

Electronic Supplementary Information for:

## **An Alternative UiO-66 Synthesis for HCl-Sensitive Nanoparticle Encapsulation**

Karen Tulig and Krista S. Walton

### **Contents**

1. Synthesis Procedures .....	2
1.1. UiO-66(ZrCl <sub>4</sub> ) and UiO-66(Zr( <i>On</i> Pr)) .....	2
1.2. AuNPs and Au@UiO-66.....	3
2. Thermogravimetric Analysis (TGA) .....	5
3. Powder X-ray Diffraction (PXRD) Analysis .....	6
3.1. Water Stability .....	6
3.2. Temperature, Solvent, and Time Variations .....	7
3.3. Acetic Acid Effect.....	10
4. Specific Surface Area Analysis.....	12
4.1. UiO-66(ZrCl <sub>4</sub> ), UiO-66(Zr( <i>On</i> Pr)), and Au@UiO-66(Zr( <i>On</i> Pr)) .....	12
4.2. Acetic Acid Effect.....	14
5. Scanning Transmission Electron Microscopy-Energy Dispersive Spectroscopy (STEM-EDS) .....	17
6. AuNP Analysis .....	18
6.1. Proton Nuclear Magnetic Resonance ( <sup>1</sup> H NMR).....	18
6.2. Transmission Electron Microscopy (TEM) .....	19

## 1. Synthesis Procedures

### 1.1. UiO-66(ZrCl<sub>4</sub>) and UiO-66(Zr(OnPr))

All chemicals were obtained commercially (Sigma-Aldrich and Fisher Scientific) and used as obtained. UiO-66(ZrCl<sub>4</sub>) is synthesized following procedures reported previously.<sup>1</sup> Briefly, zirconium chloride (ZrCl<sub>4</sub>) (0.053g, 0.227mmol) and terephthalic acid (TPA) (0.038g, 0.227mmol) are dissolved in N,N-dimethylformamide (DMF) (26.5mL, 340mmol) in a glass scintillation vial. The mixture is then stirred at 120°C for 24 hours in a silicon oil bath. The solution is allowed to cool to room temperature, then, exchanged with fresh DMF and soaked overnight three times. Finally, the solution was exchanged with fresh methanol three times.

UiO-66(Zr(OnPr)) is synthesized by stirring a mixture of 70% solution of zirconium(IV) propoxide in *n*-propanol, (71.2μL, 0.227mmol), terephthalic acid (0.075g, 0.454mmol), methanol (3.5mL, 86.5mmol), N,N-dimethylformamide (3.5mL, 45.4mmol), and glacial acetic acid (0.4mL, 6.81mmol) in a glass scintillation vial at 120°C for 24 hours. The material is washed the same as UiO-66(ZrCl<sub>4</sub>). Also, the temperature, solvent mixture, and time are varied. The synthesis procedures are tabulated below:

**Table S1:** Synthesis conditions used to synthesize UiO-66(Zr(OnPr)) with varying temperature, solvent, and time

Sample	Zr(OnPr) (mmol)	TPA (mmol)	Acetic Acid (mmol)	MeOH (mmol)	DMF (mmol)	Temp. (°C)	Time (hrs)
MeOH, 120°C, 24hrs	0.227	0.454	6.81	173	0	120	24
MeOH, 120°C, 48hrs	0.227	0.454	6.81	173	0	120	48
MeOH, 120°C, 72hrs	0.227	0.454	6.81	173	0	120	72
MeOH:DMF, 120°C, 24hrs	0.227	0.454	6.81	86.5	45.4	120	24
MeOH:DMF, 120°C, 48hrs	0.227	0.454	6.81	86.5	45.4	120	48
MeOH:DMF, 120°C, 72hrs	0.227	0.454	6.81	86.5	45.4	120	72
DMF, 120°C, 24hrs	0.227	0.454	6.81	0	90.8	120	24
DMF, 120°C, 48hrs	0.227	0.454	6.81	0	90.8	120	48
DMF, 120°C, 72hrs	0.227	0.454	6.81	0	90.8	120	72
MeOH, 70°C, 24hrs	0.227	0.454	6.81	173	0	70	24
MeOH, 70°C, 48hrs	0.227	0.454	6.81	173	0	70	48
MeOH, 70°C, 72hrs	0.227	0.454	6.81	173	0	70	72
MeOH:DMF, 70°C, 24hrs	0.227	0.454	6.81	86.5	45.4	70	24
MeOH:DMF, 70°C, 48hrs	0.227	0.454	6.81	86.5	45.4	70	48
MeOH:DMF, 70°C, 72hrs	0.227	0.454	6.81	86.5	45.4	70	72
DMF, 70°C, 24hrs	0.227	0.454	6.81	0	90.8	70	24
DMF, 70°C, 48hrs	0.227	0.454	6.81	0	90.8	70	48
DMF, 70°C, 72hrs	0.227	0.454	6.81	0	90.8	70	72
MeOH, RT, 24hrs	0.227	0.454	6.81	173	0	RT	24
MeOH, RT, 48hrs	0.227	0.454	6.81	173	0	RT	48
MeOH, RT, 72hrs	0.227	0.454	6.81	173	0	RT	72
MeOH:DMF, RT, 24hrs	0.227	0.454	6.81	86.5	45.4	RT	24
MeOH:DMF, RT, 48hrs	0.227	0.454	6.81	86.5	45.4	RT	48

MeOH:DMF,RT,72hrs	0.227	0.454	6.81	86.5	45.4	RT	72
DMF,RT,24hrs	0.227	0.454	6.81	0	90.8	RT	24
DMF,RT,48hrs	0.227	0.454	6.81	0	90.8	RT	48
DMF,RT,72hrs	0.227	0.454	6.81	0	90.8	RT	72

Additionally, the acetic acid:Zr(*OnPr*) ratio is varied and the solution is stirred at 120°C for 24 hrs. The material is filtered and washed three times with DMF and three times with methanol. The synthesis procedures are tabulated below:

