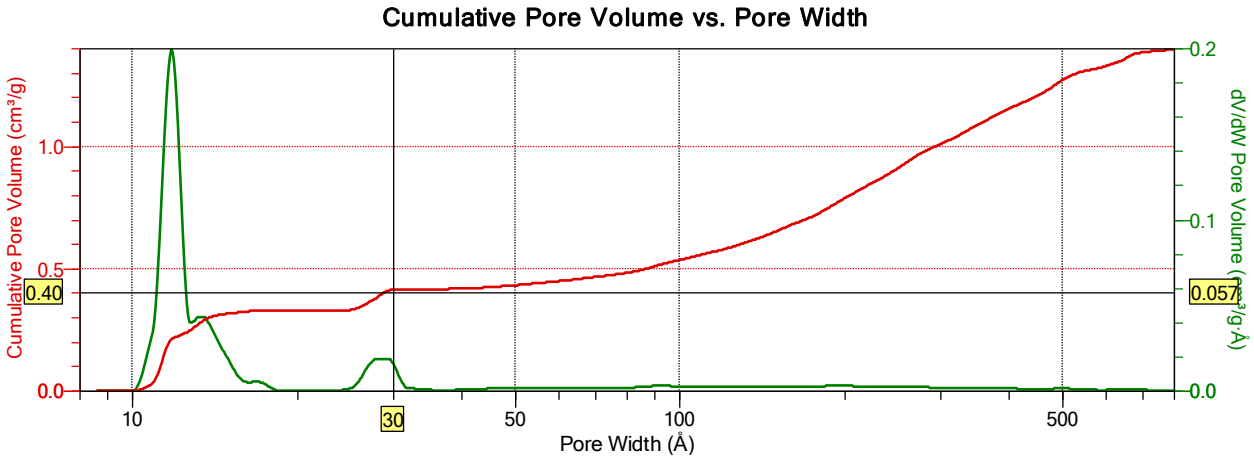

Figure S9: Cumulative pore volume and differential pore volume vs. pore width for simultaneous nucleation of 30% **L1**: 70% **L2**.

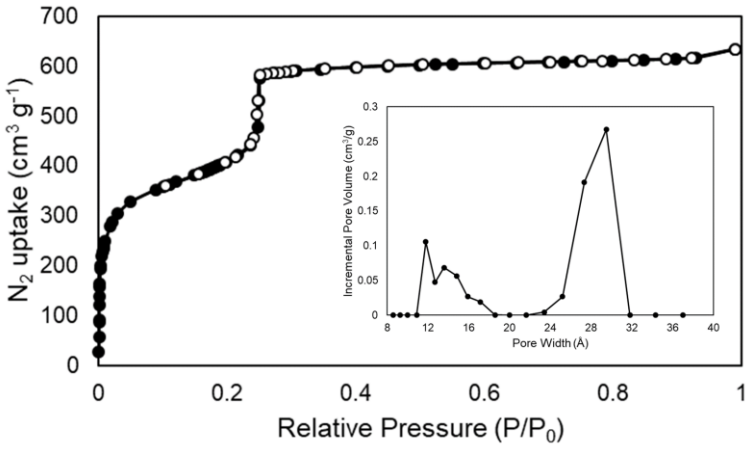

Figure S10: Isotherm and pore size distribution (inset) of NU-1008 with a BET surface area of 1420 m^2/g.

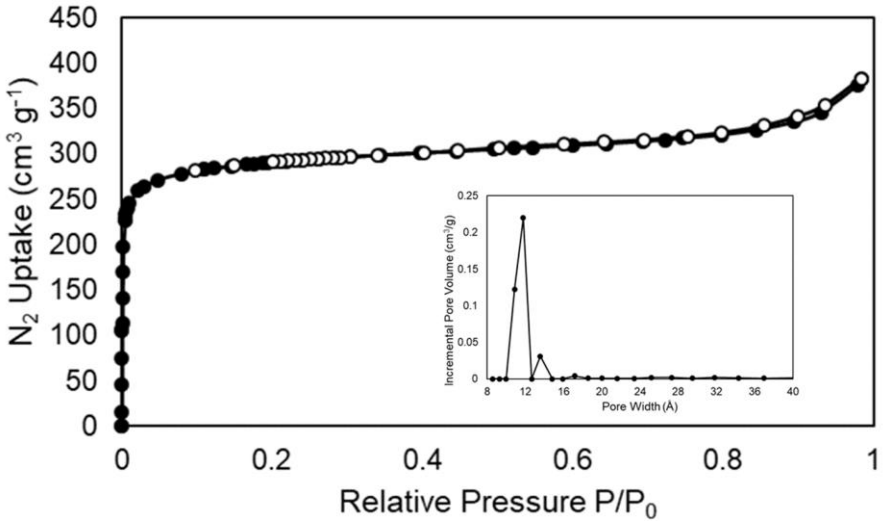

Figure S11: Isotherm and pore size distribution (inset) of NU-903 with a BET surface area of 1140 m^2/g

