

## Structural Transformation of Metal Oxo Species within UiO-66 Type Metal–Organic Frameworks

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## I) Materials

**Caution! Thorium nitrate ( $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ) is a radioactive and chemically toxic reactant. Thus, suitable care, precautions, and protection for handling such substances have been followed.**

All chemicals and solvents were obtained from commercial suppliers and used without further purification. Thorium nitrate ( $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ) ( $\geq 98\%$ , radiation clearance tested) was purchased from International Bio-Analytical Industries, Inc. Zirconium (IV) chloride, hafnium (IV) dichloride oxide octahydrate, cerium (IV) ammonium nitrate, terephthalic acid (BDC), glacial acetic acid, triethylamine, glycine, sodium chloride, benzoic acid, diethylamine, lithium formate, and N,N-dimethylformamide were purchased from Sigma-Aldrich. Ethanol was purchased from Fischer Chemical. Deionized water was used as the water source.  $\text{N}_2$  used for the adsorption and desorption measurements was Ultra High Purity Grade 5 and obtained from Airgas Specialty Gases (Chicago, IL).

## II) Methods for Materials Characterization

*Single Crystal X-Ray Diffraction Analysis and Refinement Details of NU-351:* For single-crystal X-ray diffraction measurements, one crystal of NU-351 was collected at 100 K using a Rigaku Cu-Synergy diffractometer, equipped with shutter-less electronic-noise free Hybrid Photon Counting (HPC) detector and Cryostream 80-500K (Cryostream Oxford Cryosystems, Oxford, United Kingdom),  $\text{CuK}\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) microfocus source with a beam size of  $\sim 110 \mu\text{m}$  and a 4-circle Kappa geometry goniometer. The single crystals were mounted on MicroMesh (MiTeGen) with paratone oil. The irradiation of crystals were done with the paratone oil for 20 min. The structures were determined by intrinsic phasing (SHELXT 2018/2)

and refined by full-matrix least-squares refinement (SHELXL-2018/3) using the Olex2 software packages. Refinement results are summarized in Table S1. Crystallographic data in CIF format have been deposited in the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC-2167180. The data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.).

**Table S1:** Crystallographic details of NU-351

<b>Empirical formula</b>	C <sub>72</sub> H <sub>60</sub> Ce <sub>5</sub> N <sub>4</sub> O <sub>34</sub>
<b>Formula weight</b>	2225.84
<b>Temperature/K</b>	100.02(10)
<b>Crystal System</b>	triclinic
<b>Space Group</b>	P-1
<i>a</i> /Å	13.9994(2)
<i>b</i> /Å	15.2612(3)
<i>c</i> /Å	17.7824(3)
<i>α</i> /°	89.9738(15)
<i>β</i> /°	86.8717(14)
<i>γ</i> /°	89.3377(13)
<b>Volume/Å<sup>3</sup></b>	3793.24(11)
<b>Z</b>	2
<i>ρ</i> <sub>calc</sub> /cm <sup>3</sup>	1.949
<i>μ</i> /mm <sup>-1</sup>	23.518
<b>F(000)</b>	2164.0
<b>Crystal size/mm<sup>3</sup></b>	0.2 × 0.12 × 0.1
<b>Radiation / Å</b>	Cu Kα (λ = 1.54184)
<b>2θ range for data collection/°</b>	7.638 to 159.348
<b>Index ranges</b>	-17 ≤ h ≤ 17, -19 ≤ k ≤ 19, -21 ≤ l ≤ 17
<b>Reflections collected</b>	45422
<b>Independent reflections</b>	14925 [R <sub>int</sub> = 0.0526, R <sub>sigma</sub> = 0.0393]
<b>Data/restraints/parameters</b>	14925/174/1032
<b>Goodness-of-fit on F<sup>2</sup></b>	1.128

<b>Final <i>R</i> indexes [<math>I \geq 2\sigma</math> (<i>I</i>)]</b>	$R_1 = 0.1205$ , $wR_2 = 0.3275$
<b>Final <i>R</i> indexes [all data]</b>	$R_1 = 0.1231$ , $wR_2 = 0.3285$
<b>CCDC deposition number</b>	2167180

*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-K $\alpha$ 1 X-ray radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in transmission geometry.

*N<sub>2</sub> Sorption Isotherm Measurements:* N<sub>2</sub> adsorption and desorption isotherms on activated materials were measured on a Micromeritics Tristar (Micromeritics, Norcross, GA) instrument at 77 K. Around 30 mg of sample was used in each measurement. Prior to N<sub>2</sub> isotherm measurements, the samples were placed under high vacuum at 100 °C on a Micromeritics Smart Vacprep for 18 h. The specific surface areas were determined using the Brunauer–Emmett–Teller model from the N<sub>2</sub> sorption data in the region  $P/P_0 = 0.005\text{--}0.05$ . Pore size distributions were obtained using DFT calculations using a carbon slit-pore model with a N<sub>2</sub> kernel.

