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NPG ONTOLOGY TERMS

Subjects	Physical sciences/Chemistry/Synthesis/ Physical sciences/Chemistry/Materials chemistry (porous materials)
Techniques	

PROTOCOLS KEYWORDS

Metal-organic framework (MOFs), NU-1000, mesoporous, Atomic layer

deposition In Metal organic frameworks (AIM), Solvent Assisted Ligand Incorporation (SALI)

EDITORIAL SUMMARY

Metal-organic frameworks (MOFs) are porous, crystalline materials with well-defined structures that can be used in many applications from gas storage to catalysis and drug storage. This protocol is for the preparation of the MOF NU-1000.

TWEET

Preparation and modification of metal-organic framework NU-1000.

COVER TEASER

Mesoporous metal-organic framework

Scalable Synthesis and Post-modification of a mesoporous metal-organic framework called NU-1000

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ABSTRACT

The synthesis of **NU-1000**, a highly robust mesoporous (containing pores larger than 2 nm) metal-organic framework (MOF), can be conducted efficiently on a multigram scale from inexpensive starting materials. Tetrabromopyrene and (4-(ethoxycarbonyl)phenyl)boronic acid can easily be coupled to prepare the requisite organic strut with four metal binding sites in the form of four carboxylic acids, while zirconyl chloride octahydrate is used as a precursor for the well-defined metal oxide clusters. **NU-1000** has been reported as an excellent candidate for the separation of gasses and a versatile scaffold for heterogeneous catalysis. In particular, it is ideal for the catalytic deactivation of nerve agents and shows great promise as a new generic platform for a wide range of applications. Multiple post-synthetic modification protocols have been developed using **NU-1000** as the parent material, making it a potentially useful scaffold for several catalytic applications. The procedure for the preparation of **NU-1000** can be scaled up reliably and is suitable for the production of 50 grams of the tetracarboxylic acid containing organic linker and 200 mg to 2.5 g of **NU-1000**. The entire synthesis is performed without purification by column chromatography and can be completed within 10 days.

INTRODUCTION

Metal-organic frameworks (MOFs) are a class of crystalline materials that are formed by coordination bonds between metal-based nodes and organic linkers that have multiple coordination sites. [1-4] Both the metal component and the organic linker can be viewed as multitopic building blocks that self-assemble to form a rigid crystalline polymer. As a result of their well-defined and atomically precise structures, exceptional porosities, and the tunability of nearly every aspect of this class of porous material (including particle size, pore size, surface area, density, topology and molecular affinity) MOFs are being investigated extensively for a variety of applications including, but not limited to gas storage[5-8] and separation[9,10], heterogeneous catalysis[11], sensing,[12] light harvesting[13] and drug delivery[14,15].

NU-1000, a recently reported MOF, based on zirconium oxide nodes, has several key properties that are essential in rendering it a useful platform for many applications.[10,16-18] The structural projection of **NU-1000** can be visualized (**Fig. 1**) as a 2D extended Kagome network, also referred to as a trihexagonal tiling simply described as a set of equilateral triangles and hexagons where each hexagon is surrounded by six triangles and each triangle by three hexagons,[19] built using eight-connected $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(H_2O)_4(OH)_4$ nodes[20] at each vertex and tetratopic 1,3,6,8-(p-benzoate)pyrene linkers positioned at each edge. The strong bonding between the zirconium nodes and the carboxylates of the linkers ensure the high thermal and chemical stability[21] of **NU-1000**, while the Lewis acidity of the Zr_6 nodes provides isolated reactive sites for certain chemical transformations. The exceptionally wide (31 Å) mesoporous channels extending throughout the structure can alleviate mass transport issues often encountered in catalysis applications and allow for the rapid flow of substrates and reagents throughout the entire heterogeneous framework.

Recently, we have been able to demonstrate that **NU-1000**, and the isostructural more Lewis-acidic Hf variant, **Hf-NU-1000**[22], are efficient Lewis-acid catalysts for the opening of styrene oxide using CO_2 (1 atm gauge pressure) at room temperature to form styrene carbonate, a useful monomer for polycarbonate production.[22] Furthermore, we have explored the potential of **NU-1000** toward the catalytic hydrolysis of phosphate ester-containing compounds, a key step in the destruction of phosphate-based chemical warfare agents.[23] When the nerve agent Soman, also known as GD, was tested as a substrate in a government facility, solid **NU-1000** under 50% humidity was able to degrade the nerve agent 80 times faster than the most active MOF reported to date. The rate we observed is comparable to the best heterogeneous degradation materials.[24]

Figure 1 Structure of **NU-1000** and developed post-synthetic modification methods on this platform. See refs. 9,15-17. The blue, red, and black spheres represent zirconium, oxygen,

and carbon, respectively. The perfluoro alkane SALIed into NU-1000 is represented in green and the gold sphere shows the location of a metal cluster introduced into NU-1000 using AIM.

In addition, it is possible to perform post-synthesis functionalization of **NU-1000** to prepare new materials that can be used in different applications[25]. The connectivity of **NU-1000** gives rise (**Fig. 1**) to Zr-nodes with hydroxyl containing[20] (i.e., –OH or $-OH_2$, *described in more detail below*) functional groups pointing into the large 1-D mesoporous hexagonal channels of the framework. These free and exposed —OH groups are ideal grafting sites and can be easily tailored to serve a specific function. It has been demonstrated that by doing **A**tomic Layer Deposition **I**n **M**OFs (**AIM**)[16], Zn and Al oxides can be formed with atomic precision at the exposed –OH sites of **NU-1000**. Very importantly, this process occurs without changing the overall structure of the framework. The increased Lewis acidity of the newly installed metal oxides gives rise to new catalytic activity, and since the **AIM** method can be generalized to deposit a multitude of different metals, a wide range of reactivity can be explored by implementing **AIM** within **NU-1000**.

The same –OH groups, protruding from the Zr_6 nodes, can also react with organic molecules carrying a pendent carboxylic acid or phosphonic acid group. This method, recently termed **S**olvent-**A**ssisted **L**igand **I**ncorporation (**SALI**)[10,17,18,27] has been used to enhance CO_2 adsorption within **NU-1000**, and to allow redox active motives anchored inside the framework to communicate electronically and display the property of redox conductivity[26]. Using **SALI**, task specific functionality can easily be incorporated into the robust **NU-1000** framework.

Given the demonstrated potential of **NU-1000** as an atomically defined heterogeneous platform for chemistry, it is desirable to develop a reliable and scalable synthetic procedure to prepare this particularly useful MOF. Based on the original synthetic procedure, with only subtle modifications, we demonstrate that both the organic linker and

NU-1000 can be synthesized on multigram scales. Additional experimental procedures describing the **AIM** and **SALI** processes using standard functionalization reagents is also included to serve as a guide to post-synthesis functionalization of **NU-1000**.

Overview of the Procedure // Experimental Design

The preparation of the 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid strut can be accomplished on 50 g scale using a standard Suzuki-Miyaura reaction between 1,3,6,8-tetrabromopyrene and (4-(ethoxycarbonyl)phenyl)boronic acid. The ethyl ester is used to slow down the hydrolysis of the benzoic ester during the C-C bond forming step. Without it, an insoluble mixture of mono, bis, tris, and tetra benzoic acids is formed. Simple filtration provides the tetraester**(1)** which is hydrolyzed cleanly to the tetra-acid**(2)** under basic conditions in dioxane. After acidification of the mixture, the strut is isolated by filtration on a 50 g scale. (**Fig. 2**) The synthesis of **NU-1000** from zirconyl chloride octahydrate, the tetra acid strut and benzoic acid as modulator in *N,N*-dimethylformamide can be scaled so as to prepare 2.5 g in a single reaction vessel. After removal of the modulator by washing the framework with an HCl solution, **NU-1000** is thermally activated to remove any extraneous solvent and analyzed by gas sorption and PXRD. (**Fig. 3**) The material produced from the large scale synthesis of **NU-1000** possesses identical properties to that formed from the previously reported[20] synthetic procedure used to prepare only 35 mg of activated material. In this protocol, we also provide procedures for performing **AIM** and **SALI** modification; these are scalable allowing production of up to 250 mg per batch of materials.

MATERIALS

REAGENTS

- **!CAUTION** Many of the reagents used in this synthesis procedure are hazardous. Please consult material safety data sheets for each item. Suitable personal protection equipment such as proper clothing, goggles, and gloves are required. It is highly

recommended to work inside a fume hood and to vent the MOF growth oven (VWR Symphony Oven).

- Dioxane, ≥99.0% (Sigma-Aldrich; cat. no. 360481)
- 1,3,6,8-Tetrabromopyrene, 97% (Sigma-Aldrich; cat. no. 717274)

CRITICAL: Use Aldrich 97% purity starting material. Lower purity starting material can result in unwanted products that are difficult to remove.

- 4-Ethoxycarbonylphenylboronic acid, 98% (Combi-blocks; cat. no. BB-2113)
- Potassium phosphate tribasic, ≥98% (Sigma-Aldrich; cat. no. P5629)
- Fmoc-Gly-Gly-Gly-OH, ≥97% (ChemImpex International; cat. no. 08072)
- Tetrakis (triphenylphosphine) palladium (0), 99% (Strem; cat. no. 46-2150)

CRITICAL: Only use this catalyst when it is gold to yellow color. Orange to brown color indicates some oxidation of the catalyst and may lead to impurities.

- DI water (Northwestern University)
- Acetone, chloroform, methanol (MeOH), N,N-dimethylformamide (DMF), dichloromethane (Any commercial supplier, reagent grade)
- Potassium hydroxide, 90% (Sigma-Aldrich; cat. no. 484016)
- Hydrogen chloride, 36.5-38.0% (Avantor, cat. no. 2612)
- zirconyl chloride octahydrate, 98% (Sigma-Aldrich; cat. no. 224316)

CRITICAL: Store this chemical in a dessicator as it is exceedingly hydroscopic.

- Benzoic acid, ≥99.5% (Sigma-Aldrich; cat. no. 242381)

CRITICAL: Benzoic acid purchased from other vendors has been correlated to a smaller mesoporous step observed in the isotherm, which indicates impurities formed during MOF growth.

- Dimethylaluminum isopropoxide (DMA-i) 98% (Strem; cat. no. 13-1600)

!CAUTION The atomic layer deposition (ALD) precursor, dimethylaluminum isopropoxide (DMA-i), used in this procedure is highly flammable. Please consult material safety data

sheet prior to use. Suitable personal protection equipment such as proper clothing, goggles, and gloves are required.

- High purity water (18.3 $M\Omega cm^{-1}$, Barnstead; Easypure RF)
- Nitrogen (N_2) gas (In-line Entegris Ni filtered for H_2O and O_2 removal to sub-ppb levels, liquid nitrogen boil off from Argonne National Lab)

CRITICAL: Residual moisture in the ALD carrier and purge gas will react with DMA-i, which consumes metal precursor during long exposure and reacts in a non-self-limiting fashion (CVD)

EQUIPMENT

- 5 L Three neck round bottom flask
- 12 L Three neck round bottom flask
- Weighing balance (Mettler-Toledo)
- Mechanical stirring system
- Water condenser
- Heating mantle
- Sparger (for degassing)
- Glass Buchner funnels (2000 mL, medium frit)
- 4 L Erlenmeyer flasks
- Vacuum oven (VWR)
- pH Test paper
- Ceramic Buchner funnels (4 L)
- Filter paper
- Mortar and pestle
- 500 FT-NMR spectrometer (500 MHz for ^{1}H and 126 MHz for ^{13}C, Bruker)
- Sonicator (Branson)

- Medium bottle (100 mL, 500 mL, 1 L, VWR)
- VWR Symphony Oven
- Centrifuge tube (VWR)
- Centrifuge 5430 (Eppendorf, 6-place fixed angle rotor F-35-6-30)
- Sorption tubes (Micromeritics, 1/2 in.)
- Smart VacPrep (Micromeritics)
- Tristars II 3020 (Micromeritics)
- Advance D8 Powder X-ray Diffractometer with Ni-filtered Cu Kα radiation (Bruker)
- AXS APEX2 diffractometer equipped with a CCD detector and a CuKα microfocus source with MX optics (Bruker)
- SU 8030 SEM (Hitachi)
- 8 in diameter atomic layer deposition (ALD) system (Cambridge Nanotech; Savannah 200)
- ICP-OES system (Thermo)
- 8 in diameter aluminum sample holder (Argonne National Laboratory)
- 7.125 in diameter 500 × 500 mesh screen (McMaster-Carr; cat. no. 85385T118)
- Filter paper
- Weighing balance (Mettler-Toledo)
- Scintillation vial (VWR, 20 mL)

PROCEDURE

Figure 2. The two-step synthesis of the tetra acid ligand for **NU-1000** can be accomplished in 3 days with an overall yield of 55% to produce 36 g of **H_4TBAPy (2)** without the need for chromatographic purification.

Figure 3. Synthesis of **NU-1000** from **2** and $ZrOCl_2$ with benzoic acid as modulator. **NU-1000** (2.5 g) can be prepared in one reaction.