VI) ^1H NMR Spectra

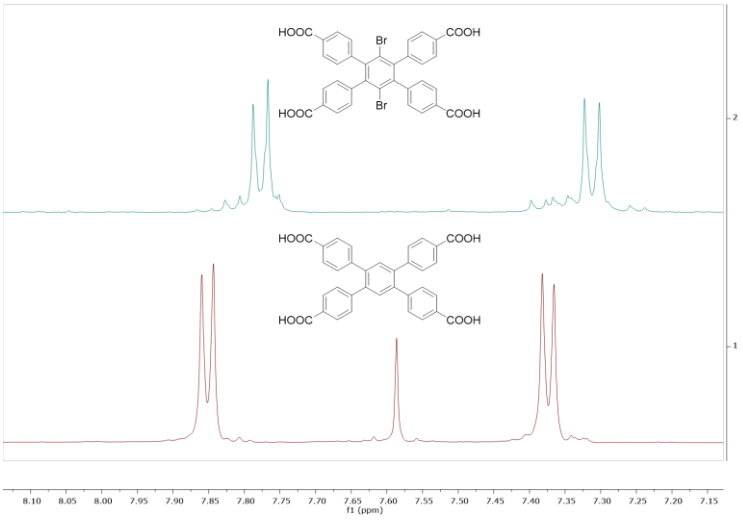

Figure S12: Stacked 500 MHz ^1H spectra of **L1** (bottom) and **L2** (top) in DMSO-d_6.