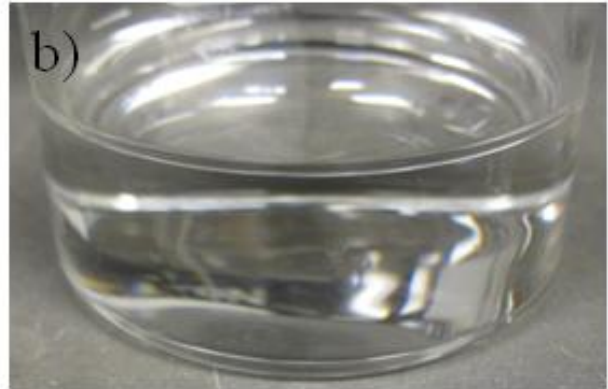
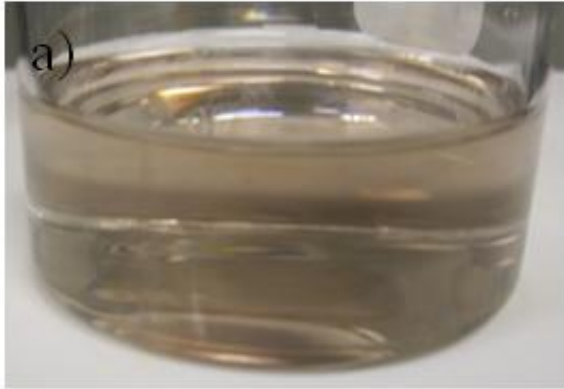
**Table S2:** Synthesis conditions used to synthesize UiO-66(Zr(*OnPr*)) with varying concentrations of acetic acid

Acetic Acid:Zr( <i>OnPr</i> )	pH	Acetic Acid (mmol)	Zr( <i>OnPr</i> ) (mmol)	TPA (mmol)	MeOH (mmol)	DMF (mmol)
0	8.3	0.000	0.227	0.454	86.5	45.4
1	6.1	0.227	0.227	0.454	86.5	45.4
7.5	5.1	1.703	0.227	0.454	86.5	45.4
15	4.4	3.405	0.227	0.454	86.5	45.4
30	4.1	6.810	0.227	0.454	86.5	45.4
60	3.4	13.620	0.227	0.454	86.5	45.4
120	2.5	27.240	0.227	0.454	86.5	45.4
240	2.1	54.480	0.227	0.454	86.5	45.4
480	1.3	108.960	0.227	0.454	86.5	45.4

Finally, acetic acid is exchanged with nitric acid (0.023mmol) yielding a mother solution with a pH of 1.5 and with benzoic acid (0.83g, 6.81mmol) yielding a solution with a pH of 3.6. Both sets of conditions, when coupled with acetic acid (pH of 1.5 and 30:1 ratio of organic acid to Zr(*OnPr*)), yield porous, crystalline UiO-66.

## 1.2. AuNPs and Au@UiO-66

Gold nanoparticles (AuNPs) capped with dodecanethiol are prepared using a previously reported procedure.<sup>2</sup> A solution of tetraoctylammonium bromide (0.3434g, 0.728mmol) in toluene (40mL) is added to a solution of gold(III) chloride trihydrate (0.1236g, 0.314mmol) in water (20mL). The mixture is stirred for 30 minutes. Then, dodecanethiol (0.065g, 0.314mmol) is added, followed by a solution of sodium borohydride (0.119g, 3.14mmol) in water (10mL). The solution is stirred vigorously for 3 hours and washed with copious amounts of water. The organic phase is then separated and reduced to approximately 10mL under vacuum at 25°C. Next, 100mL of methanol is added and the particles precipitate overnight. The solvent was decanted and the particles are washed twice more with copious amounts of methanol. Finally, the dodecanethiol monolayer is place-exchanged with 11-mercaptoundecanoic acid (0.034g, 0.154mmol) and washed with toluene.<sup>3</sup> The AuNPs are then added to the UiO-66(Zr(*OnPr*)) mother solution and stirred at 120°C for 24 hours.