*X-ray Photoelectron Spectroscopy:* X-ray photoelectron spectroscopy measurements were carried out on a Thermo Scientific ESCALAB 250 Xi equipped with an electron flood gun and a scanning ion gun. Analysis used the Thermo Scientific Advantage Data System software, and C1s peak (284.8 eV) peak was used as the reference. Oxidation states of Ce were assigned by comparison to previously published data.<sup>1</sup>

*Scanning Electron Microscopy Imaging:* Prior to observation, the samples were coated with OsO<sub>4</sub> (~9 nm) in a Denton Desk III TSC Sputter Coater. Scanning electron microscopy (SEM) images were acquired from a Hitachi SU8030 scanning electron microscope.

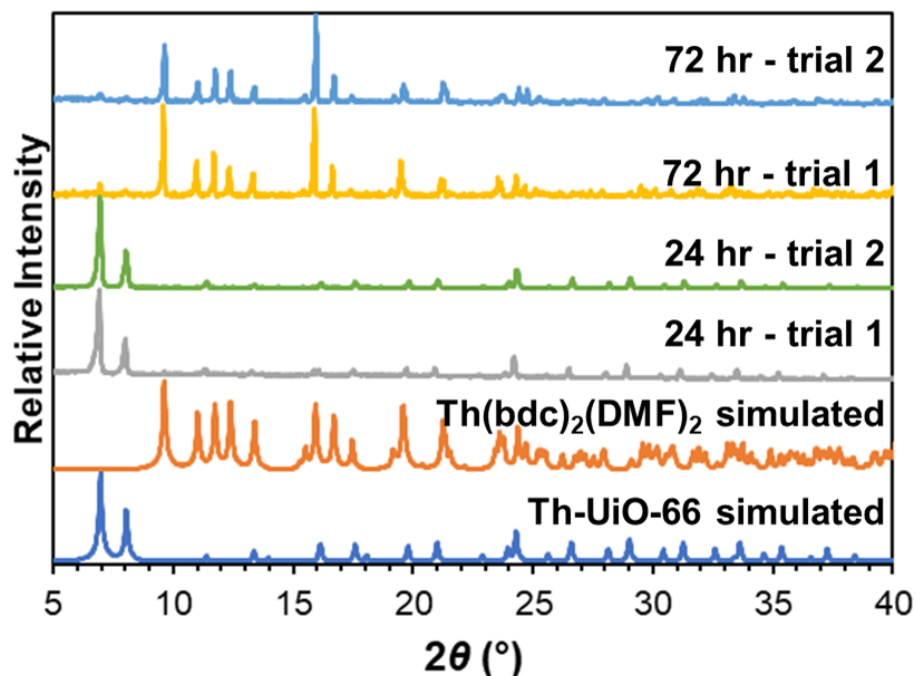
*Thermogravimetric Analysis:* Sample weight loss data was measured on a Mettler Toledo

TGA/DSC 1 Star System instrument. Samples were heated in air from 30°C to 600°C at a rate of 5°C/minute. The sample was held at 600°C for 60 minutes.

### III) Materials Syntheses and Corresponding PXRD Characterizations

#### *Phase Transition of Th-UiO-66 to Th(bdc)<sub>2</sub>(dmf)<sub>2</sub>*

1,4 benzene dicarboxylic acid (150 mg, 0.9 mmol) and Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (200 mg, 0.35 mmol), 4 mL of DMF and 1 mL of H<sub>2</sub>O were each placed a 2-dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners. A total of 4 identical vials were prepared. All vials were sonicated for approximately 10 minutes and then heated at 130 °C. 2 vials were left in the oven for 24 hr and contained a white powder corresponding to Th-UiO-66. The remaining 2 vials were removed after 72 hr and instead contained clear trapezoidal crystals. Each product was washed with DMF 3 times and then washed with ethanol 3 times prior to further characterization.



**Figure S1:** Overlaid PXRDs showing reaction time of identical vials and the evolution of the resulting products from Th-UiO-66 to Th(bdc)<sub>2</sub>(dmf)<sub>2</sub>.