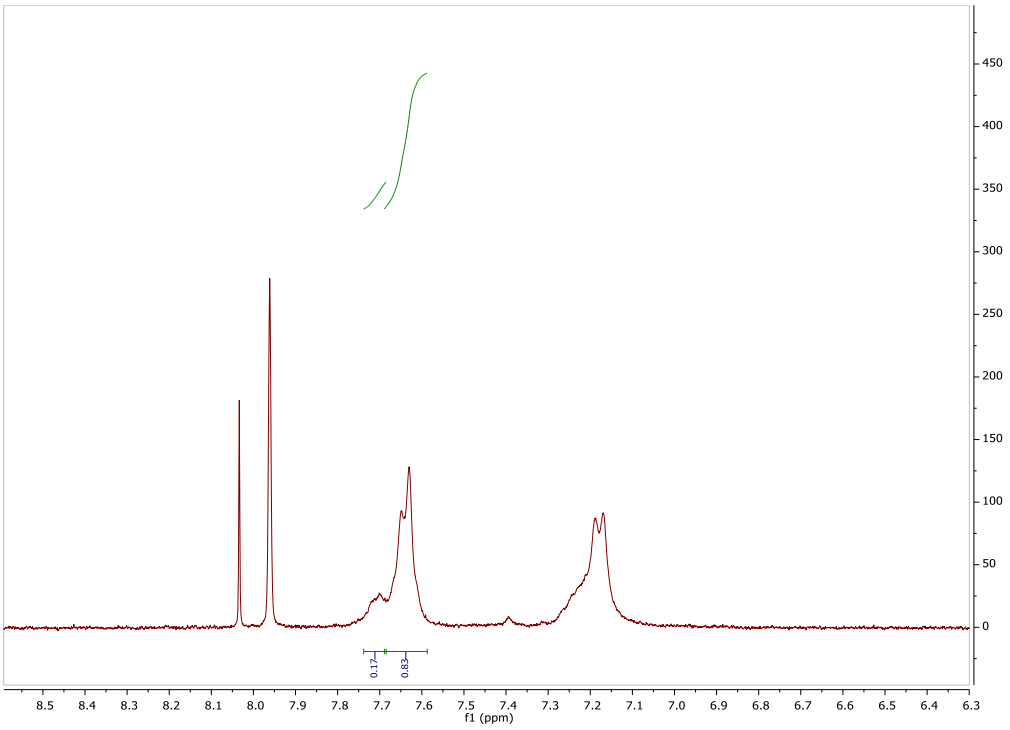

Figure S13: 10% **L1**: 90% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

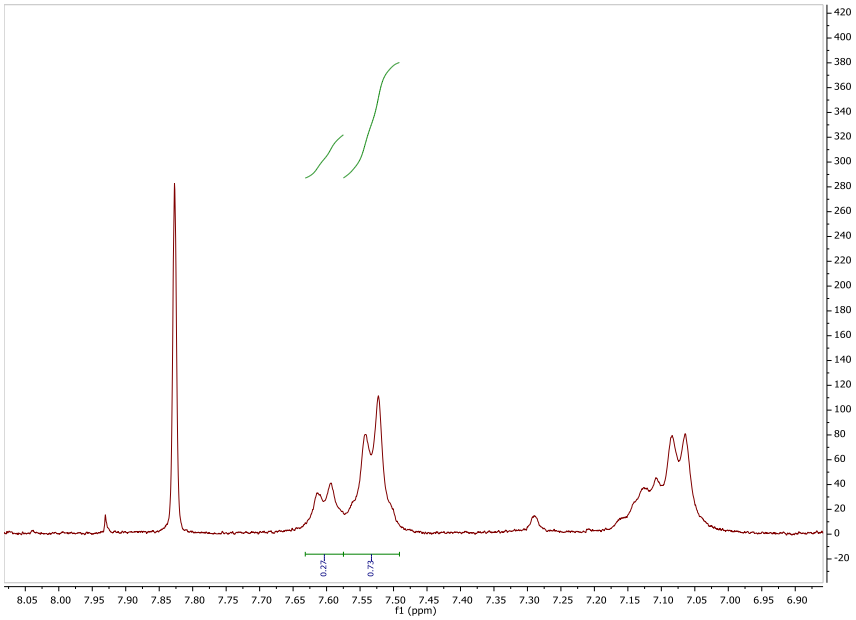

Figure S14: 20% **L1**: 80% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

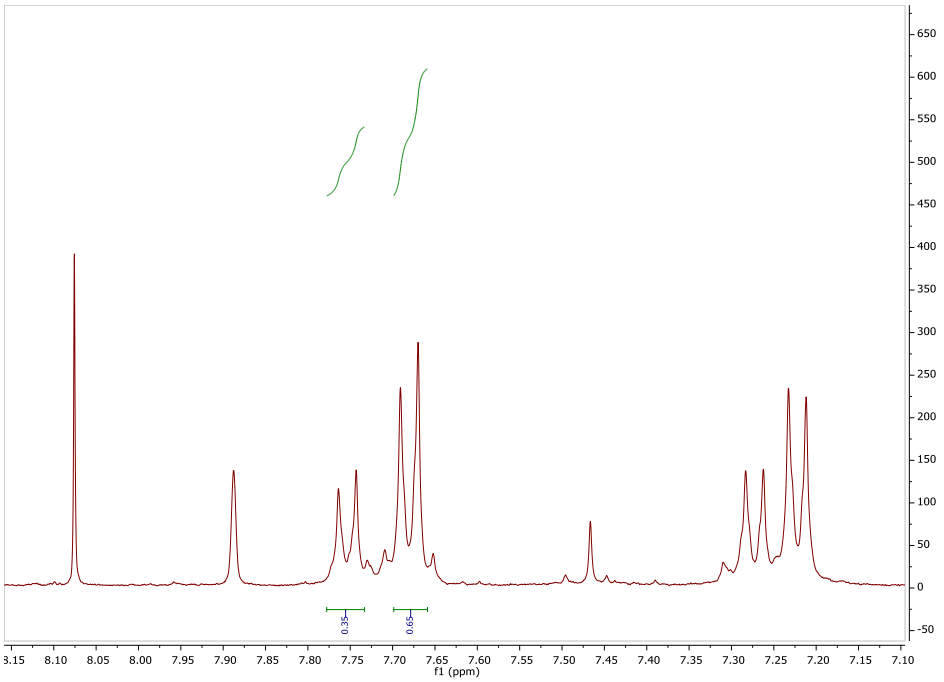

Figure S15: 30% **L1** : 70% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