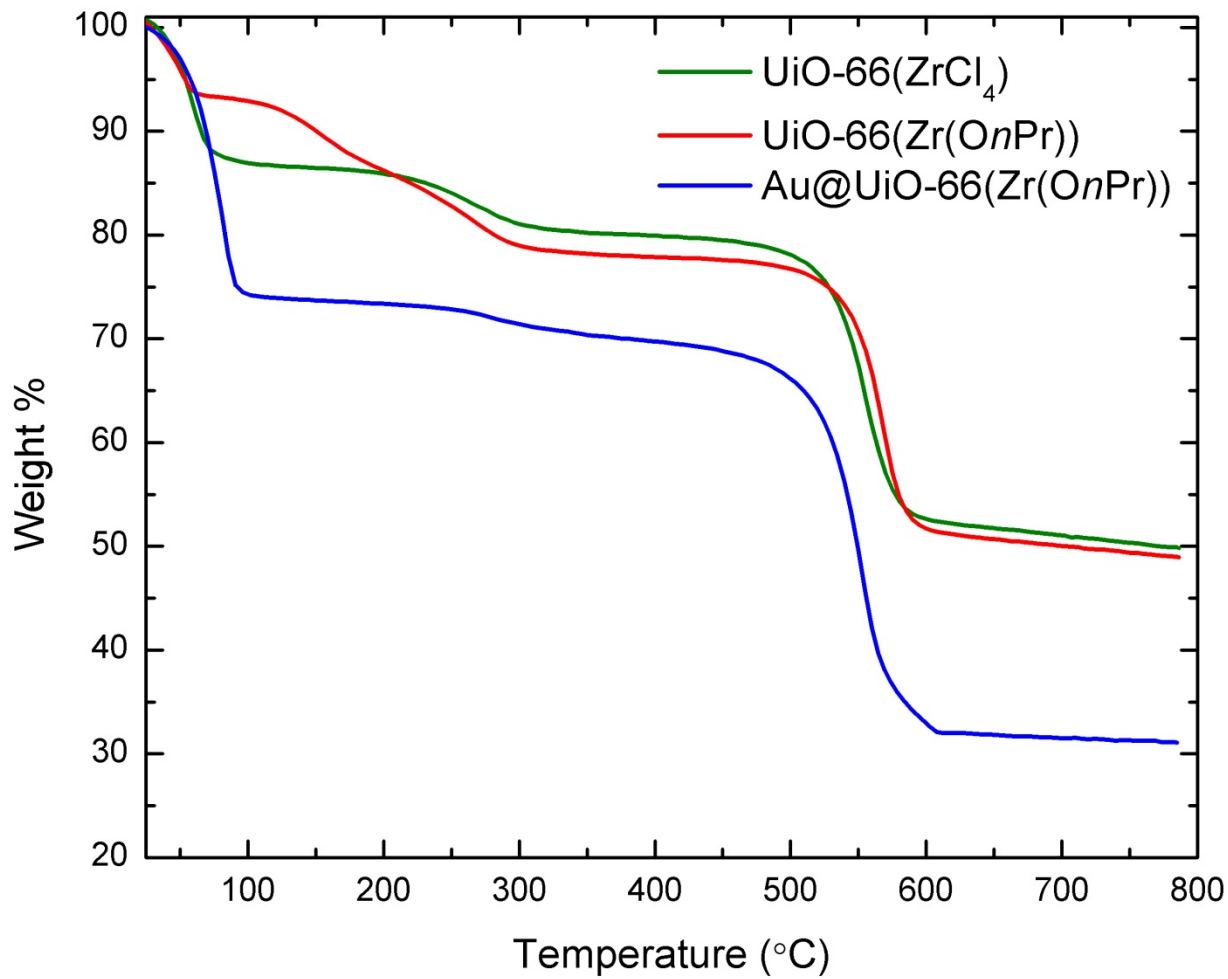


**Figure S1:** Images of AuNPs in UiO-66(ZrCl<sub>4</sub>) mother solution (a) initially and (b) after 2 min at 120°C



**Figure S2:** Images of (a) UiO-66(Zr(OnPr)) and (b) Au@UiO-66(Zr(OnPr))

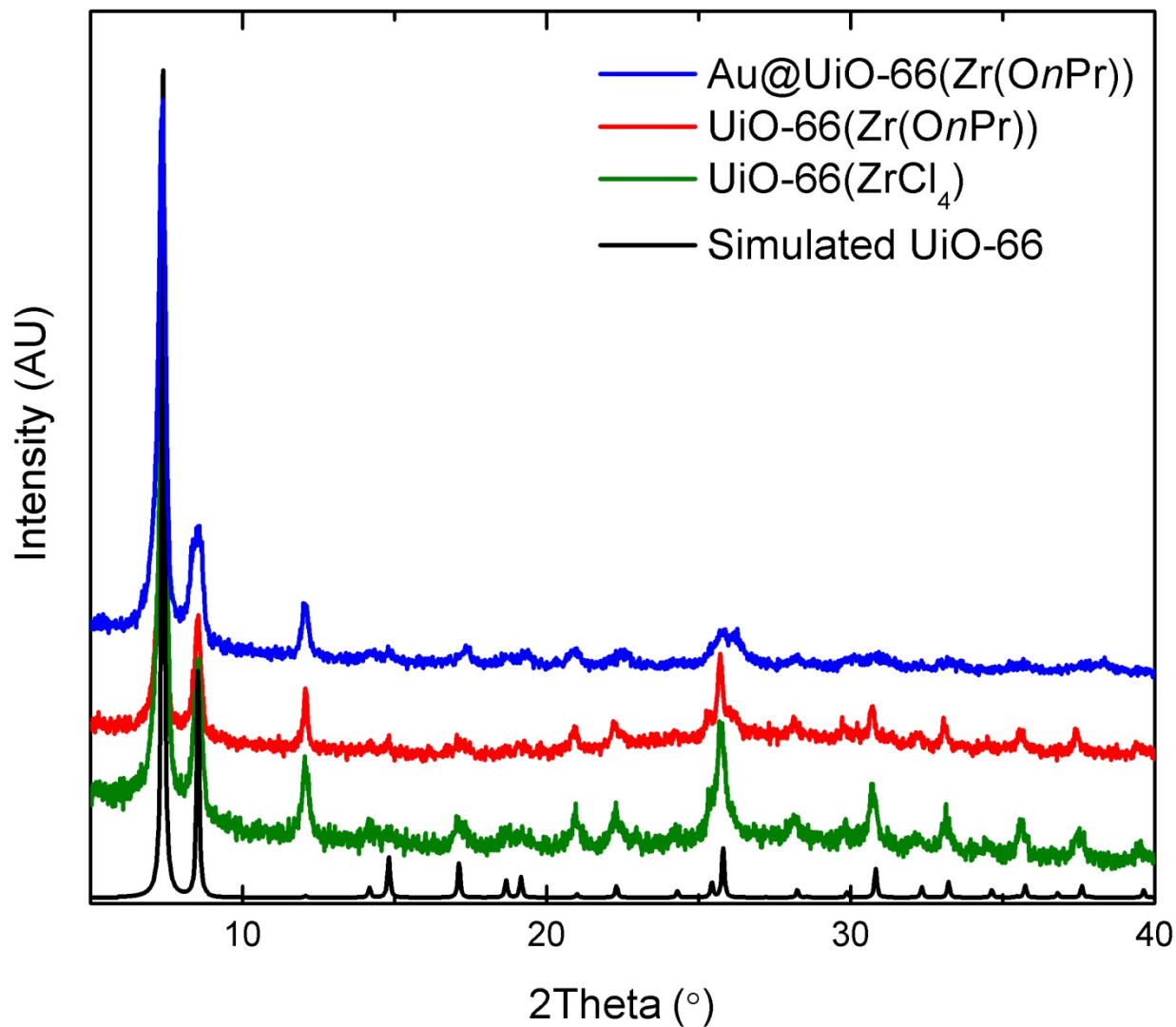
**2. Thermogravimetric Analysis (TGA):** TGA data is collected using the Netzsch STA 449 Jupiter Simultaneous TG-DSC apparatus. Approximately 10mg of material is placed in an  $\text{Al}_2\text{O}_3$  crucible and ramped at  $5^\circ\text{C}/\text{min}$  to  $800^\circ\text{C}$  under helium flow at  $20\text{cm}^3/\text{min}$ .



**Figure S3:** Thermal gravimetric analysis (TGA) of UiO-66(ZrCl<sub>4</sub>) (red), UiO-66(Zr(OnPr)) (green), and Au@UiO-66(Zr(OnPr)) (blue).

**3. Powder X-ray Diffraction (PXRD) Analysis:** Powder X-ray diffraction spectra are obtained using a PANalytical X-ray diffractometer. Approximately 5mg of sample is placed on a low background sample holder and scanned from 5-40°.

3.1. Water Stability



**Figure S4:** PXRD spectra of UiO-66(ZrCl<sub>4</sub>) (green), UiO-66(ZrOnPr) (red), and Au@UiO-66(Zr(OnPr)) (blue) after 24hrs of liquid H<sub>2</sub>O exposure.