Figure 4. Equipment setup for 50 g scale synthesis of **H_4TBAPy (2)**

Figure 5. Equipment setup for 250 mg scale **AIM** modification for **Al-AIM(4)**

Preparation of tetraethyl 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoate (1) TIMING:67h.

1 Place a 5 L three necked round bottom flask on a heating mantle, attach a water condenser and insert a mechanical stirrer in/on the flask. **(Fig. 4a)**

2 Add 2.7 L of dioxane into the 5 L three neck round bottom flask.

3 Using a high efficiency sparger, degas the dioxane for 1.5 h with argon.

4 With the argon still purging and mechanical stirrer stirring the dioxane, add 50 g of tetrabromopyrene, 82.5 g of 4-ethoxycarbonylphenylboronic acid, 165 g of potassium phosphate tribasic and 7.5 g of tetrakis (triphenylphosphine) palladium (0) into the flask. (Solution turned brown.)

5 Plug the opening of the round bottom flask with glass plug and purge the system with argon for an additional 5 min.

6 Using the heating mantle, heat the reaction to 90 °C for 48 h to 72 h. (The reaction is a suspension throughout the reaction, but the color of the suspended solid should become more and more yellow as reaction proceeds. Color of the solution turns black in the end of the reaction.)

CRITICAL STEP: Let the reaction run no less than 48 h; incomplete reaction would lead to impurities that are hard to separate. There is no significant harm for running the reaction longer. Thin Layer Chromatography could be used to track the reaction after 48 h. The color may not turn black if the system is kept in good inert condition.

7 Add 2 L of water to the reaction mixture, and let the reaction mixture cool down.

8 Filter the reaction mixture with 2 L glass Buchner funnel with medium frit, and yellow solid collected on the frit was washed with 1 L of water twice, and 2 L of acetone. **(Fig. 4b)**

9 Use 3 L of boiling chloroform (6×500 mL) to flow through the glass frit to dissolve the desired product on top of the filter.

CAUTION: Chloroform vapor is toxic and carcinogenic. Please keep conduct this step in fume hood

10 Reduce the volume of the collected chloroform solution containing desired product to 1.5 L by blowing nitrogen through it at room temperature.

PAUSE POINT: The chloroform solution can be blown fully dry, and the resulting solid can be kept in a capped round bottom flask at room temperature in dark for several weeks. To continue, just dissolve all solid in 2 L chloroform and precipitate with methanol.

11 Add 3 L of methanol into the solution, light yellow solid precipitate as the methanol is added.

12 Allow the solution to sit for 30 minutes, then collect the pale yellow solid with 2 L glass Buchner funnel with medium filter.

13 Further dry the product in a vacuum oven set at 70 °C for 12 hours, to yield 45.3 g of product (**1**).

PAUSE POINT: The resulting solid can be kept in a capped round bottom flask at room temperature in dark for several weeks.

?Troubleshooting

Preparation of tetraethyl 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoic acid or H_4TBAPy (2) TIMING: 67 h.

14 Place a 12 L three necks round bottom flask on a heating mantle, and setup water condenser and mechanical stirrer on the flask. (see **Fig.4** for detail)

15 Add 45 g of **1** into the three neck flask, and add 5 L of dioxane to suspend **1** by stirring.

16 In a 4 L Erlenmeyer flask, add 70.6 g of potassium hydroxide and 4 L of water.

17 Fully dissolve potassium hydroxide in water by sonication, and add all potassium hydroxide solution into the reaction flask.

18 Reflux the reaction with rigorous stirring for 18 h. Clear solution should be seen after the reaction. **(Fig. 4c)**

?Troubleshooting

19 Remove the heating mantle to cool down the reaction.

PAUSE POINT: The basic solution of the product can be kept under ambient condition for 3 days. Neutralization can be done later.

20 Slowly add concentrated hydrogen chloride through an addition funnel into the reaction (dropwise) with stirring. Test the pH level when the yellow precipitate persist in the solution. Keep adding until the solution is pH~1(tested by test paper). **(Fig. 4d)**

CAUTION: This procedure release a large amount of heat. Add HCl slowly; if necessary add ice into the solution to cool it down.

21 Yellow precipitate should be seen in the solution. Once this appears, stir the reaction for an additional 1 h.

22 Using vacuum filtration, filter the yellow precipitate from the solution. A small amount of yellow solid may pass through the filter paper in the beginning, so re-filtration of the first filtrate may be necessary. **(Fig. 4e)**

CRITICAL STEP: It is important NOT to let the solid fully dry before all liquid has been filtered. A crack in the collected solid cake on the funnel will again allow solid to pass through the filter paper, and re-filtration may be required again.

PAUSE POINT: The crude product can be left on the funnel overnight (loosely covered by aluminum foil).

23 When the solid is dried, transfer all of it into a 4 L Erlenmeyer flask and use 1L of water and sonicate for 1 h to fully suspend the entire solid.

CRITICAL STEP: This washing step removes salt that remains in the product. Be sure to suspend the solid thoroughly to ensure salt generated in the neutralization step can be removed.

24 Filter and wash with more water (1 L). Leave the solid on top of the vacuum filtration setup for 4 h.

PAUSE POINT: The water-washed product can be stored under ambient condition for months without loss of purity.

25 Dissolve all collected solid in boiling DMF (1 L) and filter while hot.

CAUTION: Boiling DMF is ~140 °C. Wear heat-insulating gloves and do this in a fume hood.

26 Cool down the collected solution to room temperature and add 3 L of dichloromethane while stirring.

27 Collect the yellow precipitate using vacuum filtration and wash the solid with dichloromethane. (1 L)

28 Further dry the product in a vacuum oven set at 120 °C for 36 hours; the yield for the reaction should be about 36 g of product.

29 Grind the solid to aid the suspension of the linker during MOF synthesis. **(Fig. 4f)**

PAUSE POINT: The purified organic linkers can be stored at dark in a seal vial at room temperature for months.

?Troubleshooting

Preparation of NU-1000(3)

30 There are three options depending on what scale reaction you want to do. *The purity of the ligand will significantly affect the synthesis of **NU-1000**, so it is recommended to start with a 200 mg NU-1000 procedure (option A) to ensure the purity of **H_4TBAPy** from each batch before scaling up to a 1 g or 2.5 g procedure (options B or C respectively).*

A Preparation of NU-1000(3) on 200 mg scale TIMING: ~90 h.

i. Weigh out 388 mg of zirconyl chloride octahydrate and 10.8 g benzoic acid in a 100 mL VWR medium bottle.

ii. Add 32 mL N,N-dimethylformamide (using graduated cylinder) and sonicate the solution to fully dissolve reagents.

CRITICAL STEP: Do NOT add more than required amount of DMF. Samples with a smaller mesoporous step in the nitrogen isotherm were made when too much DMF was accidentally added. Perhaps a different phase of MOF was made at the same time.

Figure 6. Nitrogen isotherm of the sample with smaller mesoporous step.

iii. Heat the reaction mixture in 80 °C oven for 1 h. (VWR symphony oven)

CRITICAL STEP: Do NOT leave it for more than 1 h. Another phase of MOF which cannot be removed may form.

iv. Cool down the solution containing zirconium precursor and benzoic acid (a water bath can be used), and add 160 mg of **H_4TBAPy (2)**.

CRITICAL STEP: The cooling down should not take more than half hour. Proceed to the synthesis once the reaction flask is cooled.

v. Use sonication (20 min) to disperse the organic ligand to an even suspension, then place the reaction bottle in 100 °C oven for 15.5 h. The ligand will dissolve as the bottle is heated, and light yellow precipitate forms as the MOF forms.

vi. Cool down the reaction mixture, and then use centrifuge (50 mL capped tube, at 7,750 *g* for 5 min, room temp.) to separate the solid from the mother solution.

vii. Discard the supernatant and add fresh N,N-dimethylformamide (45 mL on the graduation on the centrifuge tube).

CRITICAL STEP: When washing **NU-1000** with DMF, never let the MOF powder dry out from DMF since this process can collapse the MOF.

PAUSE POINT: The as-synthesized **NU-1000** can be stored under ambient conditions in DMF without loss of purity for months.

viii. Soak the MOF in fresh DMF for 2 h and repeat steps 30A (vi.- vii.) two more times.

CRITICAL STEP: In every step of washing, shake the tube to disperse the MOFs in solution.

ix. After the last centrifuge, transfer all light yellow solid into a 100 mL VWR medium bottle with 52 mL of DMF (using a graduated cylinder).

x. Add 2 mL of 8 M HCl aqueous solution into the bottle and swirl to mix the solution.

xi. Place the solution containing HCl and MOF in a 100 °C oven for 12 h.

xii. Cool down the reaction mixture, and then use centrifuge (50 mL capped tube at 7,750 *g* for 5 min, room temp.) to separate solid from mother solution.

xiii. Discard the supernatant and add fresh N,N-dimethylformamide (45 mL on the graduation on the centrifuge tube).

xiv. Soak the MOF in fresh DMF for 2 h and repeat 30A (xii.- xiii.) for two more times.

PAUSE POINT: The acid-treated **NU-1000** can be stored in DMF under ambient condition for months. The evaporation of DMF from the sealed vial is negligible unless heated at more than 120 °C.

xv. After the last centrifuge, discard the supernatant and add fresh acetone (45 mL on the graduation on the centrifuge tube).

xvi. Soak the MOF in fresh acetone for 12 h and exchange the solvent with fresh acetone for two more times soaking for 12 h each time. (Use centrifuge at 7,750 *g* for 5 min, room temp. to separate solid and solution when exchanging solvent)

CRITICAL STEP: More iterations of solvent exchange performed to shorten the time, and NMR can be used to examine the extent of solvent exchange (NO DMF should appear in the NMR after full exchange).

PAUSE POINT: NU-1000 can be stored in acetone under ambient condition for months. The acetone may evaporate from the sealed vial, but the structrual integrity would not be affected.

xvii. After the last centrifuge, do not add any acetone into the tube but place the centrifuge tube containing MOF into a vacuum oven set at 80 °C for 1 h.

xviii. Transfer the dried MOF sample into a sorption tube (Micromeritics) and activate the MOF at 120 °C for 12 h.

xix. Take a Nitrogen isotherm of the activated MOF sample to evaluate the quality of the sample.

CRITICAL STEP: The characterization of MOFs are routinely done, and the details of the procedures can be found on Karagiaridi, O. et. al. Synthesis and Characterization of Functionalized Metal-organic Frameworks. *J. Vis. Exp.* (91), e52094, doi:10.3791/52094 (2014).[28]

?Troubleshooting

B Preparation of NU-1000(3) on 1 g scale TIMING: ~90 h.

i. Weigh out 1.94 g of zirconyl chloride octahydrate and 54 g benzoic acid in a 500 mL VWR medium bottle.

ii. Add 120 mL N,N-dimethylformamide (using graduated cylinder) and sonicate the solution to fully dissolve reagents.

CRITICAL STEP: Do NOT add more than required amount of DMF. This may result in larger crystals that showed lower mesoporous step in the isotherm.

iii. Heat the reaction mixture in 100 °C oven for 1 h. (VWR symphony oven)

iv. In the meantime, weigh out 800 mg **H_4TBAPy** in a 100 mL VWR medium bottle.

v. Add 40 mL DMF into the 100 mL bottle; use sonication to evenly suspend **H_4TBAPy** in the solvent.

CRITICAL STEP: Do NOT add more than required amount of DMF. This may result in larger crystals that showed lower mesoporous step in the nitrogen isotherm.

vi. Also place the **H_4TBAPy** solution in a 100 °C oven for 1 h (VWR symphony oven). The suspension would become a clear solution after heating.

vii. Take out both bottles containing zirconium precursor and **H_4TBAPy** (Both are clear solutions) and pour the **H_4TBAPy** solution into the 500 mL bottle containing zirconium precursor.

CAUTION: Wear gloves and do this in vented hood, because boiling DMF is very hot and the vapor is toxic.

viii. Shake to mix the reagents and then place the reaction bottle in 120 °C oven for 16 h. The formation of the MOF can be seen as a yellow precipitate.

ix. Cool down the reaction mixture, and then use a centrifuge (50 mL capped tube×3, at 7,750 *g* for 5 min, room temp.) to separate solid from mother solution.

x. Discard the supernatant and add fresh N,N-dimethylformamide (45 mL on the graduation on the centrifuge tube).

PAUSE POINT: The as-synthesized **NU-1000** can be stored under ambient condition in DMF without loss of purity for months.

xi. Soak the MOF in fresh DMF for 2 h and repeat 30B (ix-x) for two more times.

xii. After the last centrifuge, transfer all light yellow solid into a 500 mL VWR medium bottle with 260 mL of DMF (using a graduated cylinder).

xiii. Add 10 mL of 8 M HCl aqueous solution into the bottle and swirl to mix the solution.

xiv. Place the solution containing HCl and MOF in a 100 °C oven for 12 h.

xv. Cool down the reaction mixture, and then use centrifuge (50 mL capped tube×3, at 7,750 *g* for 5 min, room temp.) to separate solid from mother solution.

xvi. Discard the supernatant and add fresh N,N-dimethylformamide (45 mL on the graduation on the centrifuge tube).

xvii. Soak the MOF in fresh DMF for 2 h and repeat 30B (xv-xvi) for two more times.