### *Kinetic Monitoring of Phase Transition of Th-UiO-66 to Th(bdc)<sub>2</sub>(dmf)<sub>2</sub>*

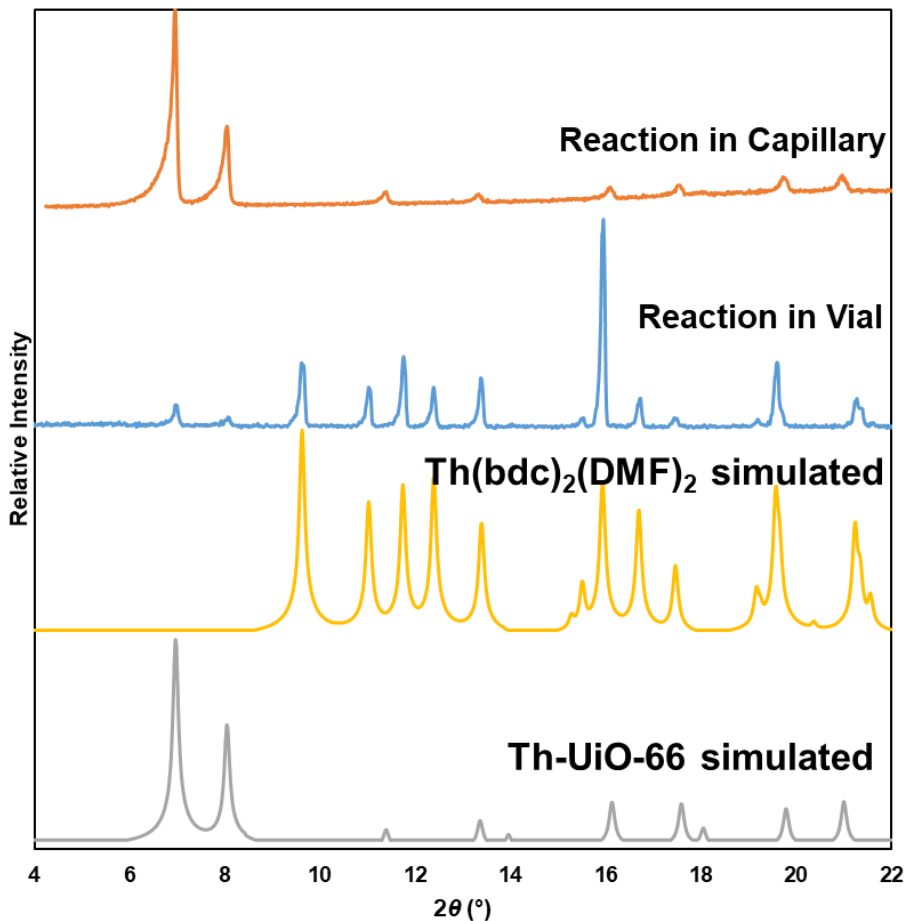
1,4 benzene dicarboxylic acid (37.5 mg, 0.225 mmol) and Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (50 mg, 0.0875 mmol), 1 mL of DMF and 0.25 mL of H<sub>2</sub>O were each placed a 0.5-dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners. A total of 6 identical vials were prepared. All vials were sonicated for approximately 10 minutes and then heated at 130 °C. A vial was removed every 12 hours beginning at 12 hours and ending at a 72 hour time point. Each product was washed with DMF 3 times and then washed with ethanol 3 times prior to further characterization.

### *Phase Transition of Th(bdc)<sub>2</sub>(dmf)<sub>2</sub> to Th-UiO-66*

20 mg of Th(bdc)<sub>2</sub>(dmf)<sub>2</sub> and 5 mL of water were added to a 2-dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners and heated for 80 °C for 24 hr.

### *Attempted Phase Transition of Th-UiO-66 to Th(bdc)<sub>2</sub>(dmf)<sub>2</sub> in a Capillary*

1,4 benzene dicarboxylic acid (150 mg, 0.9 mmol) and Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (200 mg, 0.35 mmol), 4 mL of DMF and 1 mL of H<sub>2</sub>O were each placed a 2-dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners. The vial was sonicated for approximately 10 minutes. Approximately 100 μL aliquot of the reaction mixture was placed inside a 1.5 mm boron-rich capillary, which was then flame sealed. The capillary and then mother solution were left to in an oven at 130 C and taken out after 3 days. After a first PXRD measurement, the capillary was placed in the oven for an additional 7 days, before a second measurement.