3.2. Temperature, Solvent, and Time Variations

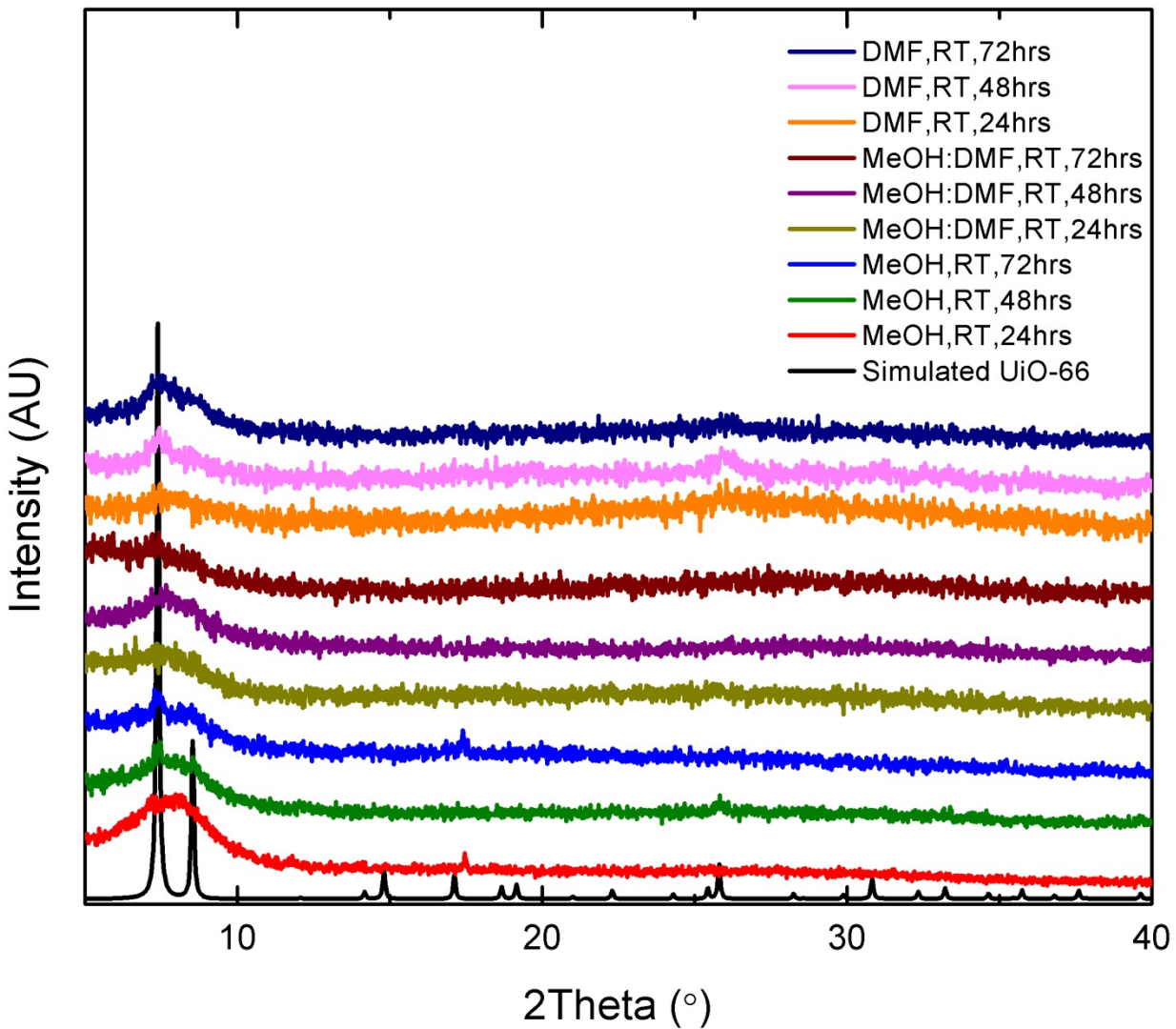


Figure S5: PXR D spectra of UiO-66(Zr(OnPr)) at room temperature with varying solvents and times.