PAUSE POINT: The acid-treated **NU-1000** can be stored in DMF under ambient condition for months.

xviii. After the last centrifuge, discard the supernatant and add fresh acetone (45 mL on the graduation on the centrifuge tube).

xix. Soak the MOF in fresh acetone for 12 h and exchange the solvent with fresh acetone for two more times. (Use centrifuge at 7,750 *g* for 5 min, room temp. to separate solid and solution when exchanging solvent)

CRITICAL STEP: More iterations of solvent exchange can be added to shorten the time, and NMR can be used to examine the extent of solvent exchange (NO DMF should appear in the NMR after full exchange).

PAUSE POINT: NU-1000 can be stored in acetone under ambient condition for months.

xx. After the last centrifuge, do not add any acetone into the tube but place the centrifuge tube containing MOF into a vacuum oven set at 80 °C for 1 h.

xxi. Transfer the dried MOF sample into a sorption tube (Micromeritics) and activate the MOF at 120 °C for 12 h.

xxii. Take a Nitrogen isotherm of the activated MOF sample (as describe in Step XX)to evaluate the quality of the sample.

?Troubleshooting

C Preparation of NU-1000(3) on 2.5 g scale TIMING: ~90 h.

i. Weigh out 4.85 g of zirconyl chloride octahydrate and 135 g benzoic acid in a 1000 mL VWR medium bottle.

CAUTION: Use 1000 mL or larger medium bottle. Adequate head space is needed for the gas expansion, too little head space can lead to overpressure and shatter the bottle in the oven.

ii. Add 300 mL N,N-dimethylformamide (using graduated cylinder) and sonicate the solution to fully dissolve reagents.

CRITICAL STEP: Do NOT add more than required amount of DMF. This may result in larger crystals that showed lower mesoporous step in the isotherm.

iii. Heat the reaction mixture in 100 °C oven for 1 h. (VWR symphony oven)

iv. In the meantime, weigh out 2 g **H_4TBAPy** in a 100 mL VWR medium bottle.

v. Add 100 mL DMF into the 100 mL bottle; use sonication to evenly suspend **H_4TBAPy** in the solvent.

CRITICAL STEP: Do NOT add more than required amount of DMF. This may result in larger crystals that showed lower mesoporous step in the isotherm.

vi. Also place the **H_4TBAPy** solution in a 100 °C oven for 1 h (VWR symphony oven). The suspension would become a clear solution after heating.

vii. Take out both bottles containing zirconium precursor and **H_4TBAPy** (Both are clear solution) and pour the **H_4TBAPy** solution into the 1000 mL bottle containing zirconium precursor.

CAUTION: Wear gloves and do this in vented hood, boiling DMF is very hot and the vapor is toxic.

viii. Shake to mix the reagents and then place the reaction bottle in 120 °C oven for 16 h. Light yellow precipitate forms as the MOF forms.

ix. Cool down the reaction mixture, and then use centrifuge (50 mL capped tube×6, at 7,750 *g* for 5 min, room temp.) to separate solid from mother solution.

x. Discard the supernatant and add fresh N,N-dimethylformamide (45 mL on the graduation on the centrifuge tube).

PAUSE POINT: The as-synthesized **NU-1000** can be stored under ambient condition in DMF without loss of purity for months.

xi. Soak the MOF in fresh DMF for 2 h and repeat 30C (ix.-x.) for two more times.

xii. After the last centrifuge, transfer all light yellow solid into a 1000 mL VWR medium bottle with 650 mL of DMF (using a graduated cylinder).

xiii. Add 25 mL of 8 M HCl aqueous solution into the bottle and swirl to mix the solution.

xiv. Place the solution containing HCl and MOF in a 100 °C oven for 12 h.

xv. Cool down the reaction mixture, and then use centrifuge (50 mL capped tube×6, at 7,750 *g* for 5 min, room temp.) to separate solid from mother solution.

xvi. Discard the supernatant and add fresh N,N-dimethylformamide (45 mL on the graduation on the centrifuge tube).

xvii. Soak the MOF in fresh DMF for 2 h and repeat 30C (xv.-xvi.) for two more times.

PAUSE POINT: The acid-treated **NU-1000** can be stored in DMF under ambient condition for months.

xviii. After the last centrifuge, discard the supernatant and add fresh acetone (45 mL on the graduation on the centrifuge tube).

xix. Soak the MOF in fresh acetone for 12 h and exchange the solvent with fresh acetone for two more times. (Use centrifuge at 7,750 *g* for 5 min, room temp. to separate solid and solution when exchanging solvent)

CRITICAL STEP: More iterations of solvent exchange can be added to shorten the time, and NMR can be used to examine the extent of solvent exchange (NO DMF should appear in the NMR after full exchange).

PAUSE POINT: NU-1000 can be stored in acetone under ambient condition for months.

xx. After the last centrifuge, do not add any acetone into the tube but place the centrifuge tube containing MOF into a vacuum oven set at 80 °C for 1 h.

xxi. Transfer the dried MOF sample into a sorption tube (Micromeritics) and activate the MOF at 120 °C for 12 h.

xxii. Take Nitrogen isotherm of the activated MOF sample to evaluate the quality of the sample.

?Troubleshooting

Post-synthetic modification

31 We have included two options that can be used modify the NU-1000 that you have prepared. Option A is an atomic layer deposition (ALD) process to deposit aluminium in NU-1000. The first part of this procedure is a vapor pressure test in order to estimate the stociometry of the reactants, and making sure the precursor holder is not empty. Postsynthesis modification of **NU-1000** via Solvent Assisted Linker Incorporation (option B) can be generalized to many ligands.[17] We decided to scale up the SALI procedure that incorporate Fmoc-gly-gly-gly-OH into **NU-1000 (F3G-SALI)** as an example and serves as an illustration of how a relatively complex biomolecule can be attached to **NU-1000 .**

A Large scale (250 mg) Atomic Layer Deposition Process to deposit Al in NU-1000 (Al-AIM) TIMING: ~42 h; the vapor pressure test takes about 5 minutes.

i. **Vapor pressure test prior to Al-AIM(4).** Set inner heater, outer heater, and precursor manifold of the ALD system at 125 °C. The DMA-I and water precursors are not heated.

ii. The carrier gas (N_2) is set to 20 sccm by default.

iii. Once the temperatures have stabilized, test the vapor pressure of precursors (DMA-i and water) following steps 31A (iv-xi).

iv. Set carrier gas flow rate to 10 sccm.

v. Wait 30 s.

vi. Pulse DMA-i for 80 ms (0.080 s), the pressure transient is ~0.20 torr.

vii. Wait 30 s.

viii. Pulse water vapor for 15 ms (0.015 s), the pressure transient is ~1.78 torr.

ix. Wait 30 s.

x. Repeat steps 31A (vi.- ix.) (5 cycles).

xi. Set carrier gas flow rate to 20 sccm.

CRITICAL STEP: This step is performed to check the status of the system, precursor availability, and to calculate the number of moles of precursor delivered. The vapor pressures of the precursors should match the values mentioned previously. If not, the pulse time for the precursors can be adjusted, or the precursor needs to be refilled.

xii. **Al-AIM(4) on 250 mg scale.** Weigh 250 mg of NU-1000 and transfer onto 8 in. diameter ALD sample holder. **(Fig. 5a)**

CRITICAL STEP: Evenly distribute NU-1000 across the sample holder and crush large chunks of MOF into smaller pieces. A deep powder bed will inhibit uniform precursor diffusion to each grain and therefore require additional reaction time.

xiii. Load sample holder into the ALD system. **(Fig. 5b)**

!CAUTION The sample chamber and lid of the ALD system are hot.

xiv. Evacuate ALD sample chamber down to ~0.4 Torr.

xv. Remove any residual solvent or physisorbed water by soaking NU-1000 at 125 °C for 20 min under the low pressure dry nitrogen flow.

CRITICAL STEP: The remove of physisorbed molecules from the high surface area framework is critical to achieving growth on the nodes alone which results in reproducible Al to Zr_6 ratios.

xvi. Decrease nitrogen flow rate to 10 sccm.

xvii. Wait 30 s.

xviii. Close stop valve.

xix. Pulse water vapor for 1 s. (1 s pulse of water vapor = 8.83×10^{-4} moles)

xx. Wait 59 s.

xxi. Open stop valve.

xxii. Wait 30 s.

xxiii. Repeat steps 31A (xviii.- xxii.) (2 cycles). (total moles of water delivered: 1.77×10^{-3} moles)

CRITICAL STEP: It is important to dose a sufficient amount of water vapor to rehydrate NU-1000 to its equilibrium node configuration prior to Al loading.

xxiv. Wait 600 s.

CRITICAL STEP: A 600 s wait step is critical for removing physisorbed water on NU-1000 prior to Al loading.

xxv. Close stop valve.

xxvi. Pulse DMA-i for 80 ms (0.080 s). (80 ms pulse of DMA-i = 7.18×10^{-7} moles)

xxvii. Wait 19.920 s.

xxviii. Open stop valve.

xxix. Wait 30 s.

xxx. Repeat steps 31A (xxv.- xxix.) (3000 cycles). (total moles of DMA-i delivered: 2.15×10^{-3} moles)

xxxi. Close stop valve.

xxxii. Pulse RO water for 1 s.

xxxiii. Wait 59 s.

xxxiv. Open stop valve.

xxxv. Wait 30 s.

xxxvi. Repeat steps 31A (xxxi.-xxxv.).(2 cycles).

xxxvii. Vent ALD sample chamber to atmospheric pressure.

xxxviii. Remove the sample holder.

!CAUTION ALD sample chamber and lid as well as sample holder are hot. Wear heat resistant gloves when removing the sample holder.

xxxix. Transfer Al-loaded NU-1000 (**Al-AIM**) into a 20 mL vial.

PAUSE POINT: Al-AIM can be stored under ambient condition for months.

B General procedure for Solvent-Assisted Ligand Incorporaion (SALI) on 250 mg scale. TIMING: ~88 h.

i. Weigh 250 mg (0.115 mmol) of **NU-1000** and 470 mg (1.15 mmol) of Fmoc-gly-gly-gly-OH into a 100 mL VWR medium bottle.

CRITICAL STEP: Generally, 8-10 equivalents per node of the ligand are used in the SALI reaction.

ii. Add 16 mL of DMSO and 24 mL of acetonitrile into the medium bottle to fully dissolve the ligand.

CRITICAL STEP: Different solvent (or solvent mixture) can be used in SALI procedure as long as the ligand can be fully dissolved.

iii. Cap the bottle and heat it up in a 60 °C oven. Leave it in the oven for 24 h.

iv. Cool down the reaction mixture, and then use centrifuge (50 mL capped tube, at 7,750 *g* for 5 min, room temp.) to separate solid from mother solution.

v. Discard the supernatant and add fresh solvent (DMSO:actetonitrile=2:3) (45 mL on the graduation on the centrifuge tube).

vi. Soak the MOF in fresh solvent for 2 h and repeat 135-136 for 8 more times. (~350 mL of solvent was used to wash the SALI modified **NU-1000**).

CRITICAL STEP: In general, the solvent (or solvent mixture) that was used in the SALI procedure was also used in the first washing process.

PAUSE POINT: At the washing step, the SALI modified **NU-1000** can be soaked in the fresh solvent for days.

vii. After the last centrifuge, discard the supernatant and add fresh acetone (45 mL on the graduation on the centrifuge tube).

viii. Soak the MOF in fresh acetone for 12 h and exchange the solvent with fresh acetone for two more times. (Use centrifuge at 7,750 *g* for 5 min, room temp. to separate solid and solution when exchanging solvent).

CRITICAL STEP: More iterations of solvent exchange can be added to shorten the time, and NMR can be used to examine the extent of solvent exchange (NO DMF should appear in the NMR after full exchange).

PAUSE POINT: SALI modified **NU-1000** can be stored in acetone under ambient condition for days.

ix. After the last centrifuge, do not add any acetone into the tube but place the centrifuge tube containing MOF into a vacuum oven set at 80 °C for 1 h.

x. Transfer the dried MOF sample into a sorption tube (Micromeritics) and activate the MOF at 120 °C for 12 h.

xi. Take a Nitrogen isotherm of the activated MOF sample. Perform NMR of the dissolved sample to quantify the incorporation of the ligand.

32. General Procedure for MOF characterization

A. Procedure for collecting Powder X-Ray Diffraction (PXRD) ~35 mins/ sample

The procedure using a single crystal x-ray diffractometer can be found in reference 28, and if the powder x-ray diffractometer is used, the procedure can be described as following.

i. Transfer sample (~1 mg) on a clean Si (100) substrate.

ii. Densely pack Al-loaded NU-1000 by pressing on the powder with a spatula.

iii. On a Bruker Advance D8 Powder X-ray Diffractometer with Ni-filtered Cu Kα radiation operating at 40 kV and 40 mA, scan the diffraction pattern between 2° and 20° with 0.01° steps at a collection speed of 1 s/step.