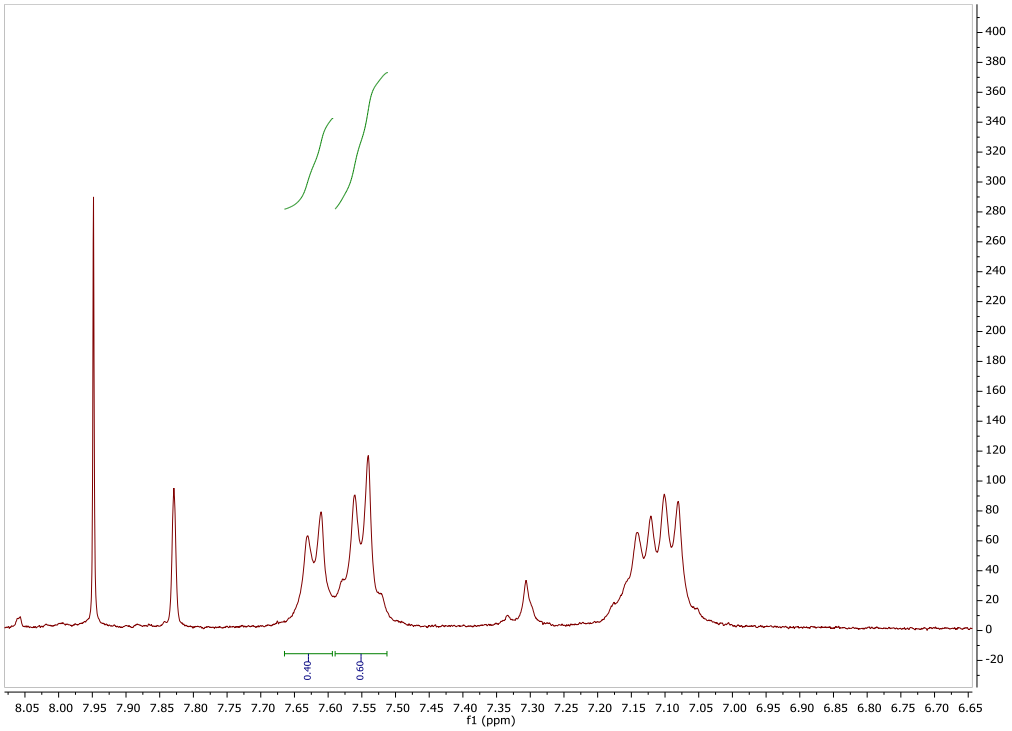

Figure S16: 40% **L1**: 60% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

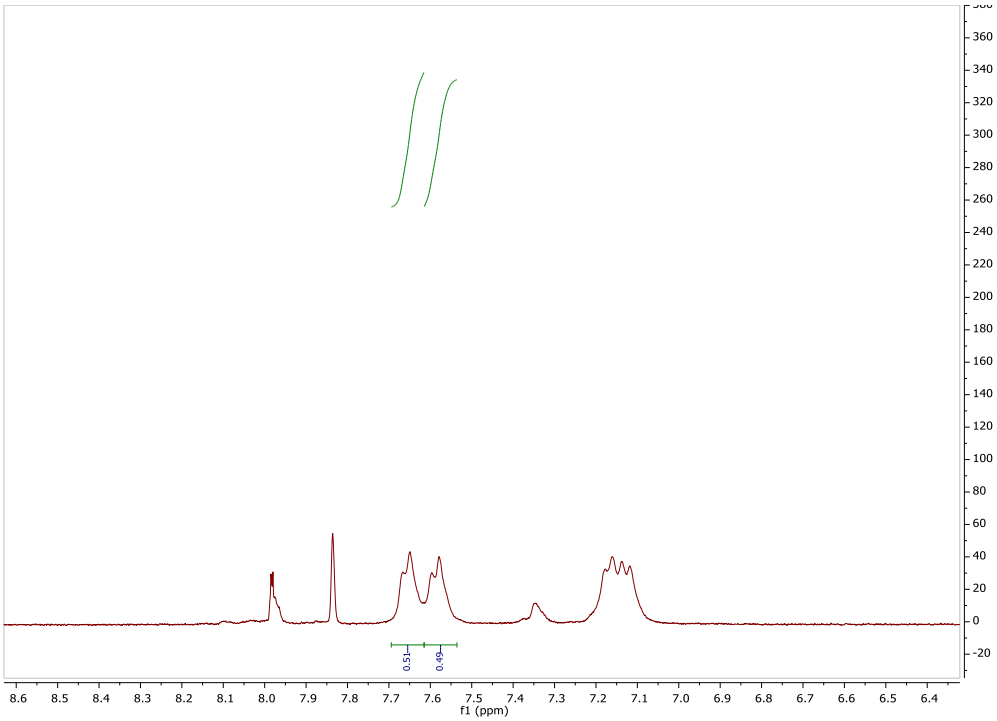

Figure S17: 50% **L1**: 50% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

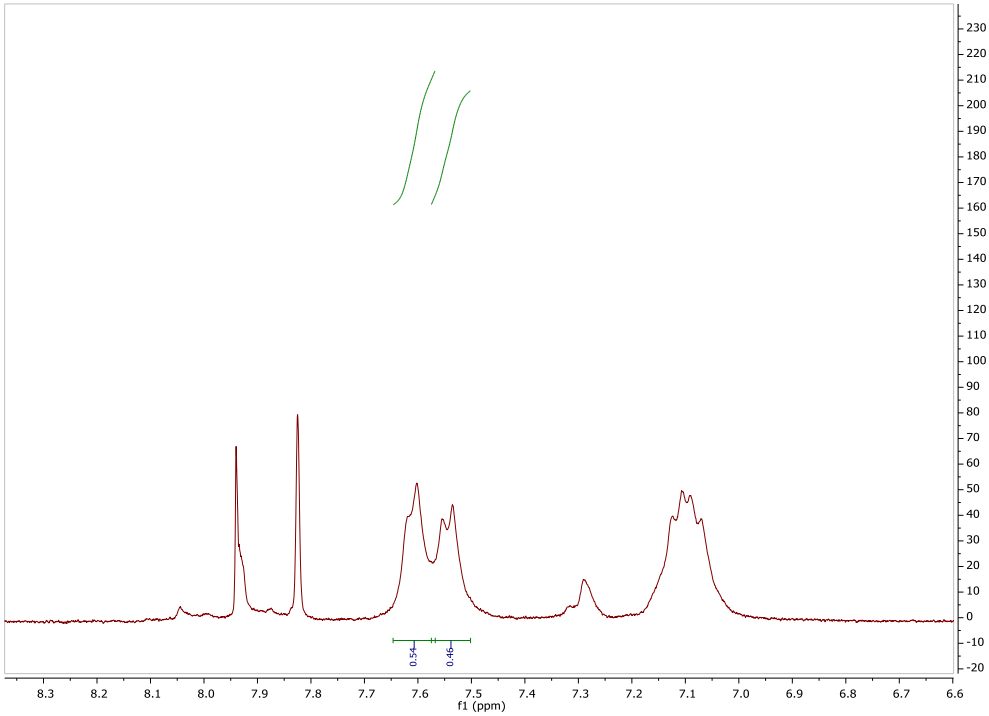

Figure S18: 60% **L1**: 40% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