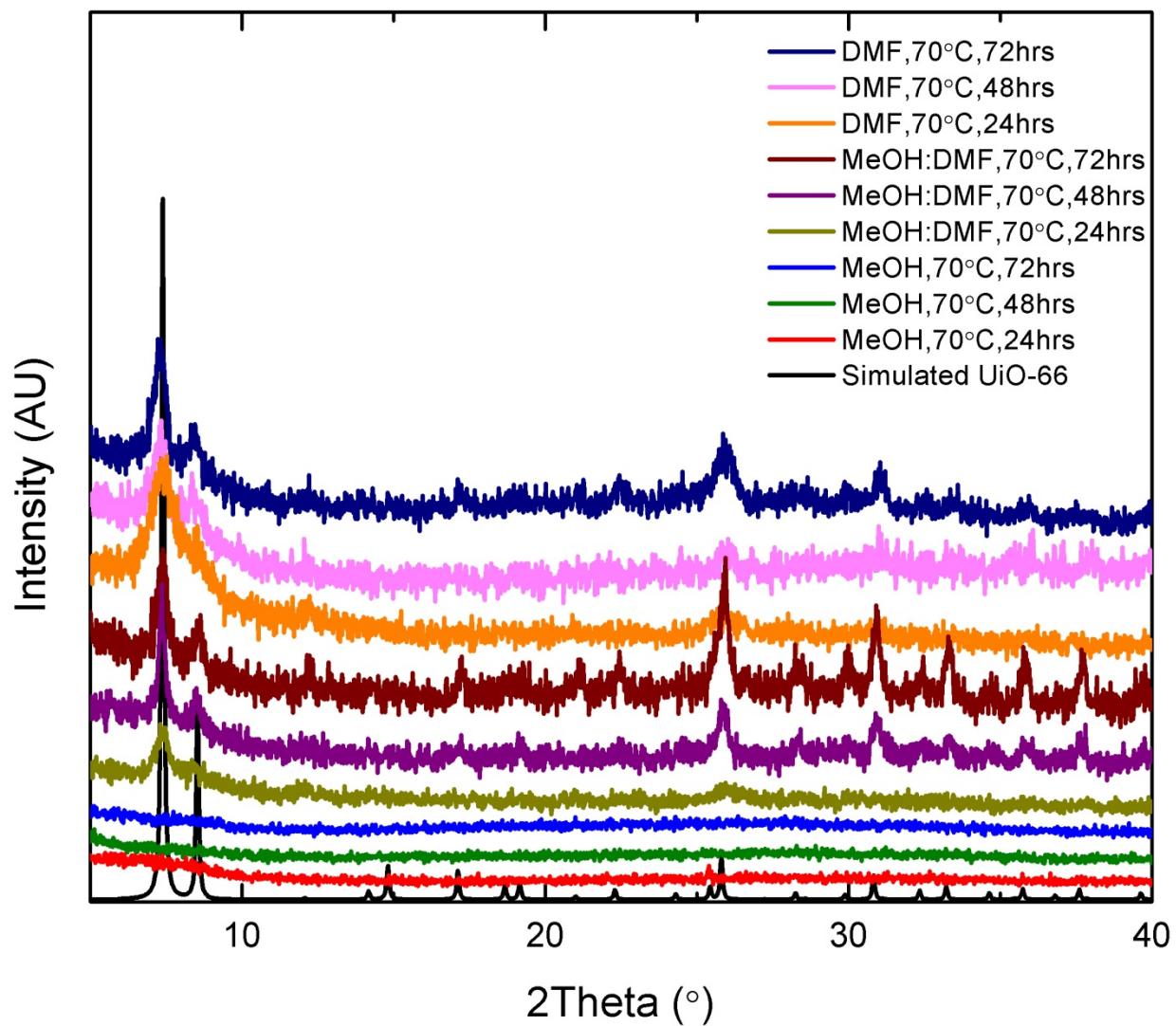
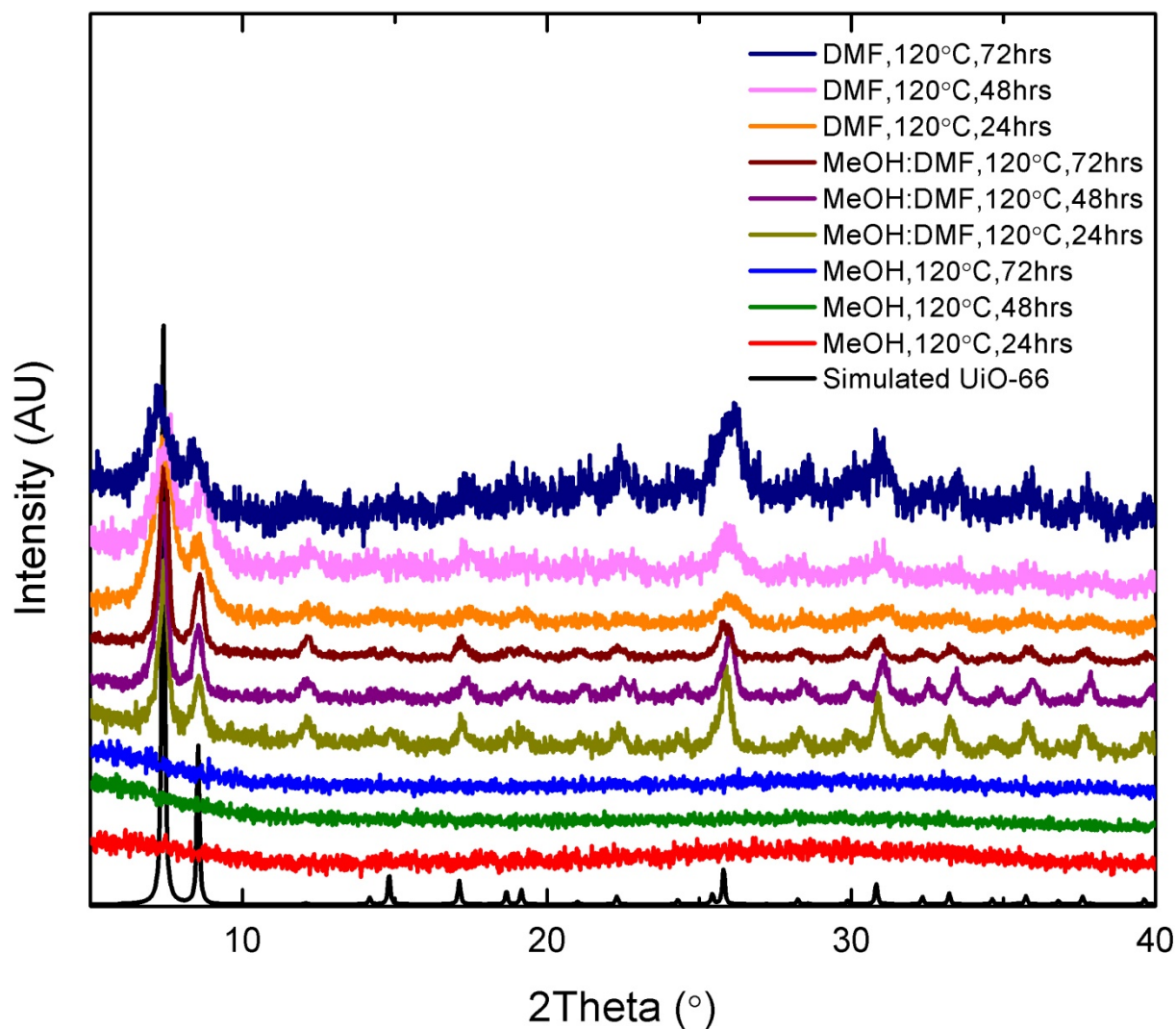


Figure S6: PXR D spectra of UiO-66(Zr(OnPr)) at 70°C with varying solvents and times.





**Figure S7:** PXRD spectra of UiO-66(Zr(OnPr)) at 120°C with varying solvents and times.

Figure S5 shows that UiO-66(Zr(OnPr)) crystals do not form at room temperature. Figure S6 and Figure S7 show that at 70°C and 120°C, crystals form in both DMF and a mixture of MeOH:DMF but not in pure methanol. Finally, Figure S7 shows that at 120°C the mixture of MeOH:DMF yields a more crystalline material.