B. Procedure for collecting nitrogen isotherm ~24 h/ sample

i. Transfer the vacuum oven dried samples into a sorption tube. (tared, and record the empty weight of the tube)

ii. Activate the sample at 120 °C under vacuum on a SmartVacPrep (Micromeritics) for 12 h.

iii. Record the sample weight after activation, and transfer the sorptuion tube onto a Tristar II. (Micromeritics) Measure the nitrogen isotherm from P/P_0=0 to 0.99 at 77 K. (held by liquid nitrogen bath)

C. Procedure for making samples for ^{1}H NMR ~5 mins/ sample

The MOF should not have residual solvent in the pores when being dissolved, if not, start from step i. If it is activated, start from step iv.

i. Soak wet MOF sample in acetone for 5 mins, and separate the solution for the solid. Repeat this twice to exchange the residual solvent in the MOF to acetone.

ii. Dried under vacuum oven to remove the residual solvent in the MOF

iii. Add ~1 mg of sample into a 1 dram vial. Then add 5 drop of D_2SO_4, sonicate the mixture to form a brown slurry.

iv. Add ~1 mL of DMSO-d_6 to dissolve the slurry, and the solution should be clear. NMR can then be recorded on this sample.

D. Procedure for making samples for ICP-OES ~30 mins/ sample

In order to perform ICP-OES, Al-loaded NU-1000 must first be dissolved in piranha solution (3:1 99.999% sulfuric acid to 30 wt% hydrogen peroxide solution).

CAUTION: Piranha solution is highly corrosive. Wear proper clothing and gloves, and handle with care.

i. Transfer ~1 mg of Al-loaded NU-1000 into a 25 mL volumetric flask.

ii. Add 750 μL of sulfuric acid (solution will turn purple) into the flask followed by 250 μL of hydrogen peroxide solution (solution will turn orange brown). Fully dissolve Al-loaded NU-1000 with gentle sonication.

iii. Once Al-loaded NU-1000 has been fully dissolved, add 24 mL of RO water. The final solution will be colorless.

iv. Measure the sample on ICP-OES, and calcuate the metal to node ratio.

TIMING

Step 1-5: 2.5 h

Step 6: 48 h

Step 7-10: 3.5 h

Step 11-13: 13 h

Step 14-17: 1 h

Step 18-19: 20 h

Step 20-22: 3.5 h

Step 23-27: 6.5 h

Step 28-29: 36 h

Step 30A (i.-iv.): 2 h

Step 30A (v.-vii.): 16 h

Step 30A (viii.-xiv.):: 20 h

Step 30A (xv.-xix.): : 55 h

Step 30B (i.-vii.): : 1.5 h

Step 30B (viii.-x.): : 16 h

Step 30B (xi.-xvii.): : 20 h

Step 30B (xviii.-xxii.): : 55 h

Step 30C (i.-vii.):: 1.5 h

Step 30C (viii.-x.): : 16 h

Step 30C (xi.-xvii.): : 20 h

Step 30C (xviii.-xxii.): : 55 h

Step 31A (i.-xi.): 5 min

Step 31A (xii.-xxxix.): 42 h (total hands-on operational time: 30 min)

Step 31B (i.-vi.): 40 h

Step 31B (vii.-xi.): 48 h

TROUBLESHOOTING

Troubleshooting advice can be found in Table 1.

Table 1 Troubleshooting

Step	Problem	Possible Reason	Solution
13	NMR Spectrum shows impurities	Some of the partial Suzuki coupling product (mono- di- tri- coupled) formed.	Boil the solid in THF (10 mL /g) for 6 h and filter the solid. The partial coupled compound should be more soluble in THF than **H_4TBAPy**.
18	The reaction mixture did not turn clear	The hydrolysis of the tetraester is not complete	Add more water (1-2 L) and let the reaction go longer.
28	Some DMF remains after drying	The DMF is trapped in the chunk of solid	Use mortar and pestle to grind the chunks into powder after 2 h in vacuum oven, and leave it for 36 h. If DMF still remains, suspend the **H_4TBAPy** in Methanol, and then filter the solid. Keep the sample in vacuum oven at 100 °C for 12 h to completely dry it.
47, 69 & 90	Nitrogen isotherm showed smaller mesoporous step, or generally lower isotherm	The ligand used in the MOF synthesis contains certain amount of KCl salt that formed during the	Try suspending the ligand in water, do steps 23-28 again to purify the ligand. It is also possible that decreasing the

	neutralization. Or the amount of DMF used in MOF synthesis is too much.	solvent (DMF) amount in **NU-1000** synthesis would help form pure phase material. After re-purify the ligand, try with 200 mg procedure first to check the anticipated outcome is achievable. If so, try with the larger scale procedures.

ANTICIPATED RESULTS

Tetraethyl 4,4',4'',4'''-(pyrene-1,3,6,8-tetrayl)tetrabenzoate (1)

Pale yellow solid,

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 8H), 8.14 (s, 4H), 8.01 (s, 2H), 7.75 (d, *J* = 8.1 Hz, 8H), 4.46 (q, *J* = 7.1 Hz, 8H), 1.45 (t, *J* = 7.1 Hz, 12H)

4,4',4'',4'''-(Pyrene-1,3,6,8-tetrayl)tetrabenzoic acid (2)

Bright yellow solid,

^{1}H NMR (500 MHz, DMSO-d_6) δ 13.12 (s, 4H), 8.22 (s, 4H), 8.18 (d, *J* = 8.0 Hz, 8H), 8.10 (s, 2H), 7.88 (d, *J* = 8.0 Hz, 8H)

NU-1000 (3)

NU-1000 is synthesized as a pale yellow solid. (With color much lighter than **H_4TBAPy**)

Figure 7. Powder X-Ray Diffraction Data for **NU-1000**

The data is collected on a single crystal x-ray diffractometer Bruker AXS APEX2.

Figure 8. Nitrogen Isotherms for **NU-1000**

Figure 9. ^{1}H NMR Spectrum of dissolved **NU-1000**

As-synthesized NU-1000 has ~ 4 benzoic acid attached to every node, as quantified by the ^{1}H NMR spectrum. The acid-treated sample showed very little of benzoic acid, which indicates the benzoic acid is removed from the node, and the active —OH on the nodes are exposed for further functionalization. The ^{1}H NMR spectrum can also determine the extent of solvent exchange.

Figure 10. SEM Images of **NU-1000**

Scanning electron microscopy (SEM) images were collected on a Hitachi SU8030 SEM.

Al-AIM (4)

ICP-OES of Al-AIM

Anticipated Al to Zr_6 ratio is ~6.2.

Figure 11. Powder X-Ray Diffraction Data of **Al-AIM**

The data is collected on a Bruker Advance D8 Powder X-ray Diffractometer

Figure 12. Nitrogen Isotherms

F3G-SALI (5)

Figure 13. ^{1}H NMR Spectrum of dissolved **F3G-SALI**

The highlighted integral in the NMR corresponds to the proton on the fluorene. Therefore, the incoporation of the Fmoc-glyglygly-OH is 2/ node in this study.

Figure 14. Powder X-Ray Diffraction Data of **F3G-SALI**

The data is collected on a Bruker Advance D8 Powder X-ray Diffractometer

Figure 15. Nitrogen Isotherms of **F3G-SALI**

Author Contributions Statements

T.C.W. N.A.V., and O.K.F designed the experiments; T.C.W. and N.A.V. performed the synthesis of the strut and analyzed the collected data while T.C.W. designed and performed the synthesis of **NU-1000** with guidance from O.K.F.; I.S.K. performed the ALD experiments with guidance from A.B.F.M.; T.C.W., N.A.V., I.S.K., A.B.F.M., J.F.S., J.T.H. and O.K.F. wrote the manuscript.

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Competing financial interests

J.T.H. and O.K.F. have a financial interest in the start-up company NuMat Technologies, which is seeking to commercialize metal–organic frameworks.

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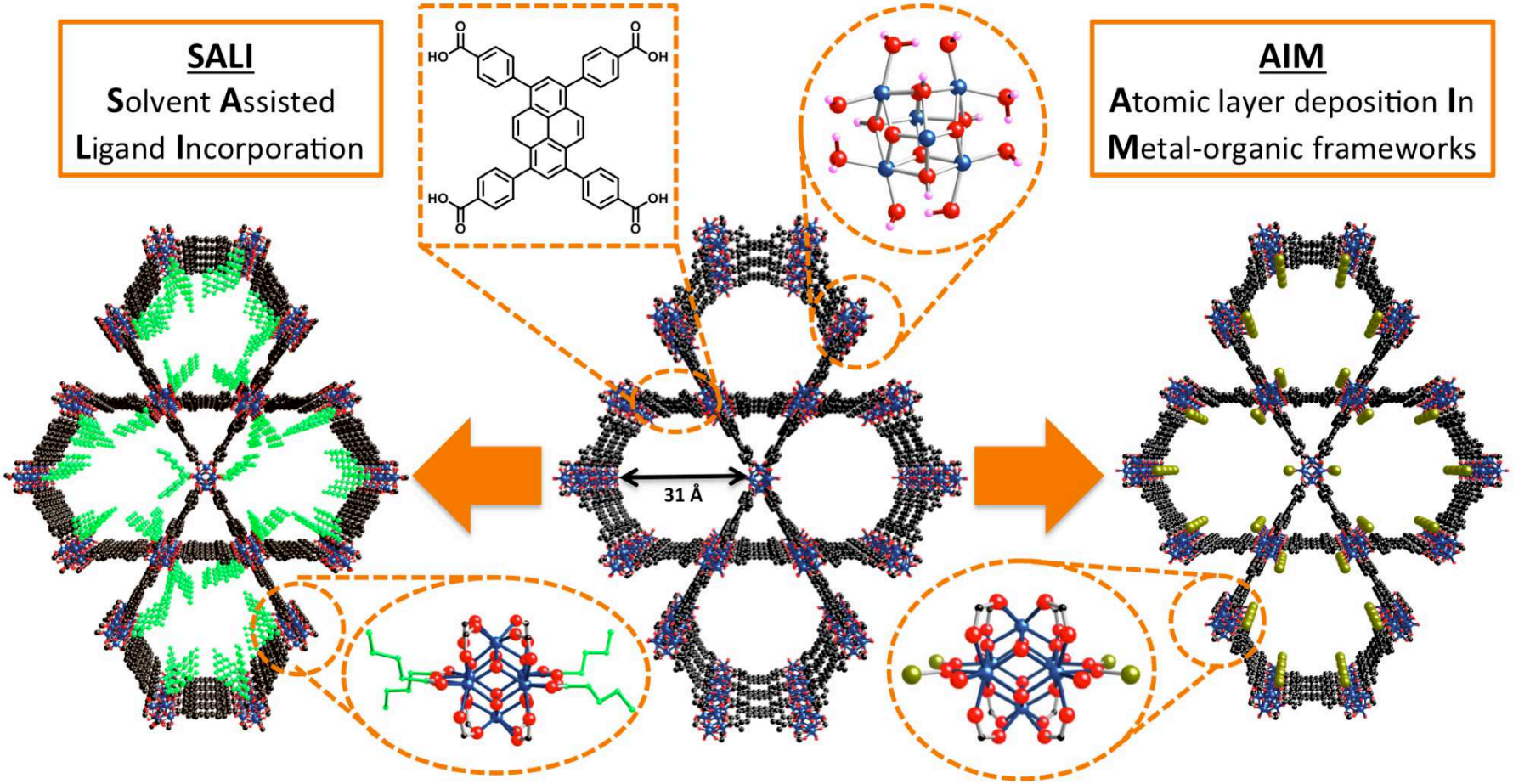
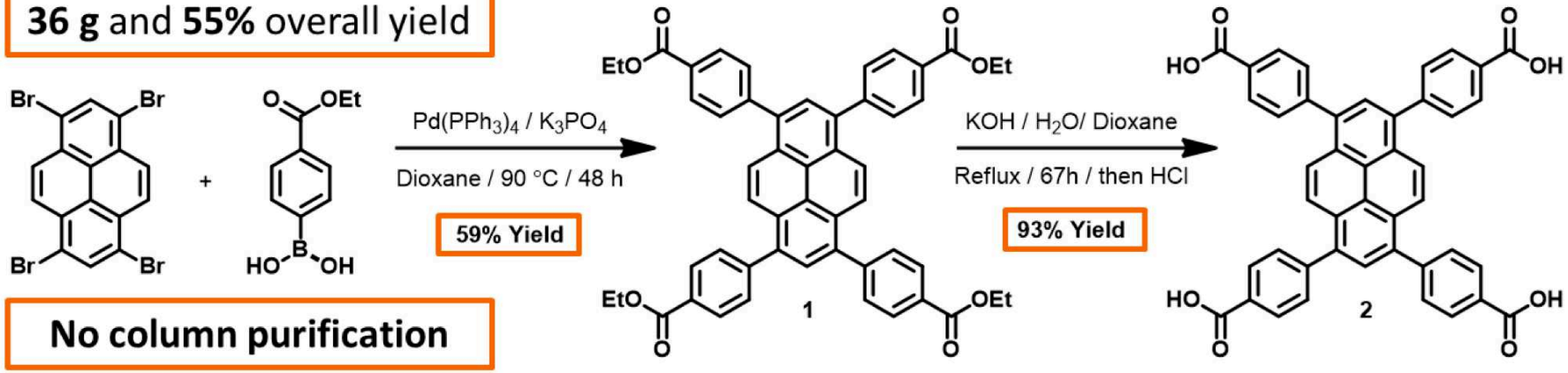
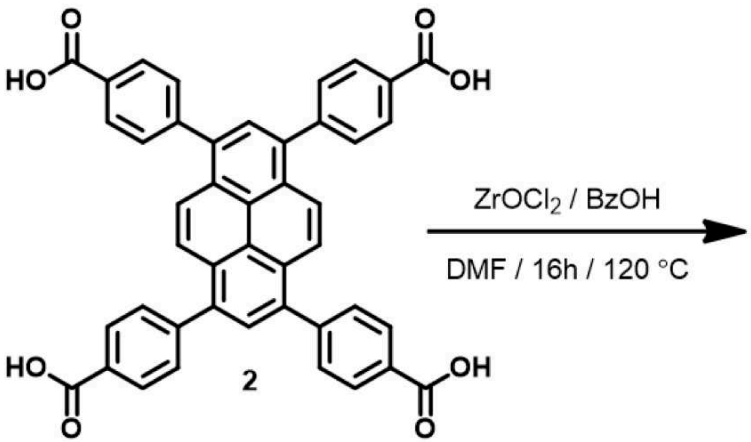