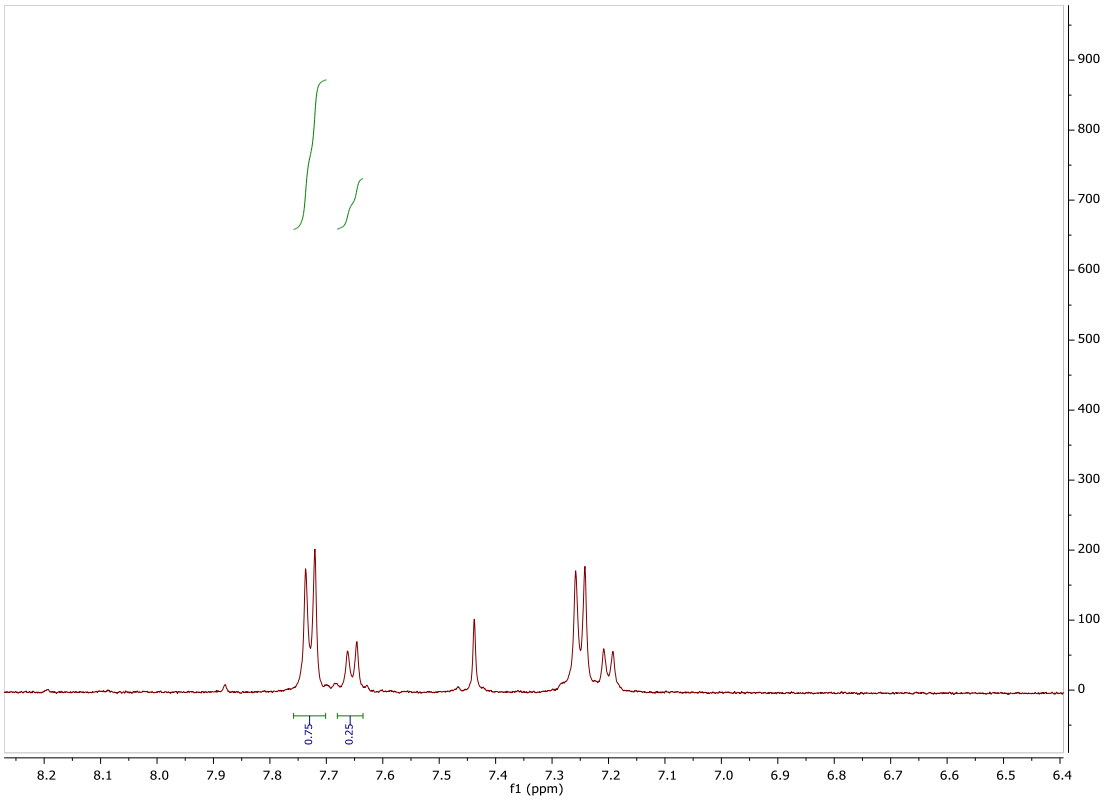

Figure S19: 70% **L1**: 30% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

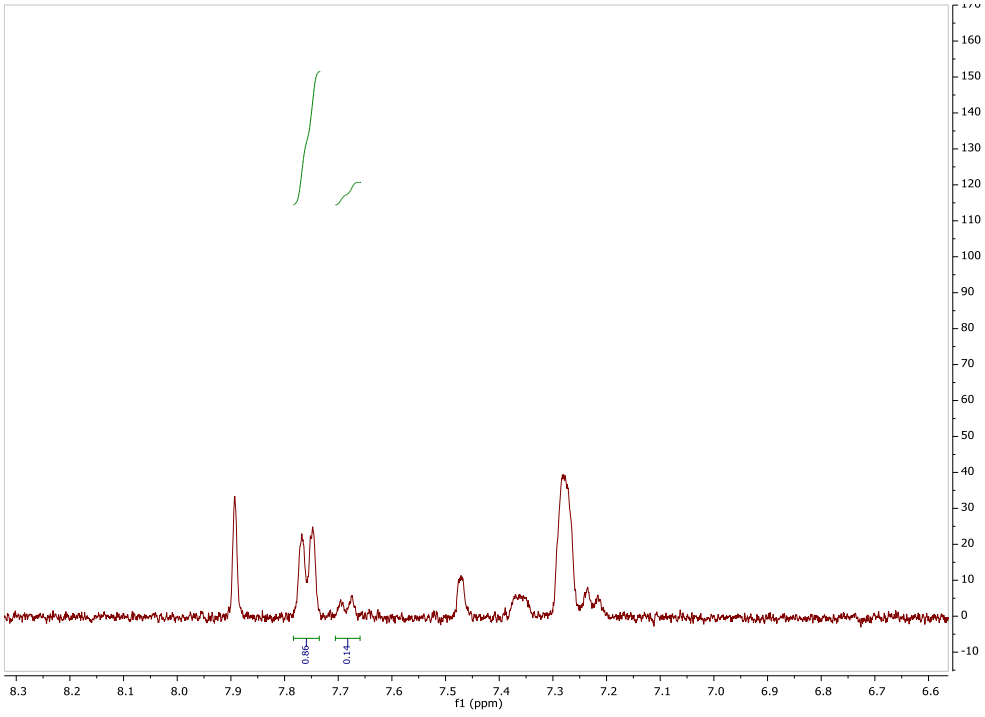

Figure S20: 80% **L1**: 20% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

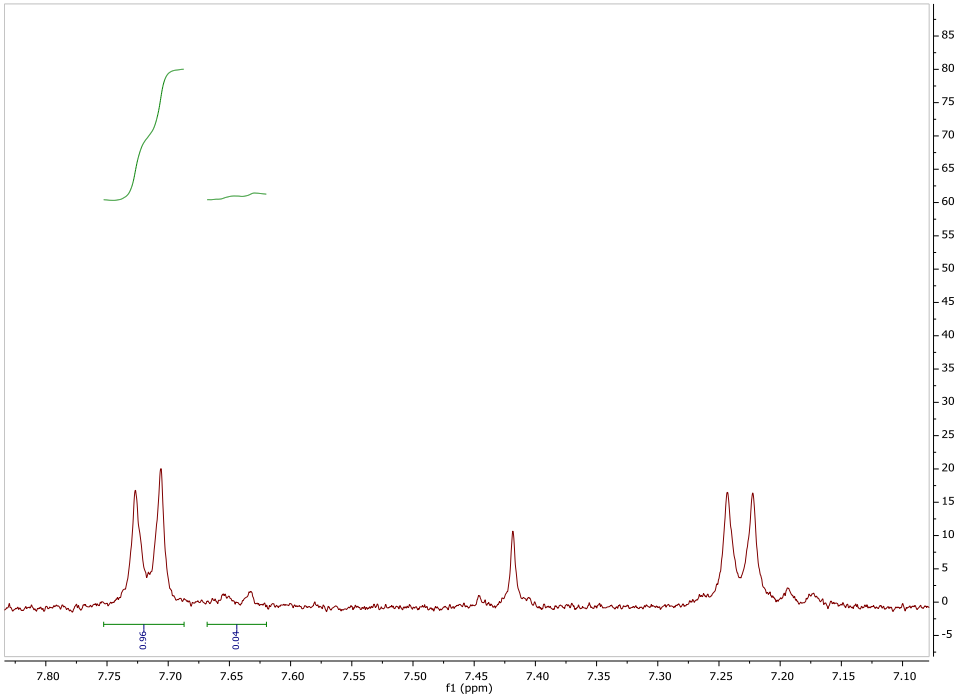