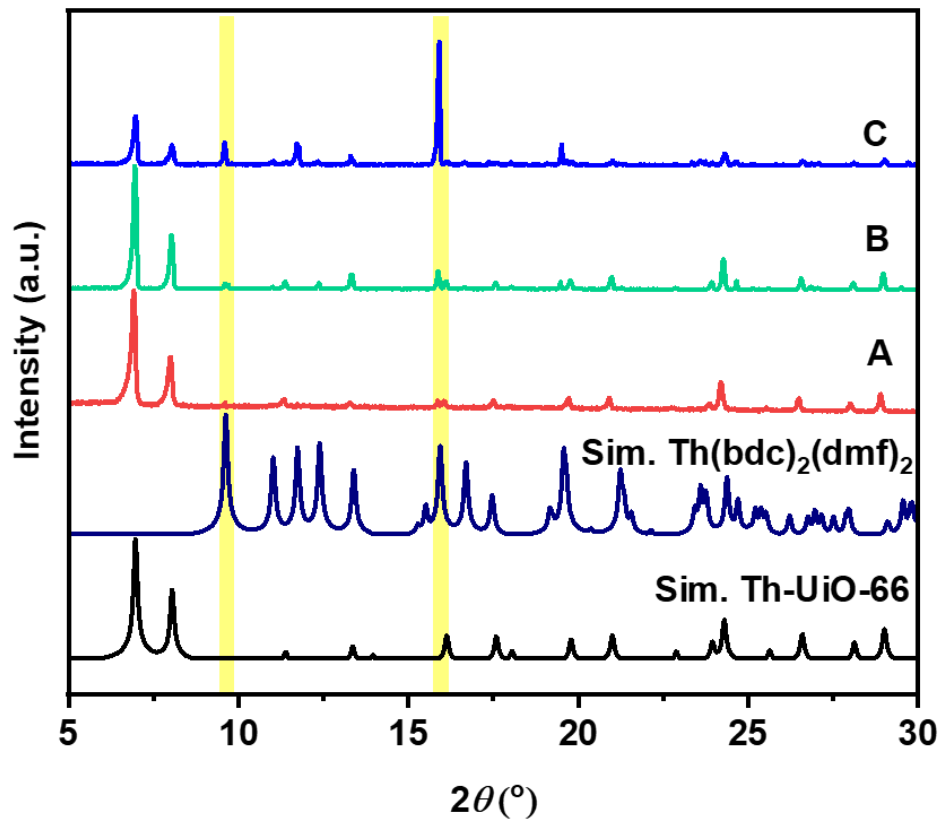


**Figure S2:** Comparing attempted phase transition of flame sealed capillary with polyvinyl-based vial.

*Varying Concentration in Attempted Phase Transition of Th-UiO-66 to Th(bdc)<sub>2</sub>(dmf)<sub>2</sub>*

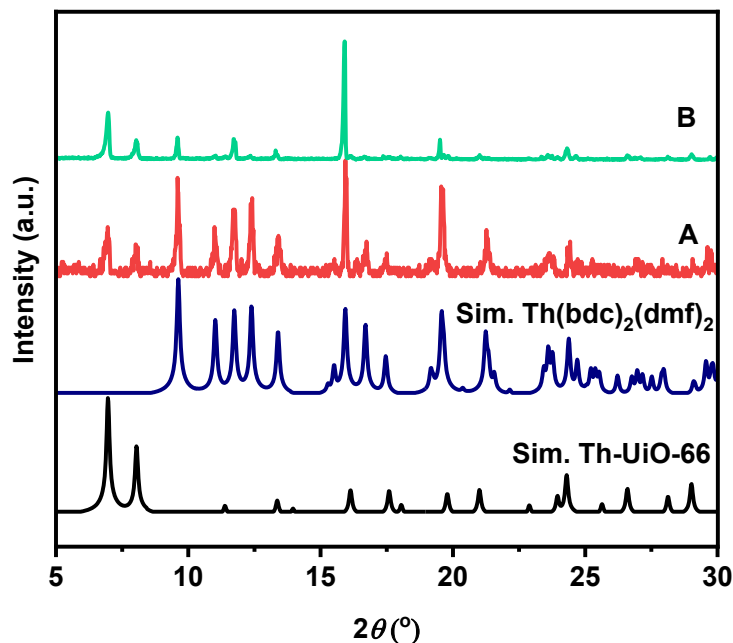
1,4 benzene dicarboxylic acid (75 mg, 0.45 mmol) and Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (100 mg, 0.175 mmol) were each placed a 1-dram DWK Life Sciences screw-thread vial lined with PTFE/rubber. Vial A contained 2 mL DMF and 0.5 mL water (same concentration as original synthesis); vial B contained 1 mL DMF and 0.25 mL water (2x concentration of reactants as original synthesis); vial C contained 0.67 mL DMF and 0.17 mL water (3x concentration of reactants as original synthesis). The vials were sonicated for approximately 10 minutes and then were placed in an oven at 130 °C

for 72 hr. Each product was washed with DMF 3 times and then washed with ethanol 3 times prior to further characterization.



**Figure S3:** Overlaid PXRDs of A) 1X concentration B) 2X concentration and C) 3X concentration within PTFE-lined vials. Highlighted regions added to aid in monitoring the growth of Th(bdc)<sub>2</sub>(dmf)<sub>2</sub> peaks.





**Figure S4:** Overlaid PXRDs of 3X concentration reaction solutions within PTFE-lined vials after A) 24 hr and B) 48 hr.

*Effect of Amine and Formate Additive in Attempted Phase Transition of Th-UiO-66 to Th(bdc)<sub>2</sub>(dmf)<sub>2</sub>*