3.3. Acetic Acid Effect

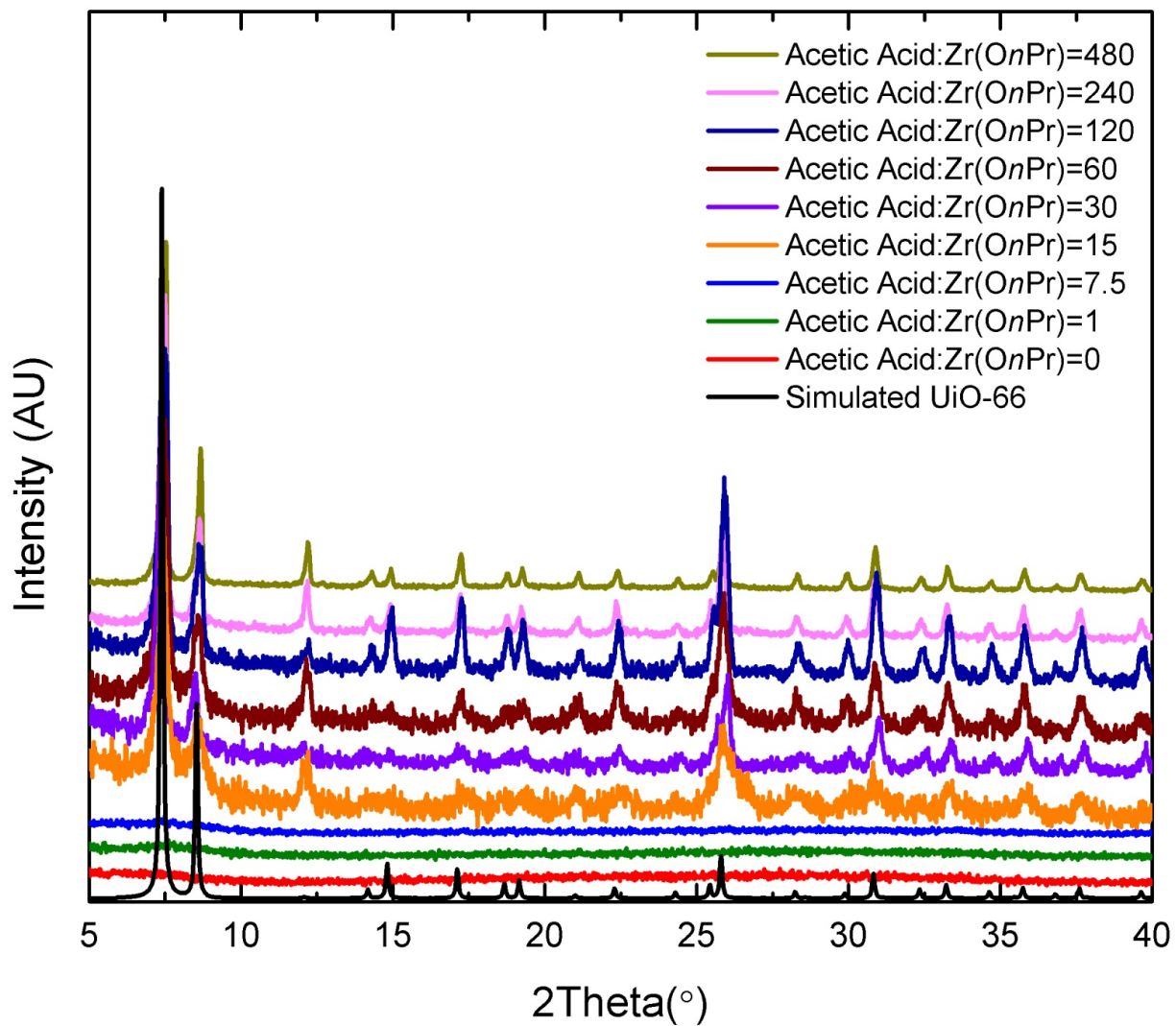
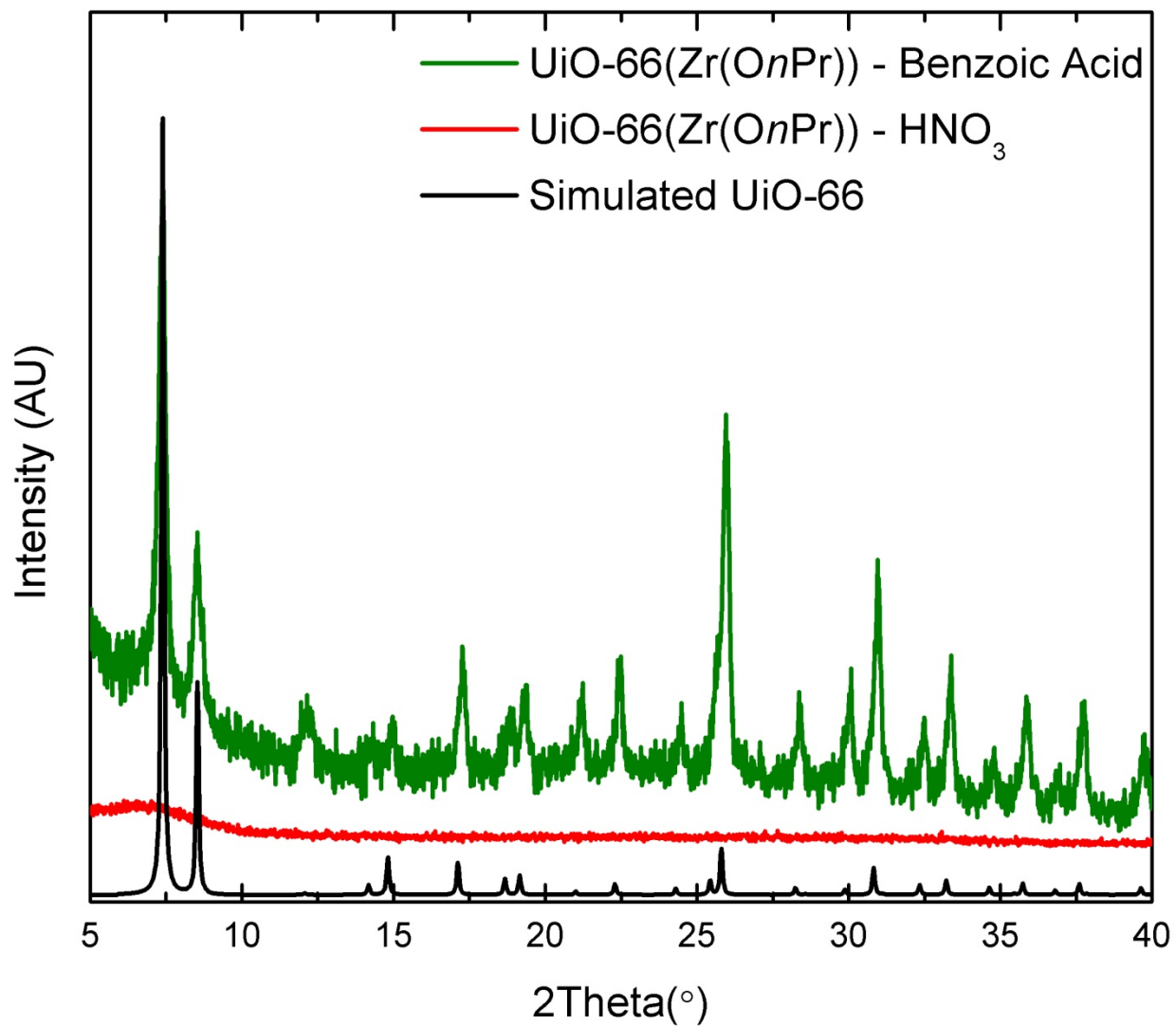