Figure S21: 90% **L1**: 10% **L2** simultaneous nucleation MOF digested in D_2SO_4 / DMSO-d_6

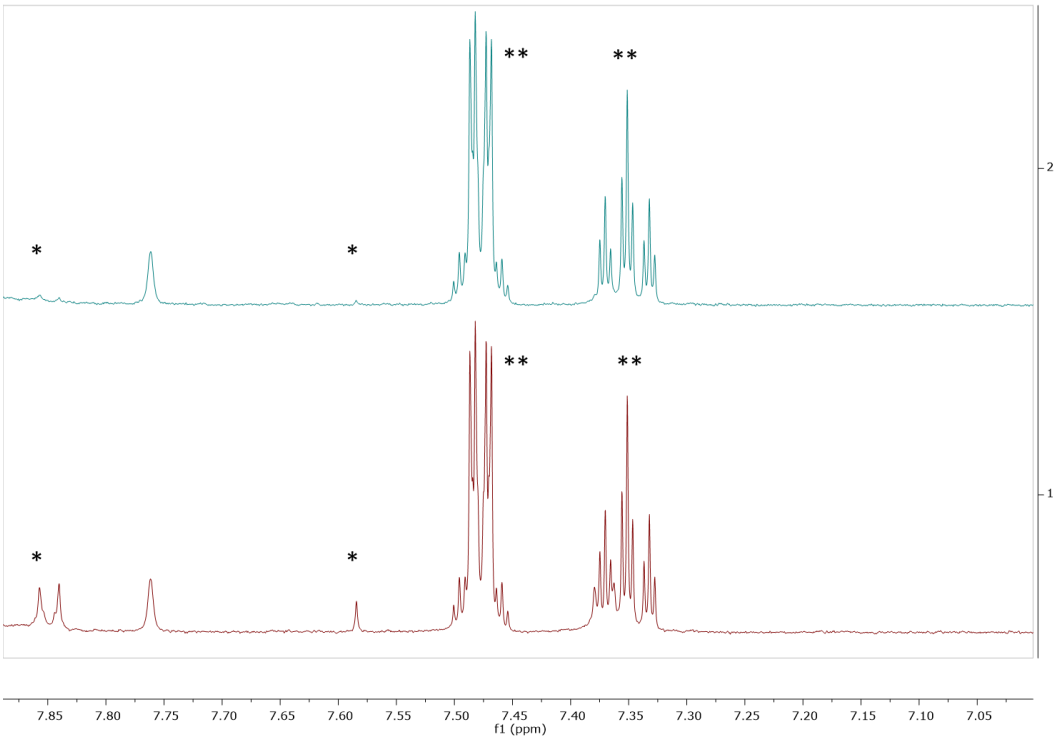

Figure S22: Stacked ^{1}H NMR spectra of time = 0 min (bottom) and time = 30 min (top) of 50% **L1** nucleation of Zr_6 node solution, (* refers to **L1** peaks, ** refers to internal standard 1-bromo-3,5-difluorobenzene)