SALI
Solvent Assisted
Ligand Incorporation
AIM
Atomic layer deposition In
Metal-organic frameworks
31 Å

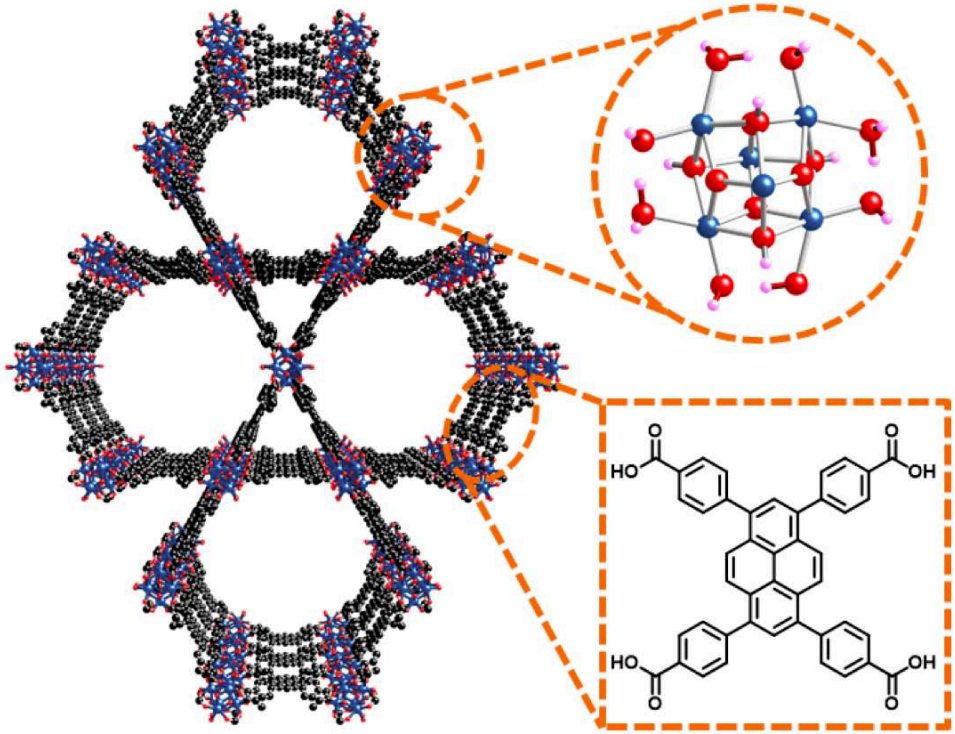
36 g and **55%** overall yield



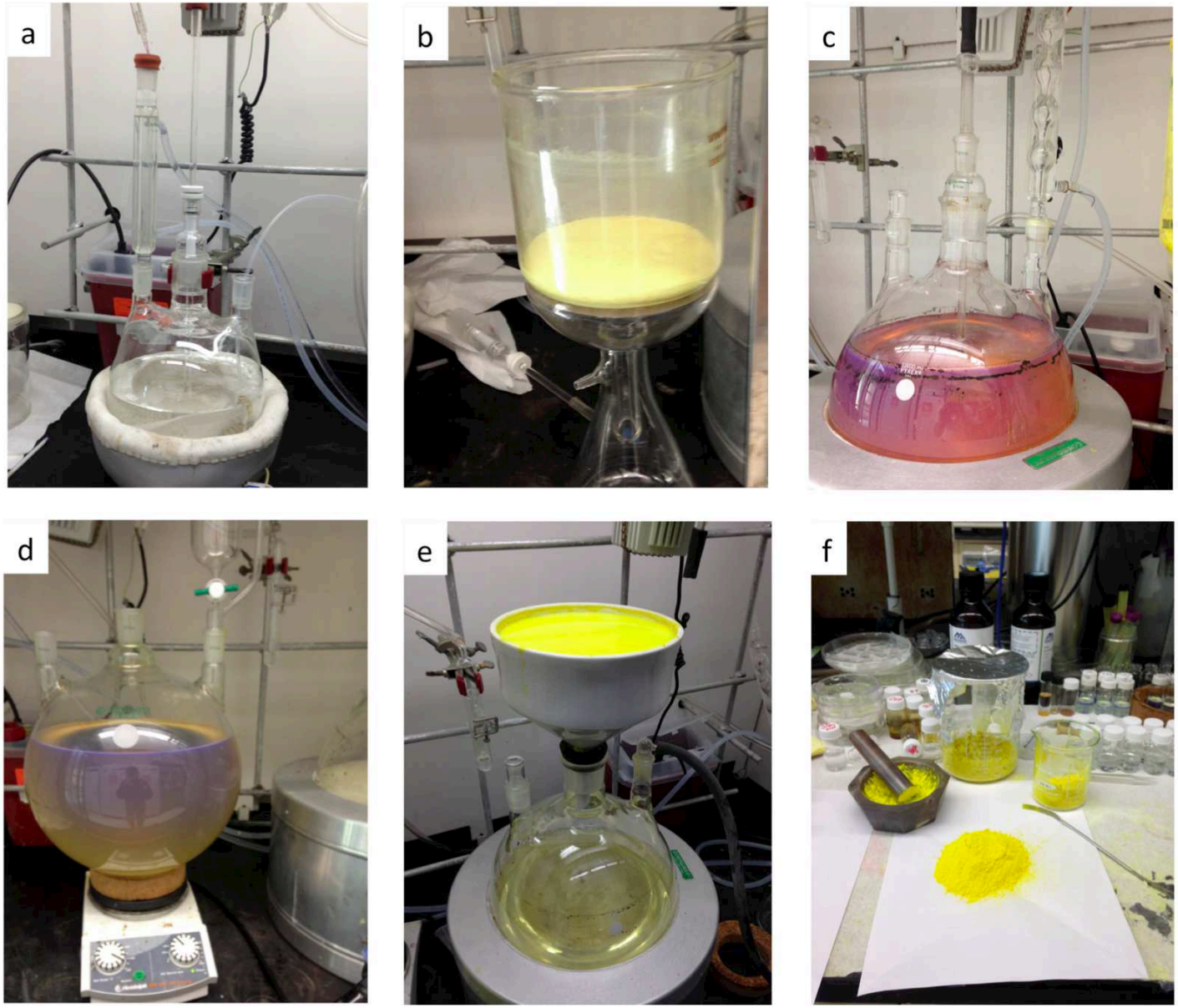
No column purification

Easy purification and isolation