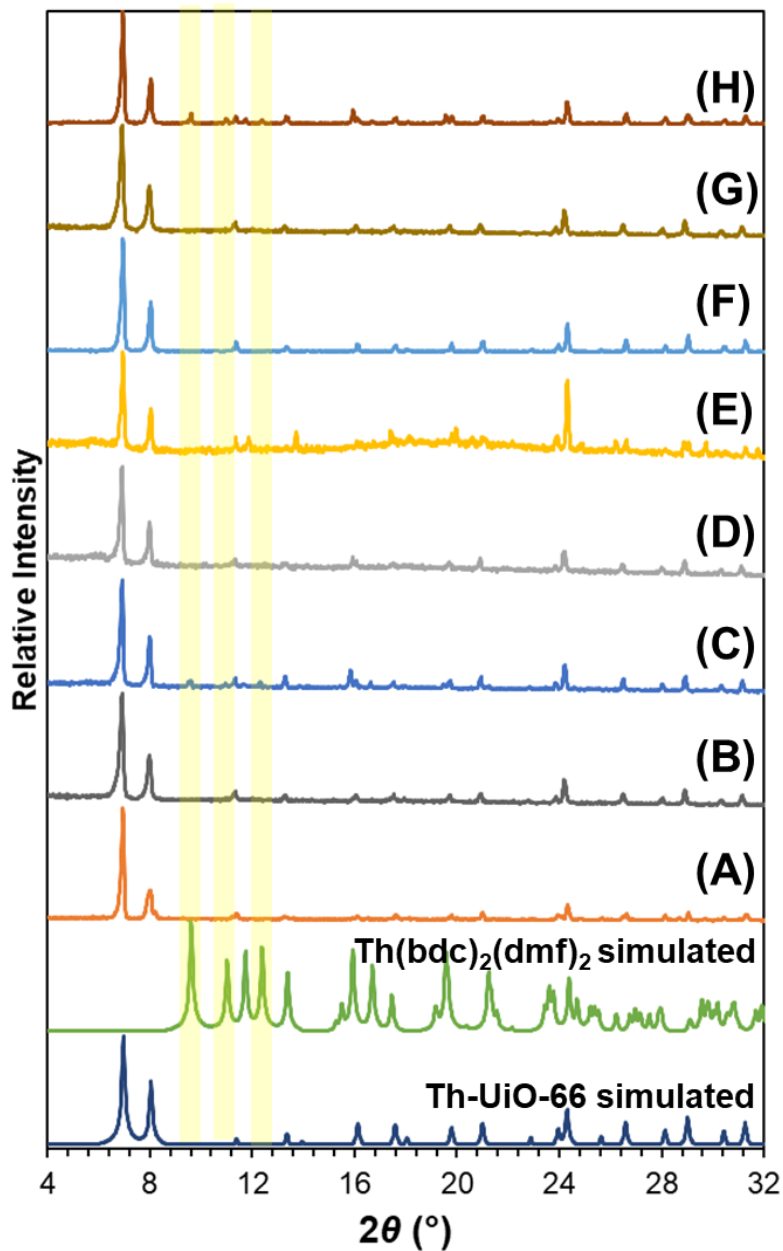
Pure phase Th-UiO-66 was synthesized first by reacting 1,4 benzene dicarboxylic acid (150 mg, 0.9 mmol) and Th(NO<sub>3</sub>)<sub>4</sub>·5H<sub>2</sub>O (200 mg, 0.35 mmol), 4 mL of DMF and 1 mL of H<sub>2</sub>O in a 2-dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners. The vial was sonicated for approximately 10 minutes and then heated at 130 °C for 24 hours. The product was washed with DMF 3 times and then washed with ethanol 3 times before it was heated on a Smart Vac Prep instrument under vacuum for 18 hours at 100 °C.

20 mg of isolated Th-UiO-66 was placed in 2-dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners with the following solvent conditions:

- A) 4 mL DMF
- B) 4 mL DMF + 1 mL water

- C) 4 mL DMF + 0.4 mL diethylamine (3.85 mmol)
- D) 4 mL DMF + 1 mL water + 0.400 mL diethylamine (3.85 mmol)
- E) 4 mL DMF + 200 mg lithium formate (3.85 mmol)
- F) 4 mL DMF + 200 mg lithium formate (3.85 mmol) + 1 mL water
- G) 2 mL DMF + 2 mL diethylamine
- H) 4 mL DMF + 0.4 mL diethylamine (1 week)

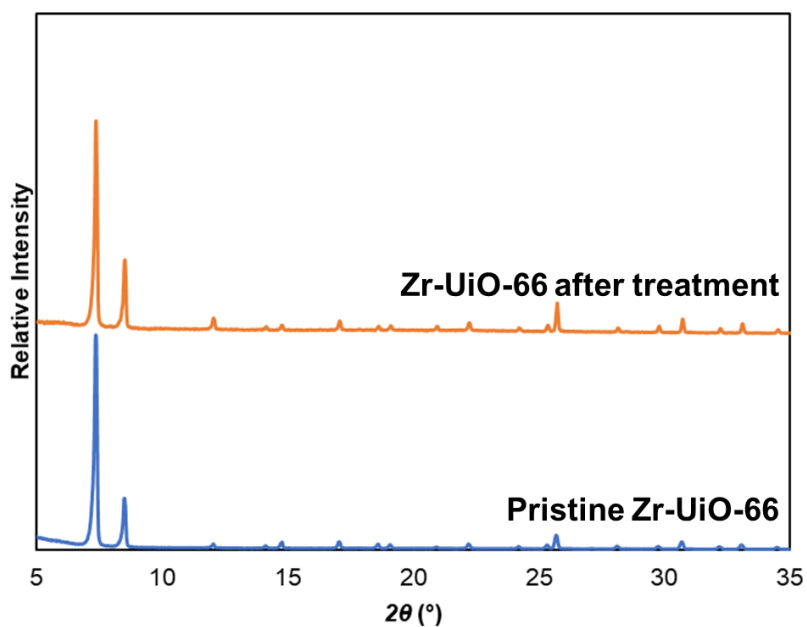
The vials were sonicated for 10 minutes, and then the vials were placed in a 130 °C oven for 48 hours unless otherwise indicated