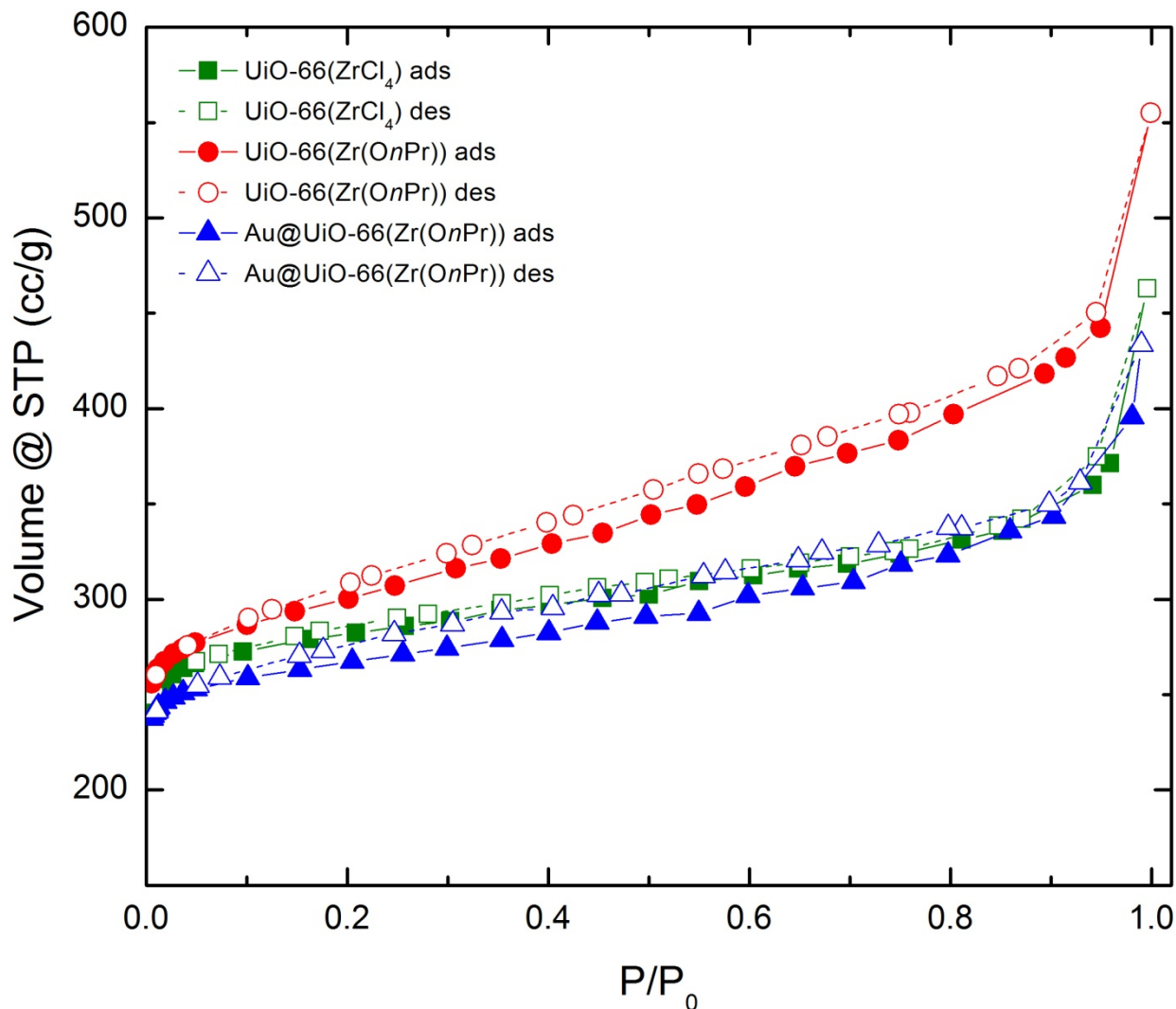
Figure S8: PXRD spectra of synthesis procedures with varying acetic acid:Zr(OnPr) ratios.



**Figure S9:** PXRD spectra when substituting acetic acid with nitric acid (red) and benzoic acid (green).

**4. Specific Surface Area Analysis:** Nitrogen sorption measurements at 77K are completed using a Quantachrome Quadrasorb SI volumetric analyzer. The isotherms are measured over a range of relative pressures from 0.003 to 0.990 using high purity nitrogen (99.998%) obtained from Airgas. Prior to the measurement, the samples are outgassed in a Quantachrome FloVac Degasser at 473K under dynamic vacuum for approximately 18 hours. The surface areas are calculated using the Brunauer, Emmett, and Teller (BET) theory using relative pressures ranging from 0.005-0.03 and the total pore volume is calculated at a relative pressure ( $P/P_0$ ) of 0.6.

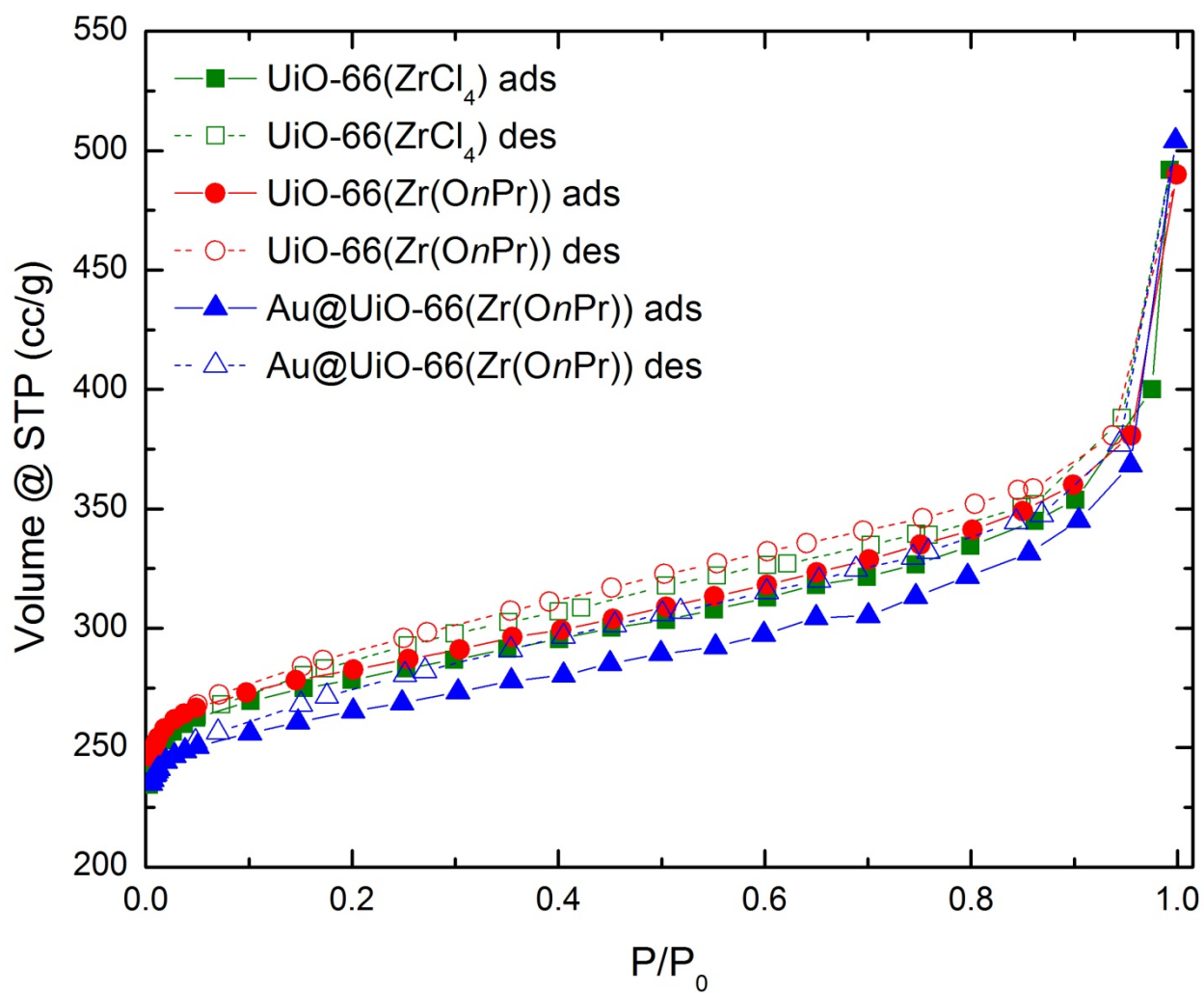
**4.1. UiO-66( $ZrCl_4$ ), UiO-66( $Zr(OnPr)$ ), and Au@UiO-66( $Zr(OnPr)$ )**