Up to 2.5 g of NU-1000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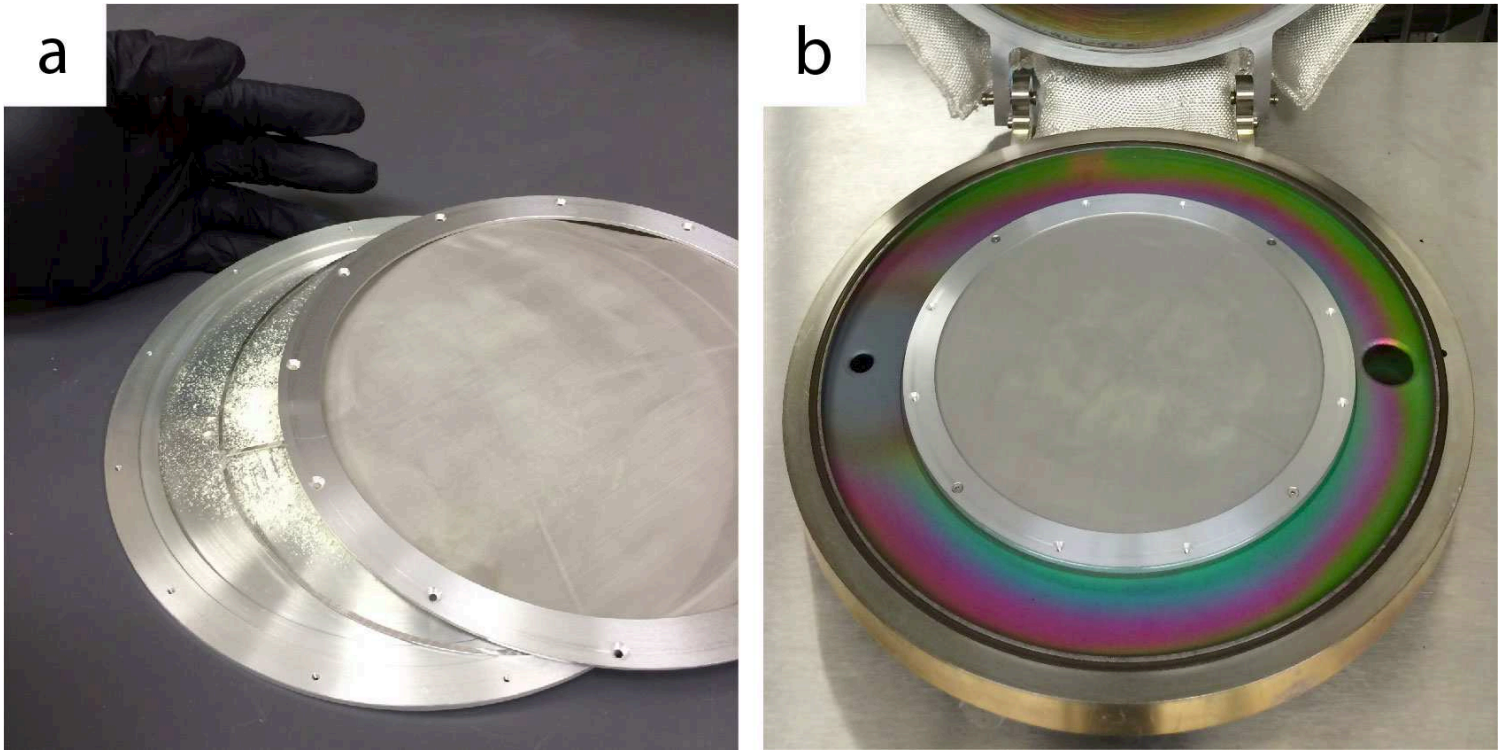
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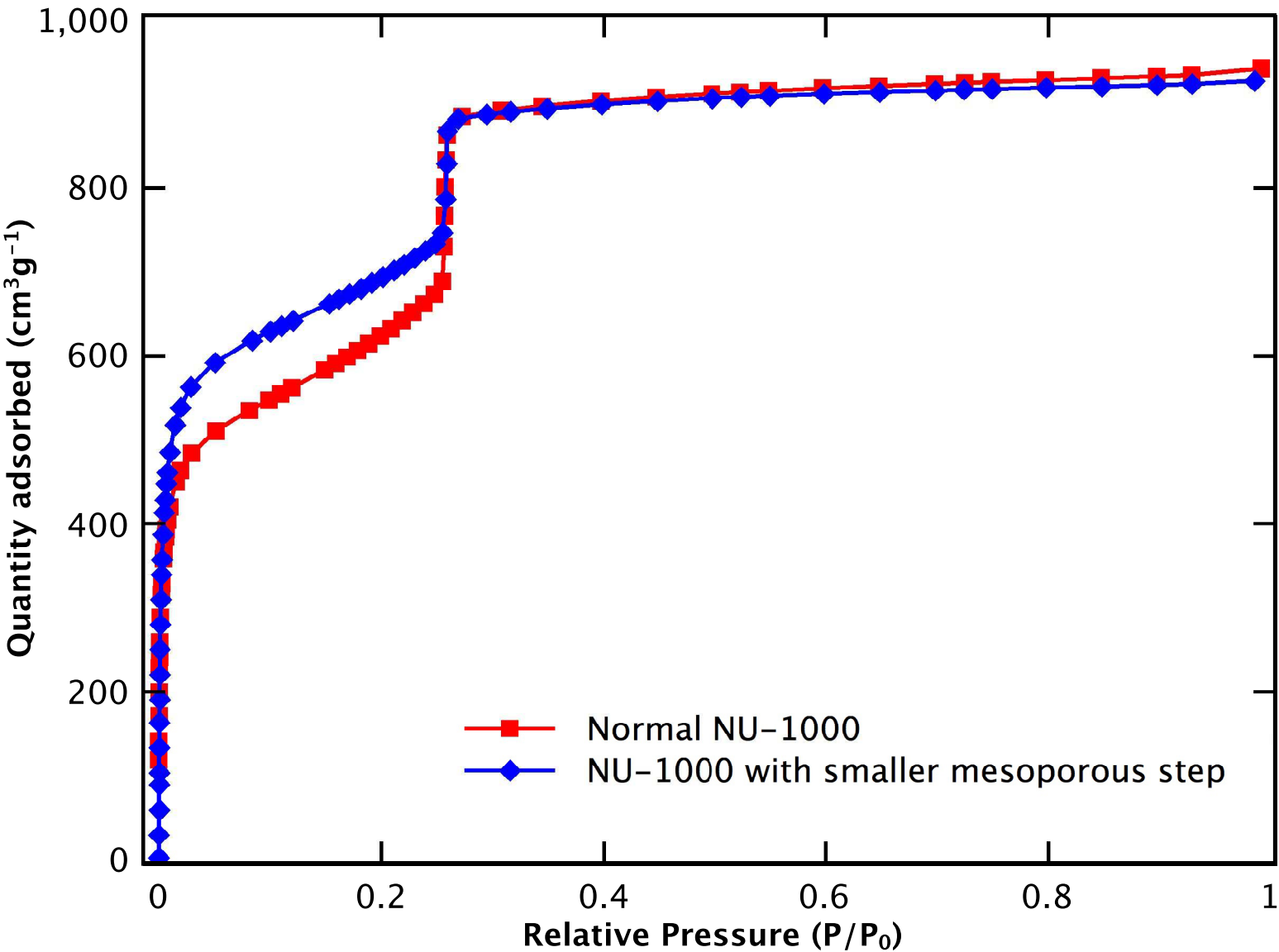
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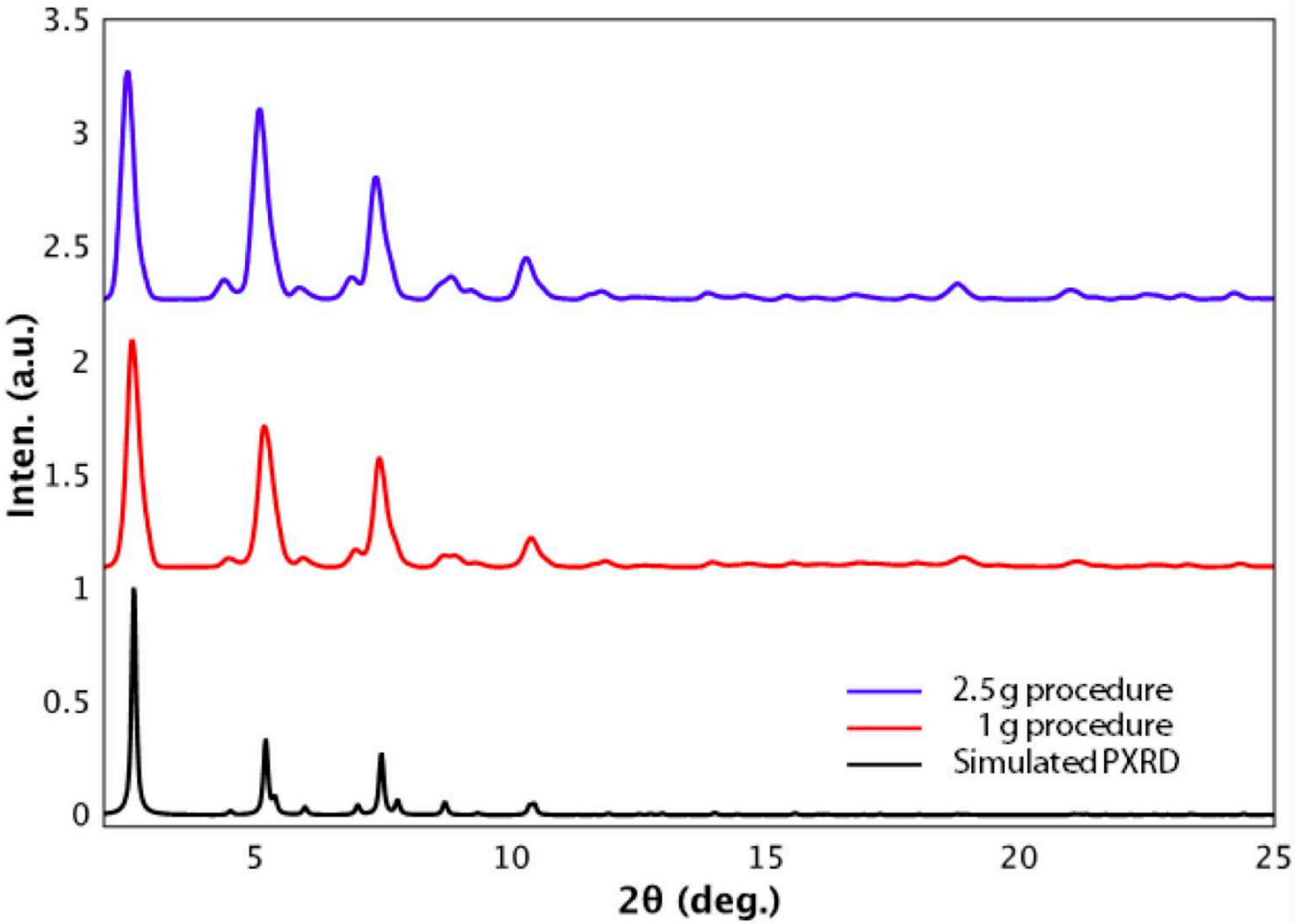
Relative Pressure (P/P$_0$)
Normal NU-1000