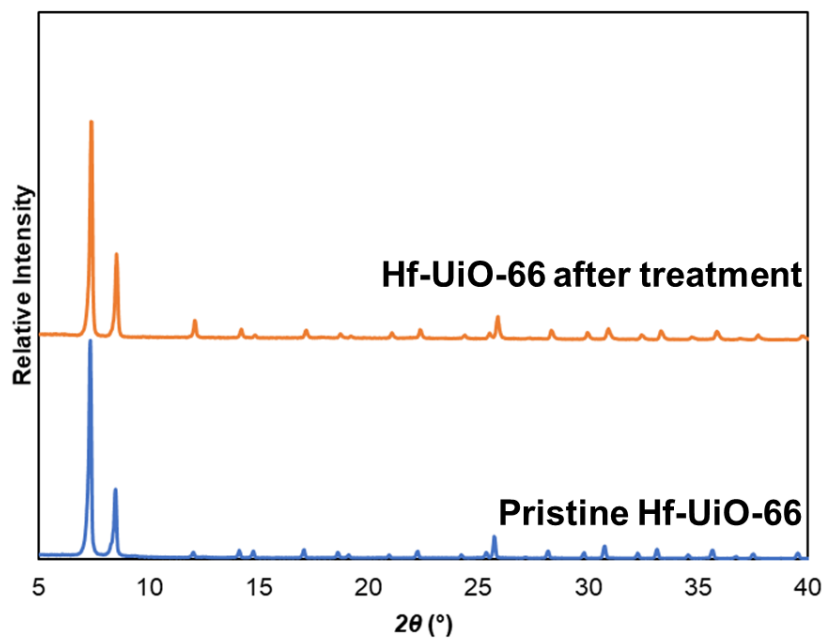
**Figure S5:** PXRD Patterns of Th-UiO-66 product exposed to: A) 4 mL DMF; B) 4 mL DMF + 1 mL water; C) 4 mL DMF + 0.4 mL diethylamine (3.85 mmol); D) 4 mL DMF + 1 mL water + 0.400 mL diethylamine (3.85 mmol); E) 4 mL DMF + 200 mg lithium formate (3.85 mmol); F) 4 mL DMF + 200 mg lithium formate (3.85 mmol) + 1 mL water; G) 4 mL DMF + 0.4 mL diethylamine (1 week); H) 2 mL DMF + 2 mL diethylamine

*Attempted Phase Transition of Zr-UiO-66, Hf-UiO-66, and Ce-UiO-66*

Zr, Hf, and Ce-UiO-66 were synthesized according to literature procedure.<sup>2-4</sup> 20 mg of a selected MOF, 4 mL of DMF, and 1 mL of water were placed in a 2 dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners and reacted for 48 hours at 130 °C. Each product was washed with DMF 3 times and then washed with ethanol 3 times prior to further characterization.



**Figure S6:** Zr-UiO-66 (top) after heating in 4:1 DMF : water at 130 °C for 48 hr stacked over as-synthesized Zr-UiO-66.

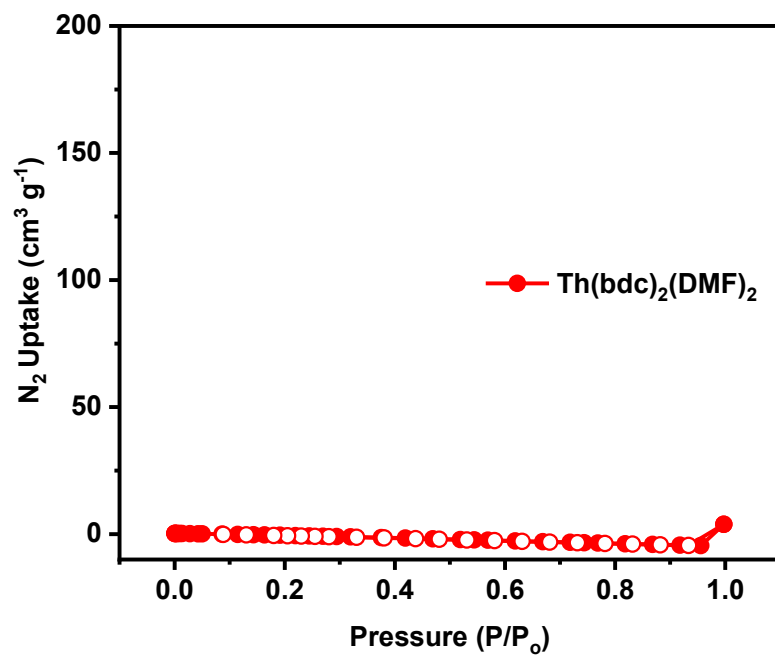


**Figure S7:** Hf-UiO-66 (top) after heating in 4:1 DMF : water at 130 °C for 48 hr stacked over as-synthesized Hf-UiO-66.