VII) PXRD Patterns

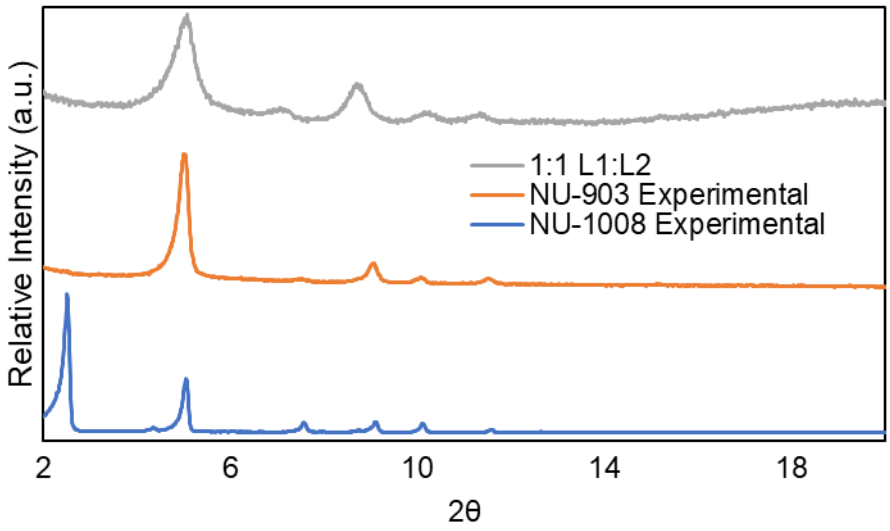

Figure S23: PXRD patterns of pure-phase NU-903, NU-1008, and 1:1 **L1**: **L2** under simultaneous nucleation.

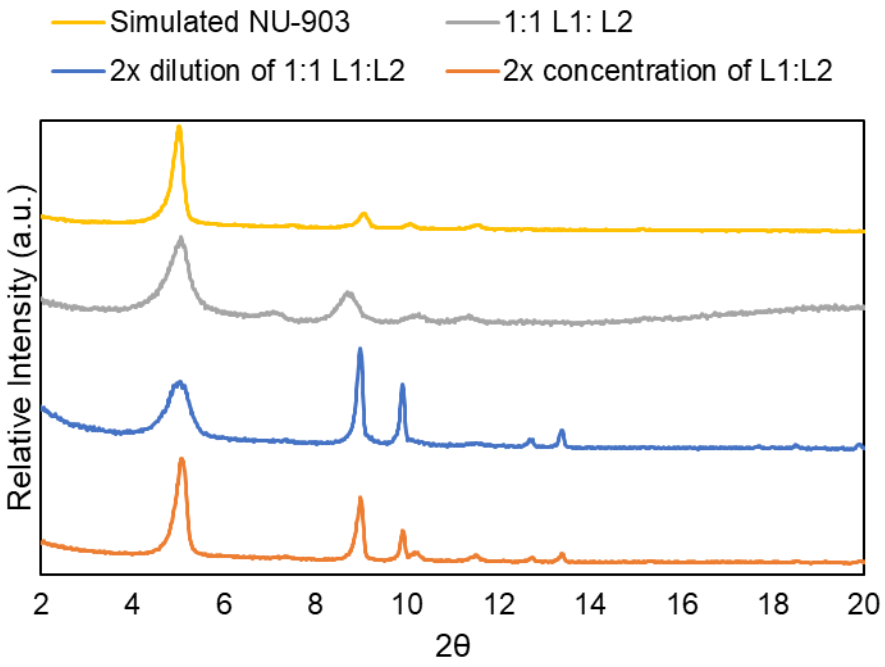

Figure S24: PXRD patterns examining the role of absolute concentration of the linker in solution to determine a possible change in kinetic product for the 1:1 **L1**: **L2** reaction conducted under simultaneous nucleation. While the 9, 10, 12.8, and 13.4 2θ peaks increase in intensity, the prediction of these shifts from the simulated pattern suggests that a change in the concentration of the system can slightly affect the crystallinity of the MOF particle, yet we did not observe a

phase change.

VIII) SEM Images

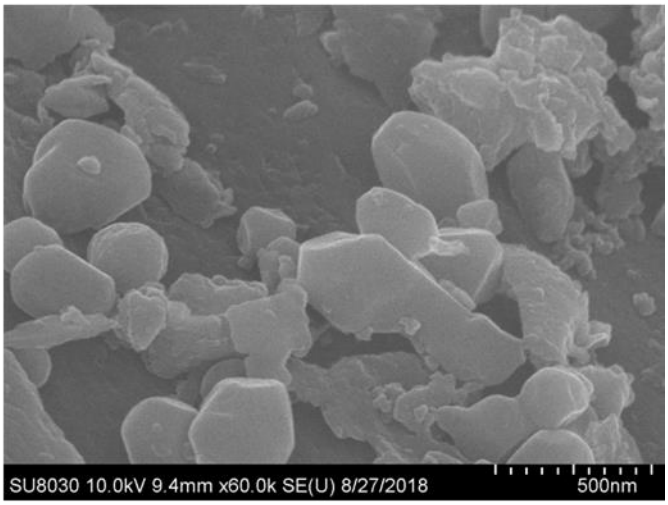

Figure S25: Image of simultaneous nucleation of 50% **L1**: 50% **L2**.