NU-1000 with smaller mesoporous step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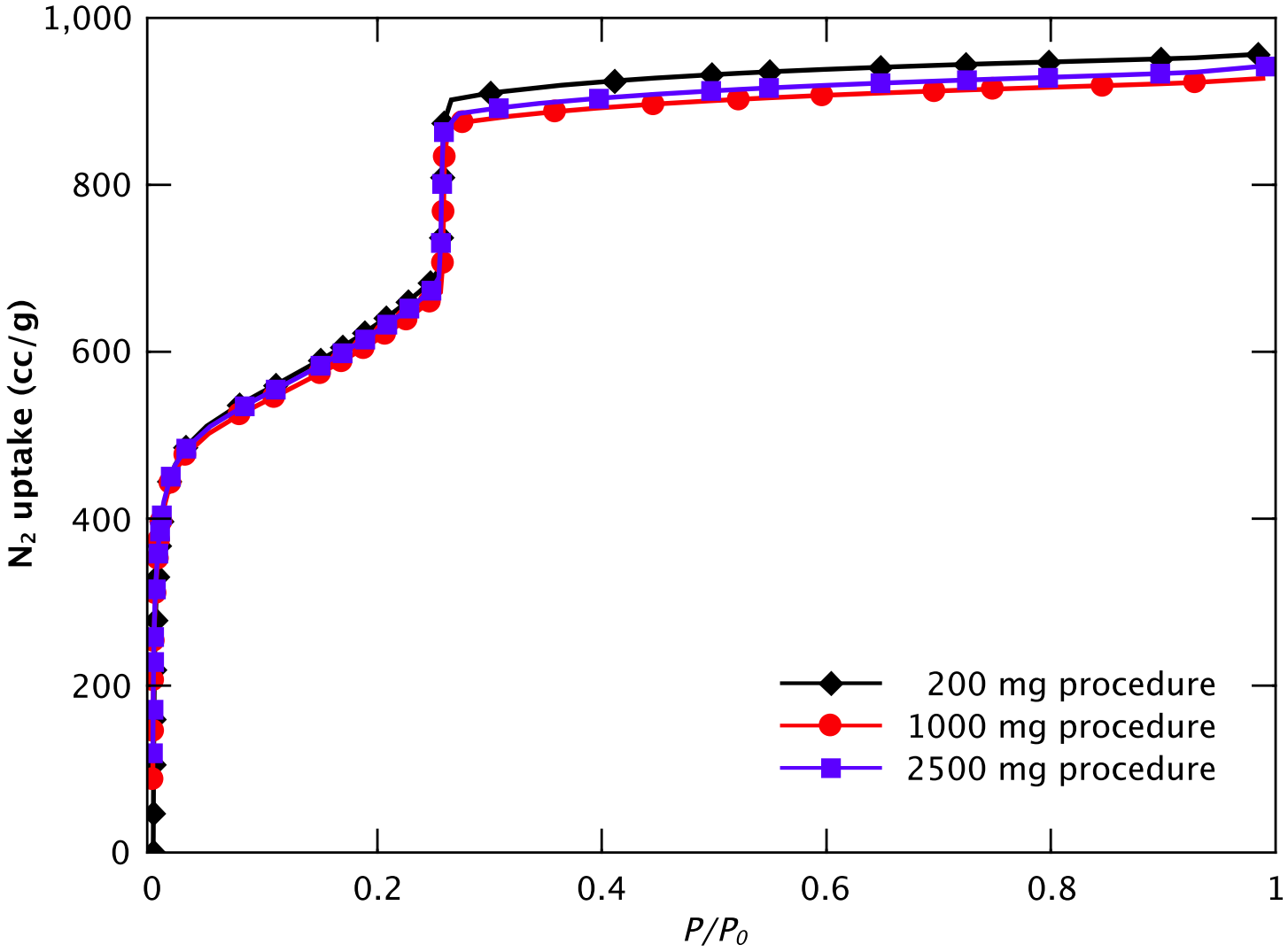
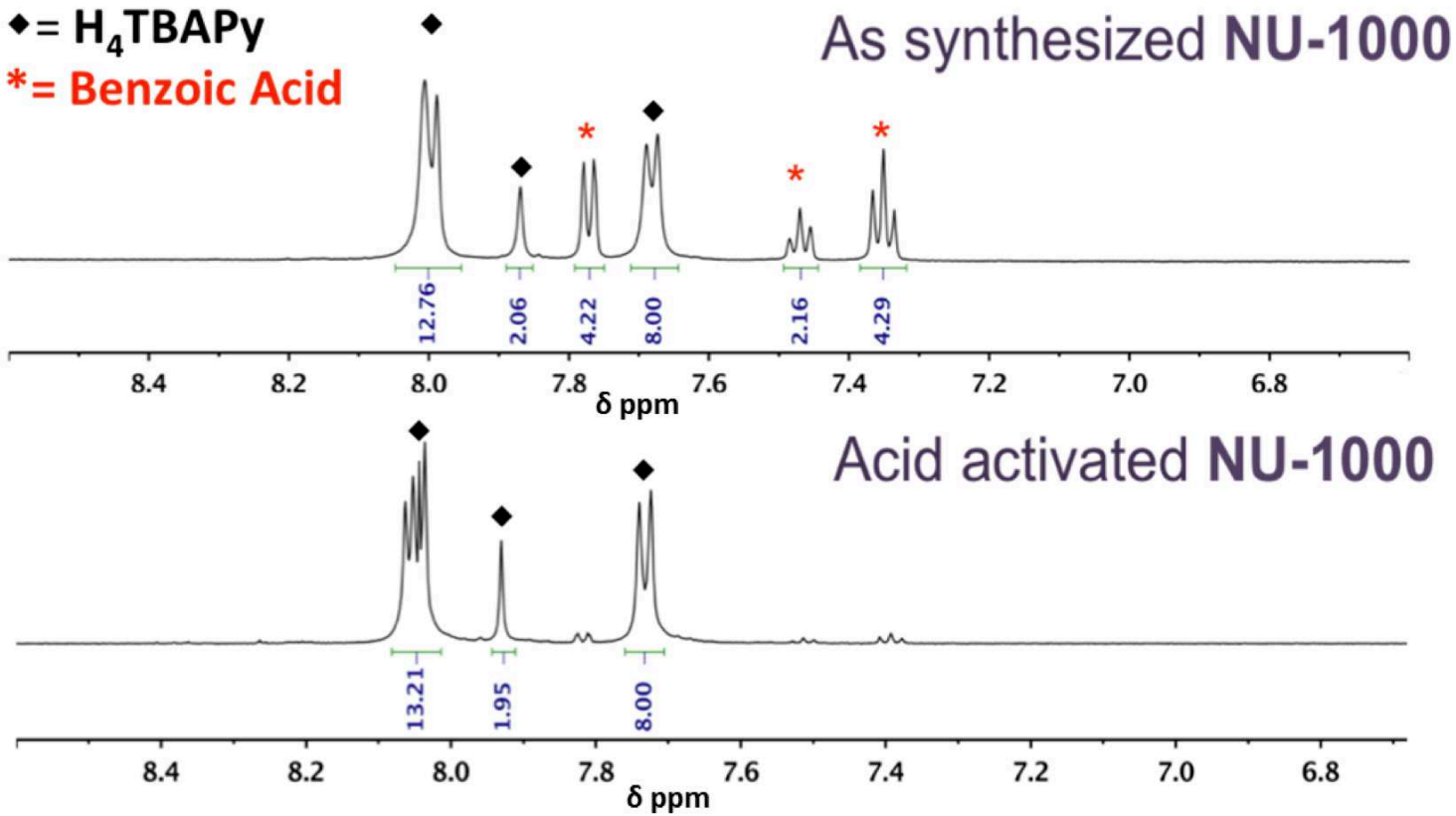
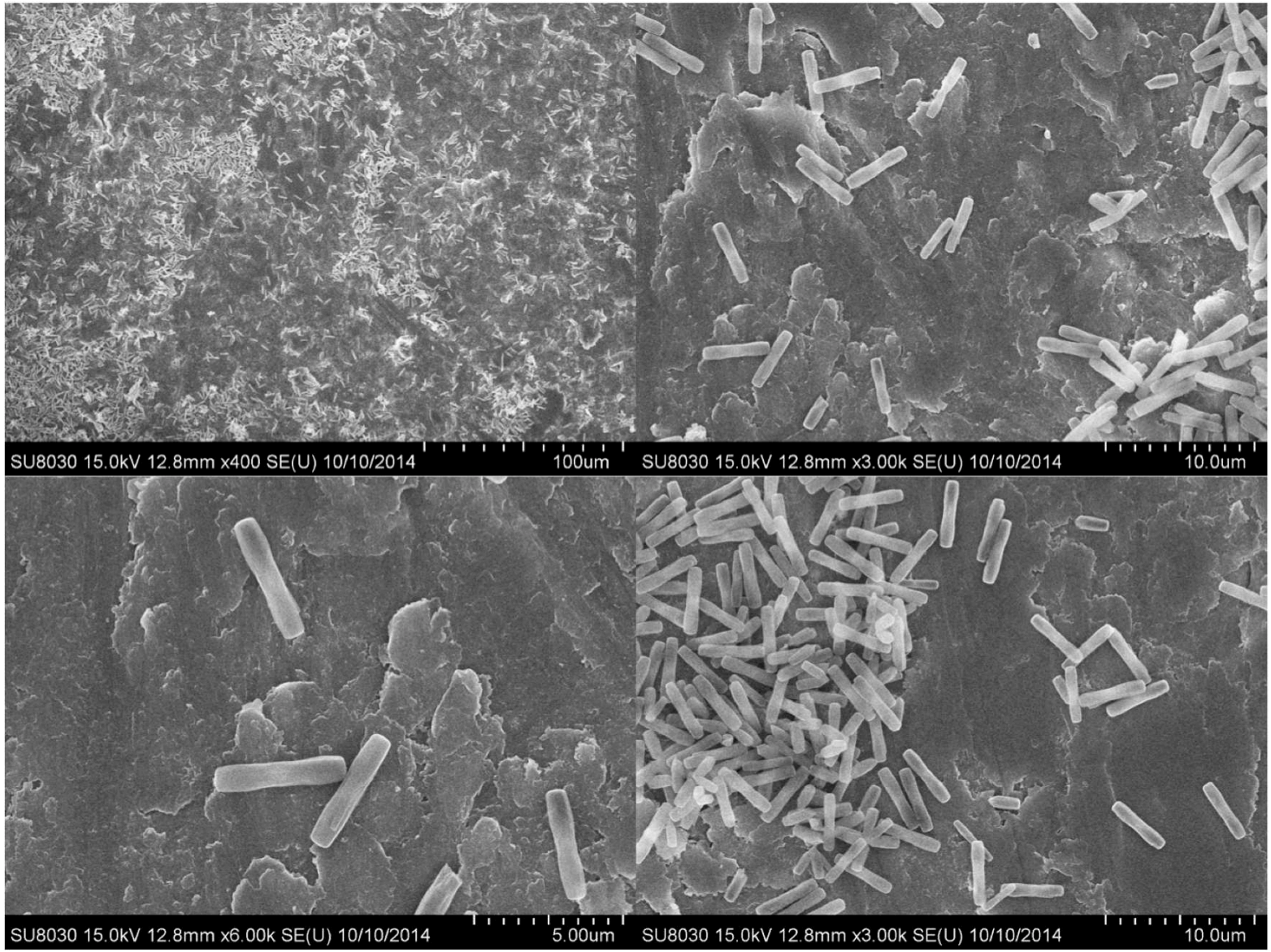
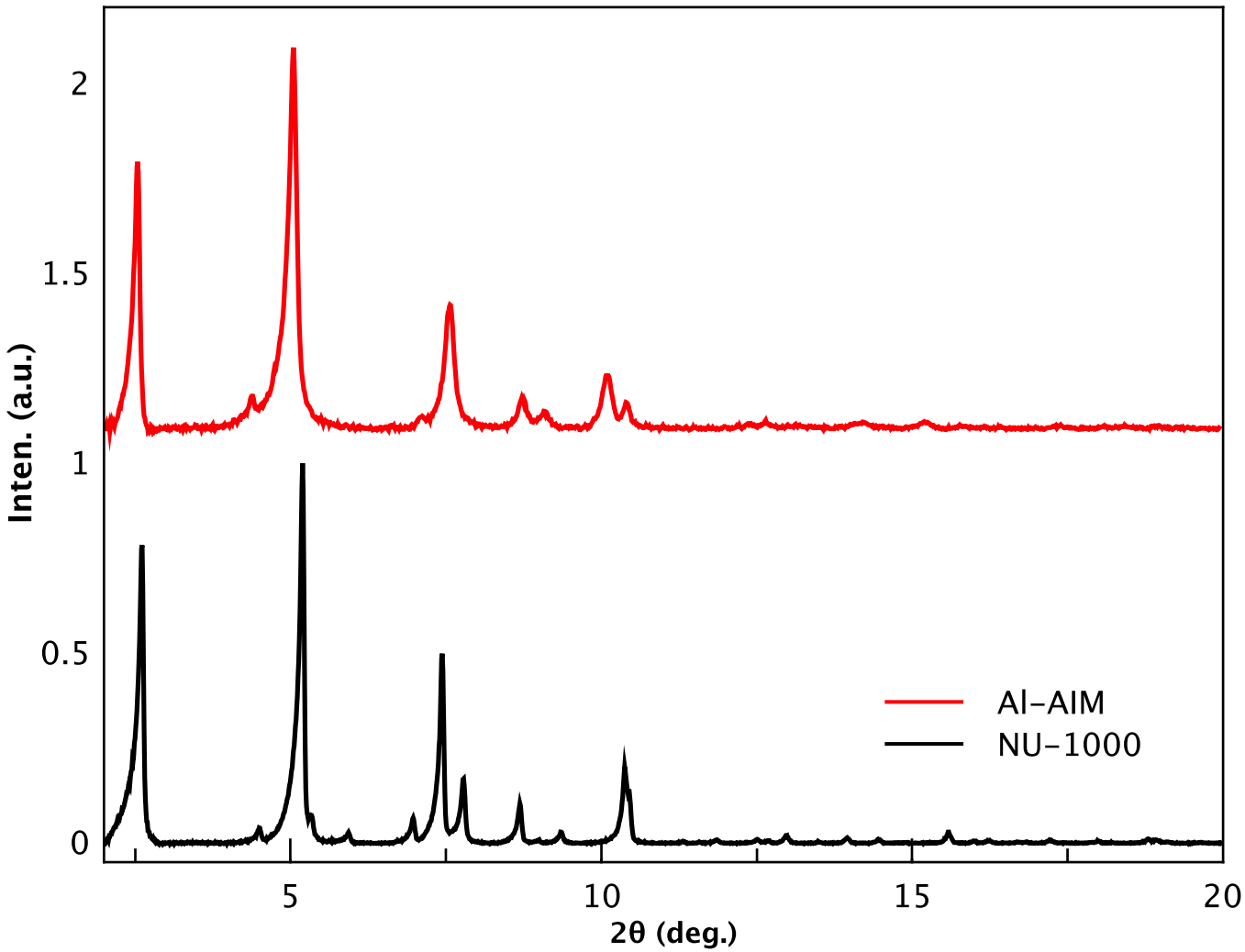
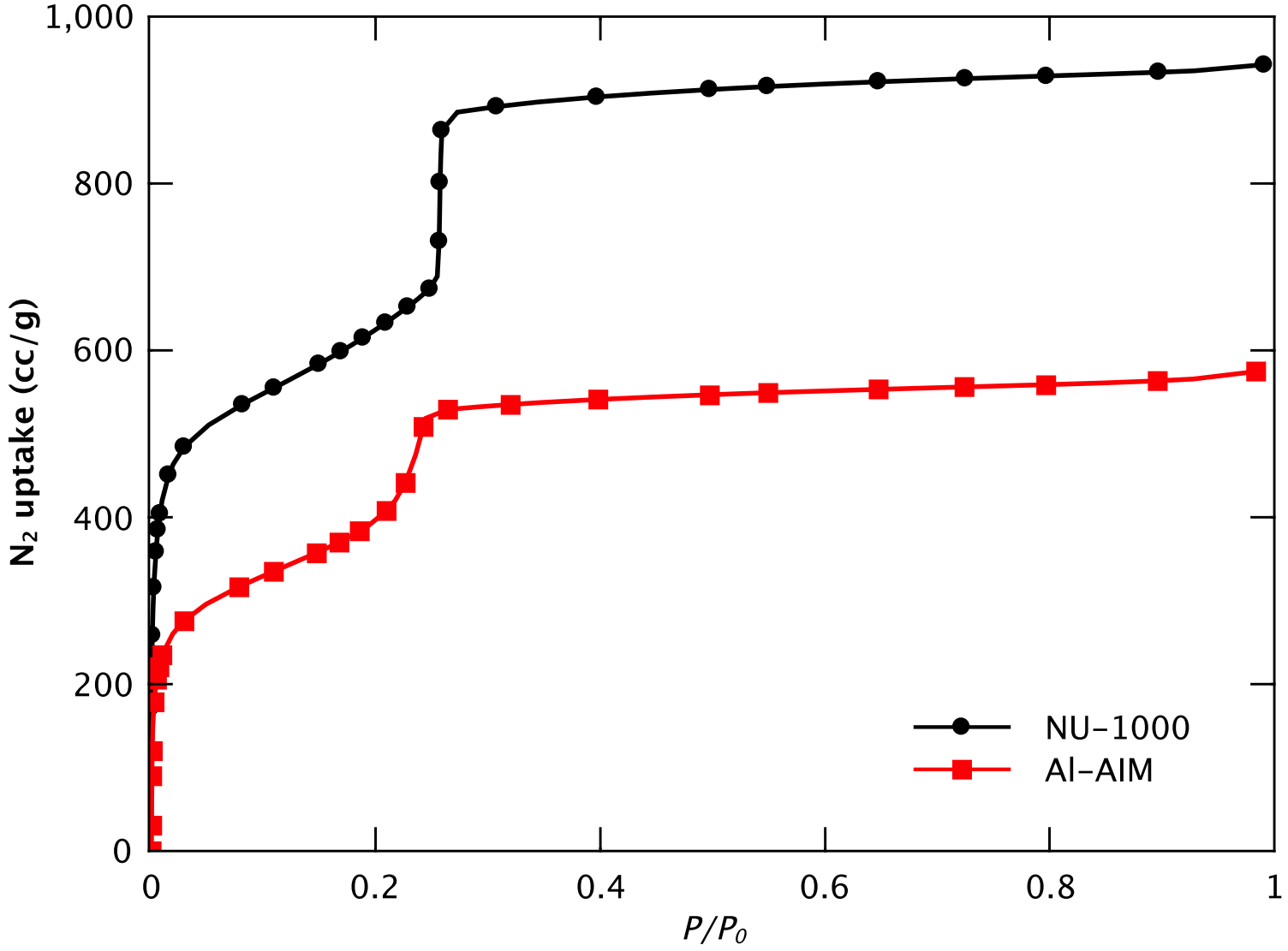
1 g procedure
Simulated PXRD