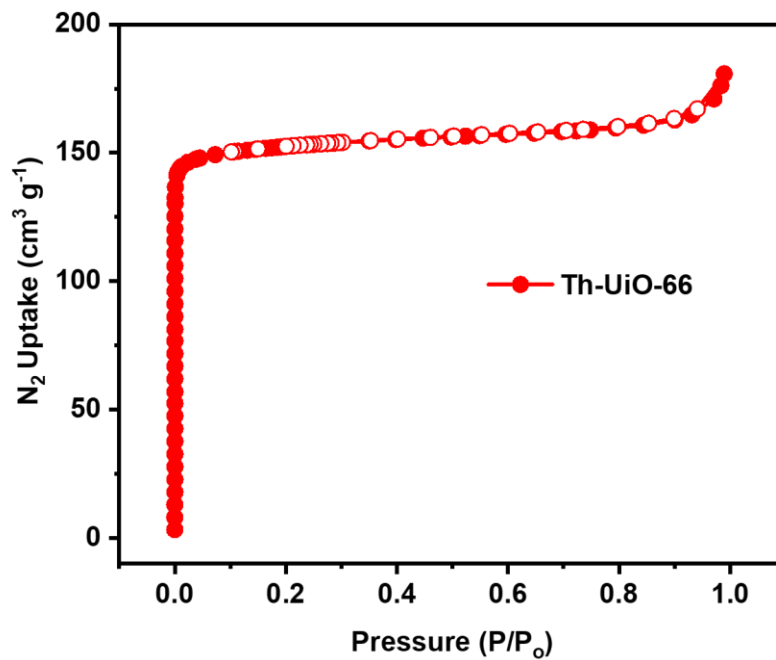
### *NU-351 Single Crystal Synthesis*

352 mg of a C<sub>6</sub> precursor (0.15 mmol), which was synthesized according to literature procedures<sup>5</sup>, 150 mg of 1,4 benzene dicarboxylic acid (0.90 mmol), 4 mL of DMF, and 1 mL of water were added to a 2 dram DWK Life Sciences screw-thread vial lined with polyvinyl-faced pulp liners. The vial was sonicated for 10 minutes and was placed in a 130 °C oven for 72 hours. The clear rod-shaped crystals were washed with DMF 3 times and then washed with ethanol 3 times prior to further characterization.