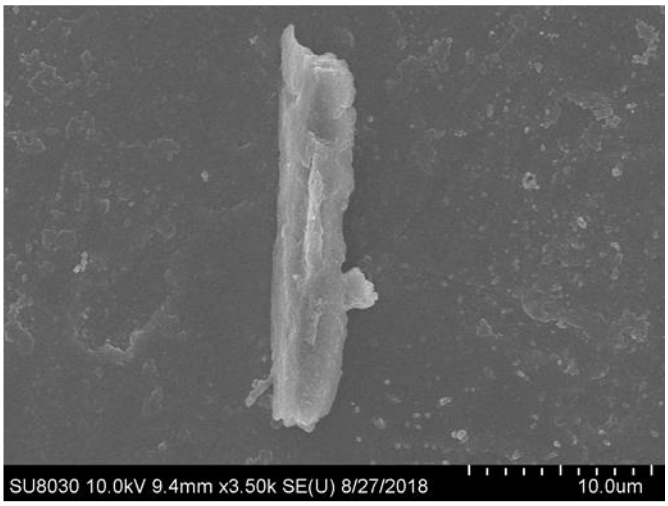

Figure S26: Image of simultaneous nucleation of 30% **L1**: 70% **L2.**

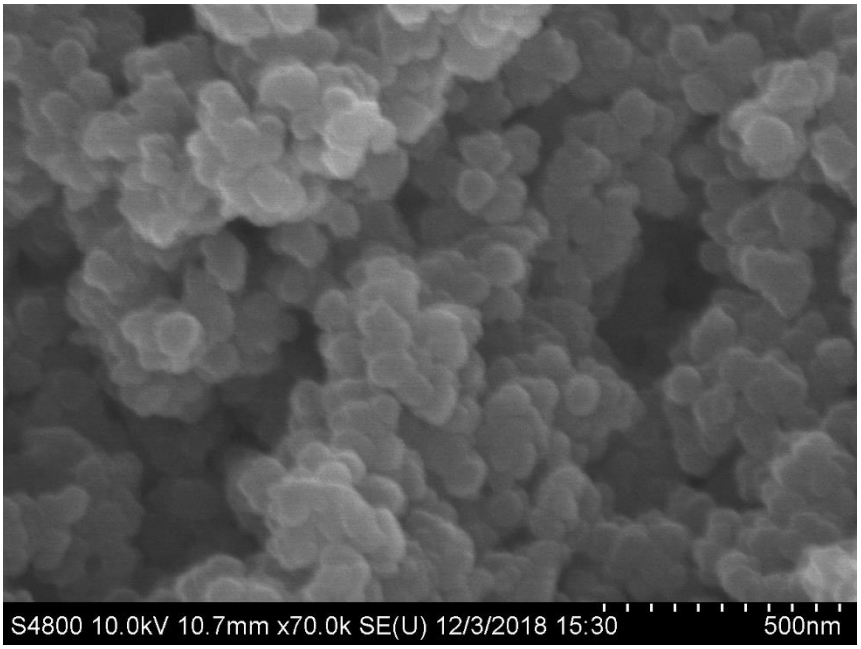

Figure S27: Image of simultaneous nucleation of 50% **L1**: 50% **L2** with 2x concentration of system**.**

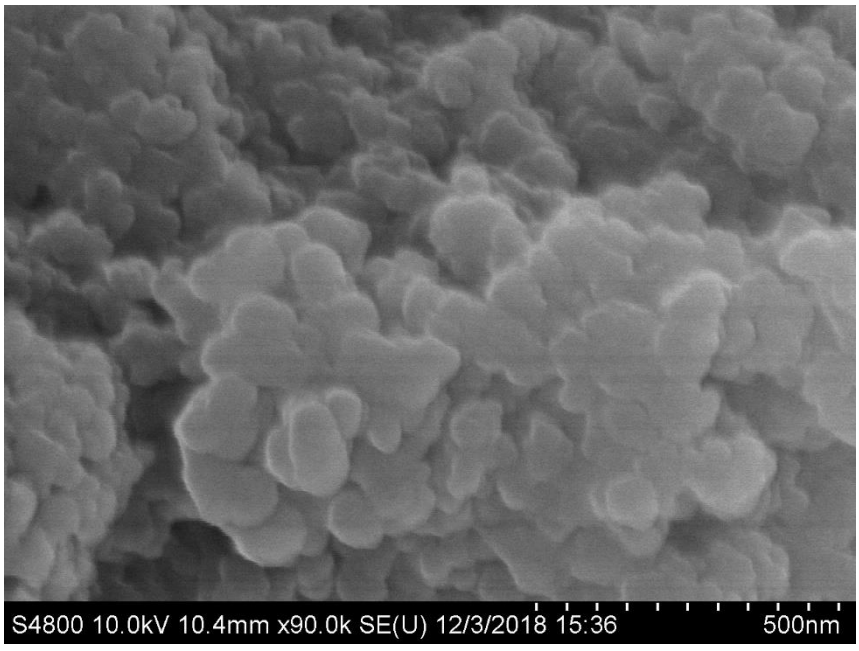

Figure S28 Image of simultaneous nucleation of 50% **L1**: 50% **L2** with 2x dilution of system**.**

References

1. Lyu, J.; Zhang, X.; Otake, K.-i.; Wang, X.; Li, P.; Li, Z.; Chen, Z.; Zhang, Y.; Wasson, M. C.; Yang, Y.; Bai, P.; Guo, X.; Islamoglu, T.; Farha, O. K., Topology and porosity control of metal–organic frameworks through linker functionalization. *Chem. Sci.* **2019**, 10.1039/C8SC04220A.