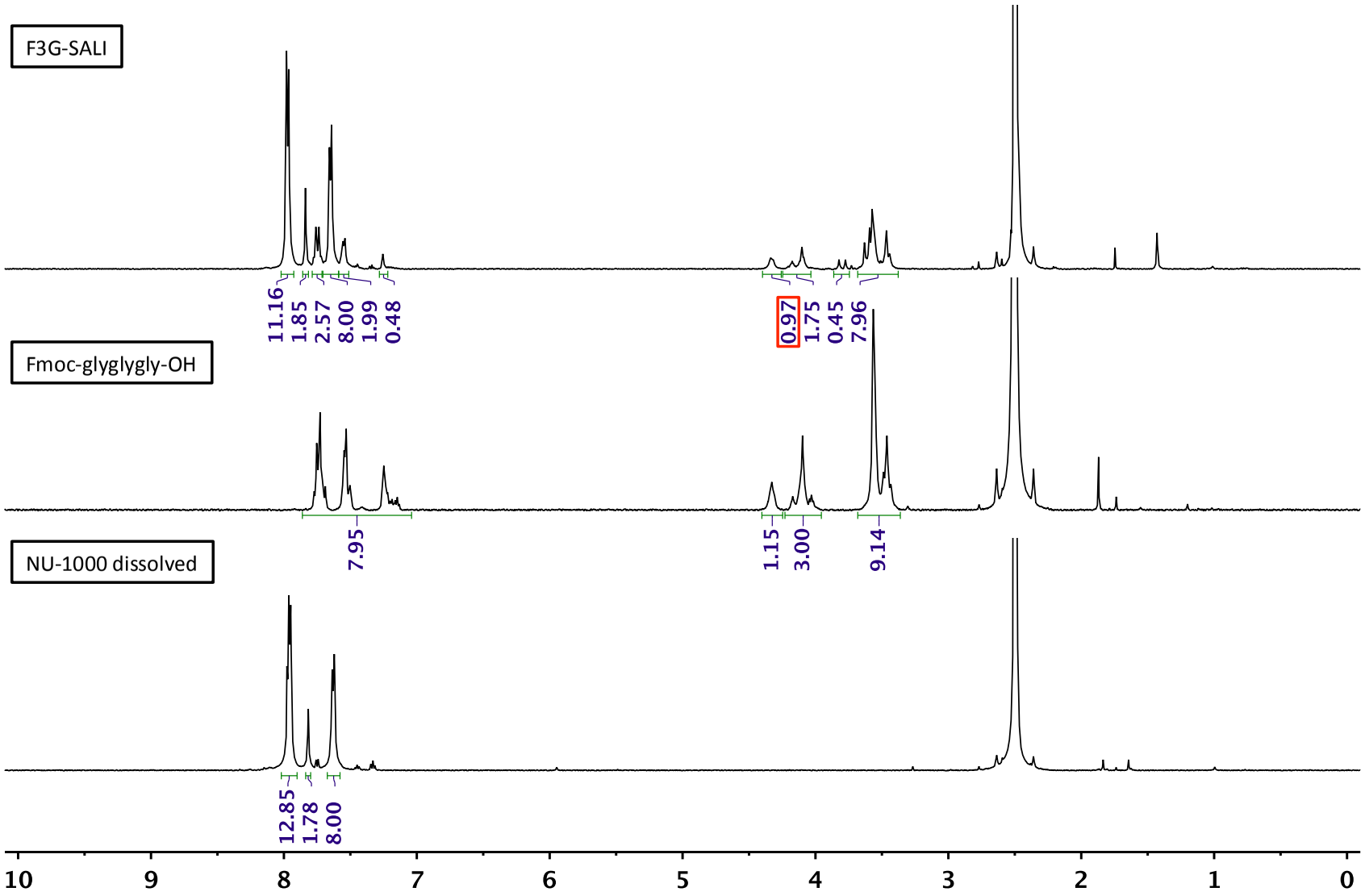

1,000
800
600
400
200
0
N2 uptake (cc/g)
0
0.2
0.4
0.6
0.8
1
P/P0
200 mg procedure
1000 mg procedure
2500 mg procedure

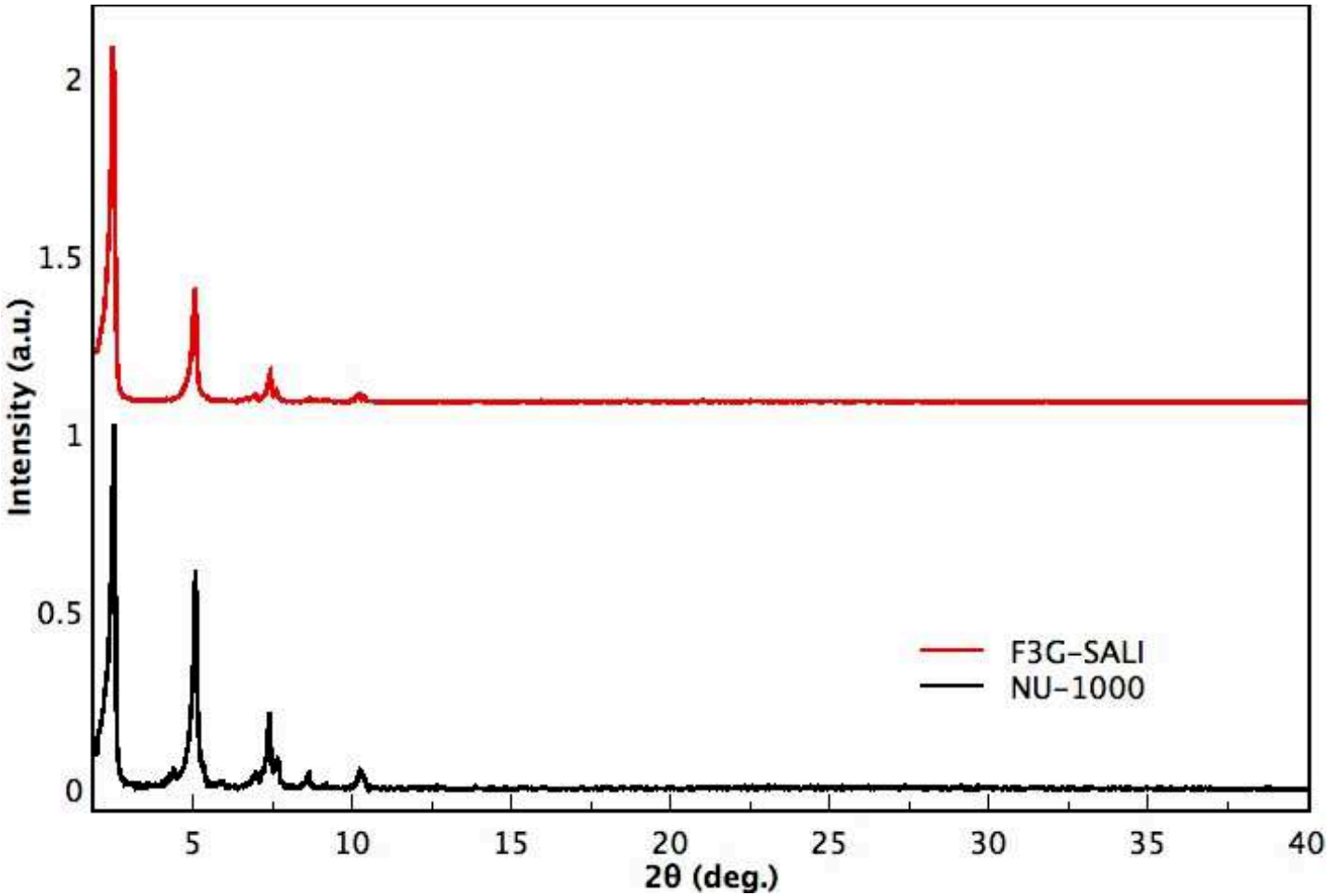

◆= H4TBAPy
*= Benzoic Acid
As synthesized NU-1000
12.76
2.06
4.22
8.00
2.16
4.29
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
δ ppm
Acid activated NU-1000
13.21
1.95
8.00
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
δ ppm

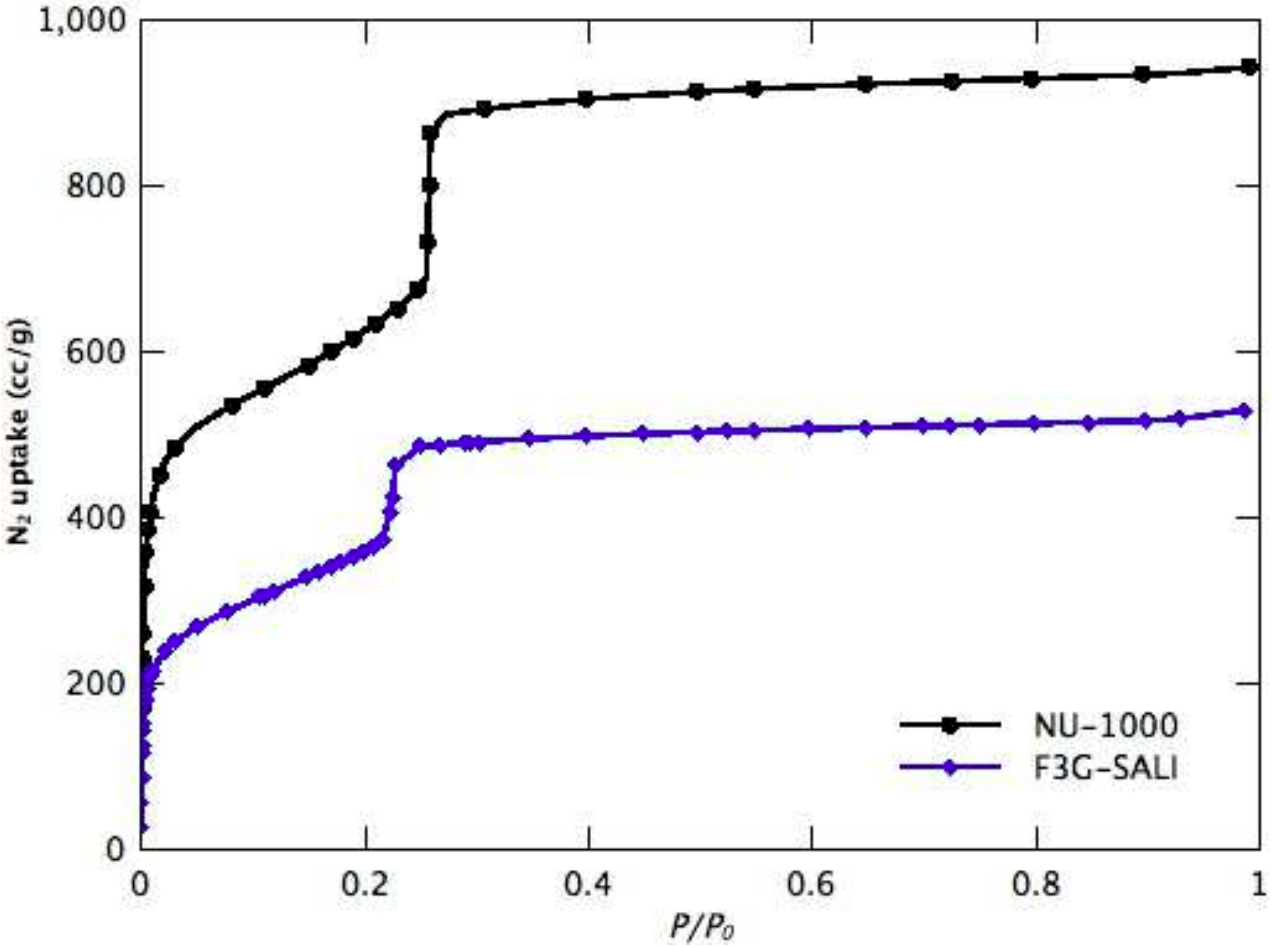

SU8030 15.0kV 12.8mm x400 SE(U) 10/10/2014
100um
SU8030 15.0kV 12.8mm x3.00k SE(U) 10/10/2014
10.0um
SU8030 15.0kV 12.8mm x6.00k SE(U) 10/10/2014
5.00um
SU8030 15.0kV 12.8mm x3.00k SE(U) 10/10/2014
10.0um


Inten. (a.u.)
2
1.5
1
0.5
0
5
10
15
20
2θ (deg.)
Al–AIM
NU–1000


1,000
800
600
400
200
0
N₂ uptake (cc/g)
0
0.2
0.4
0.6
0.8
1
P/P0
NU–1000
Al–AIM


F3G-SALI
11.16
1.85
2.57
8.00
1.99
0.48
0.97
1.75
0.45
7.96
Fmoc-glyglygly-OH
7.95
1.15
3.00
9.14
NU-1000 dissolved
12.85
1.78
8.00
10
9
8
7
6
5
4
3
2
1
0


Intensity (a.u.)
2
1.5
1
0.5
0
5
10
15
20
25
30
35
40
2θ (deg.)
F3G-SALI
NU-1000


1,000
800
600
400
200
0
N₂ uptake (cc/g)
0
0.2
0.4
0.6
0.8
1
P/P₀
NU-1000
F3G-SALI