IV) N<sub>2</sub> Physisorption Isotherms

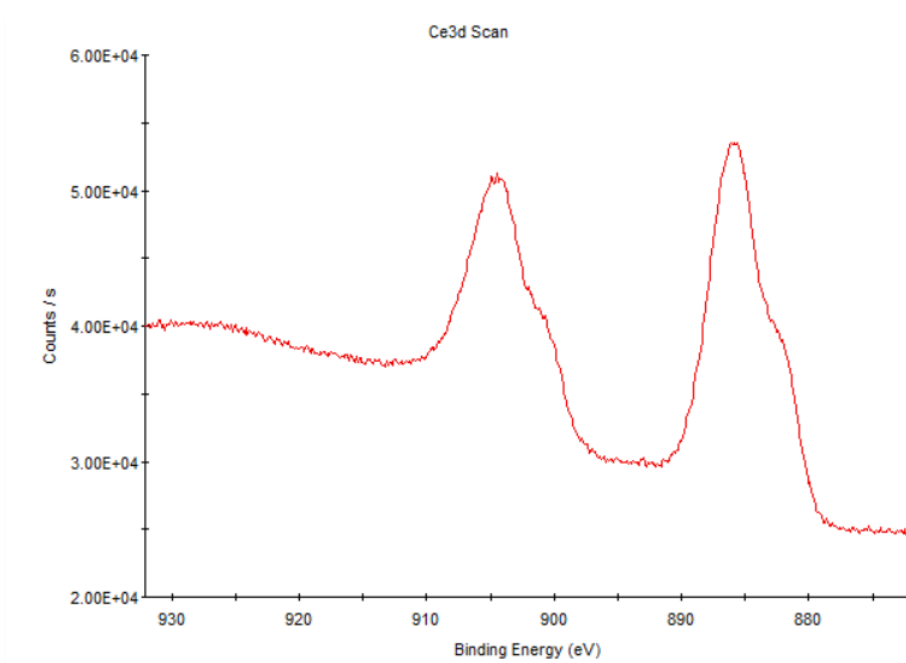


**Figure S8:** N<sub>2</sub> physisorption isotherm collected at 77 K. Apparent BET area was < 5 m<sup>2</sup>/g.



**Figure S9:** N<sub>2</sub> physisorption isotherm collected at 77 K. Apparent BET area was 620 m<sup>2</sup>/g.

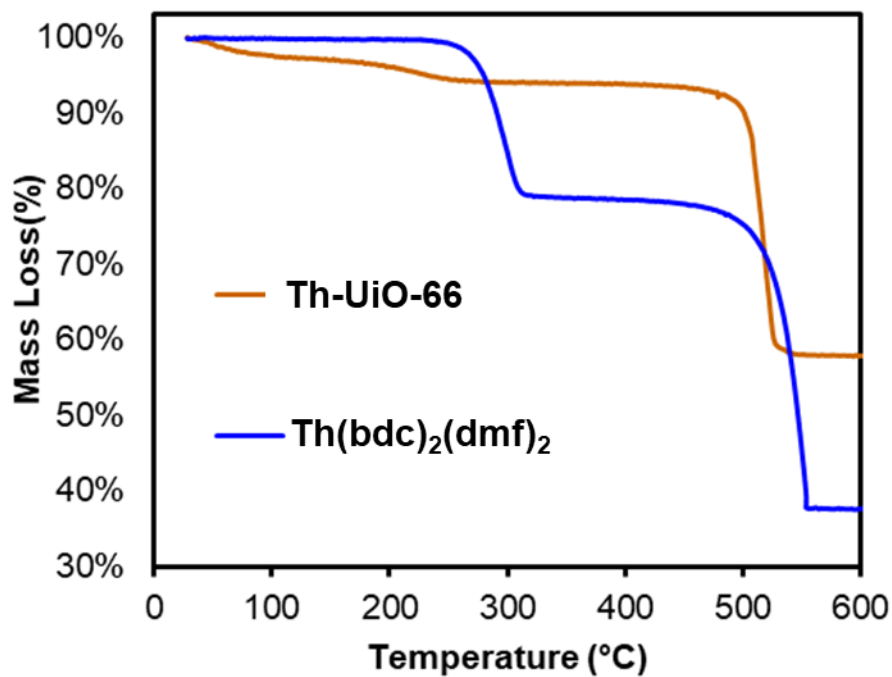
V) XPS Data



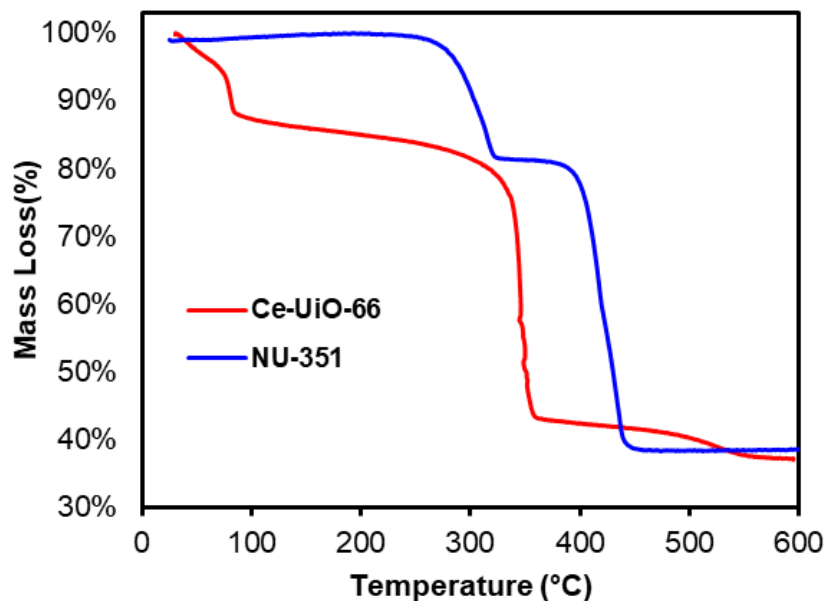
**Figure S10:** XPS Ce3d spectrum of NU-351 showing characteristic Ce(III) peaks.



VI) TGA Data



**Figure S11:** TGA data of Th-UiO-66 and Th(bdc)<sub>2</sub>(dmf)<sub>2</sub> under air. Within Th-UiO-66, the residual mass loss from 100-300 °C is attributed to loss of residual solvent used to wash MOFs (ethanol) or any initial solvent used in the synthesis (DMF/water), and the mass loss at 500 °C is attributed to the loss of BDC linkers. Within Th(bdc)<sub>2</sub>(dmf)<sub>2</sub>, the mass loss at 300 °C is attributed to loss of DMF molecules, and the mass loss at 500 °C is attributed to the loss of BDC linkers.



**Figure S12:** TGA data of Ce-Uio-66 and NU-351 under air. Within Ce-Uio-66, the mass loss < 100 C is attributed to loss of residual solvent used to wash MOFs (acetone / ethanol) and the mass loss starting at 300 C is attributed to loss of BDC linkers. Within NU-351, the mass loss at 300 °C is attributed to loss of DMF molecules, and the mass loss at 400 °C is attributed to the loss of BDC linkers.

## VII) References

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