**Figure S10:** Nitrogen sorption isotherms at 77K of UiO-66( $ZrCl_4$ ) (squares), UiO-66( $Zr(OnPr)$ ) (circles), and Au@UiO-66( $Zr(OnPr)$ ) (triangles).

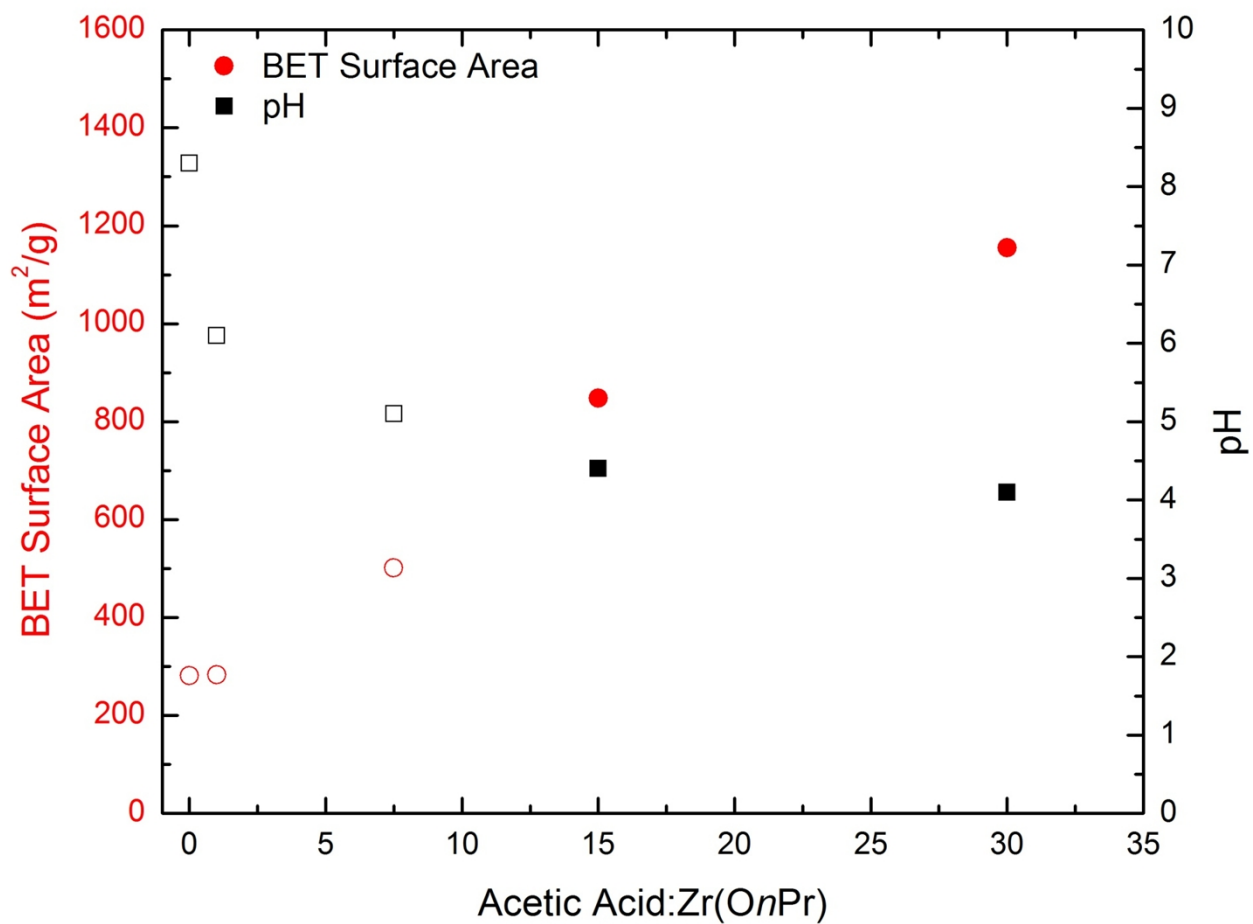
**Table S3:** BET surface areas after H<sub>2</sub>O Exposure

Sample	BET Surface Area Before H <sub>2</sub> O (m <sup>2</sup> /g)	BET Surface Area After H <sub>2</sub> O (m <sup>2</sup> /g)	% Loss
UiO-66(ZrCl <sub>4</sub> )	1118	1103	1.3
UiO-66(Zr(OnPr))	1160	1119	3.5
Au@UiO-66(Zr(OnPr))	1061	1050	1.0



**Figure S11:** Nitrogen sorption isotherms at 77K of UiO-66(ZrCl<sub>4</sub>) (squares), UiO-66(Zr(OnPr)) (circles), and Au@UiO-66(Zr(OnPr)) (triangles) after soaking in water for 24hrs.

#### 4.2. Acetic Acid Effect

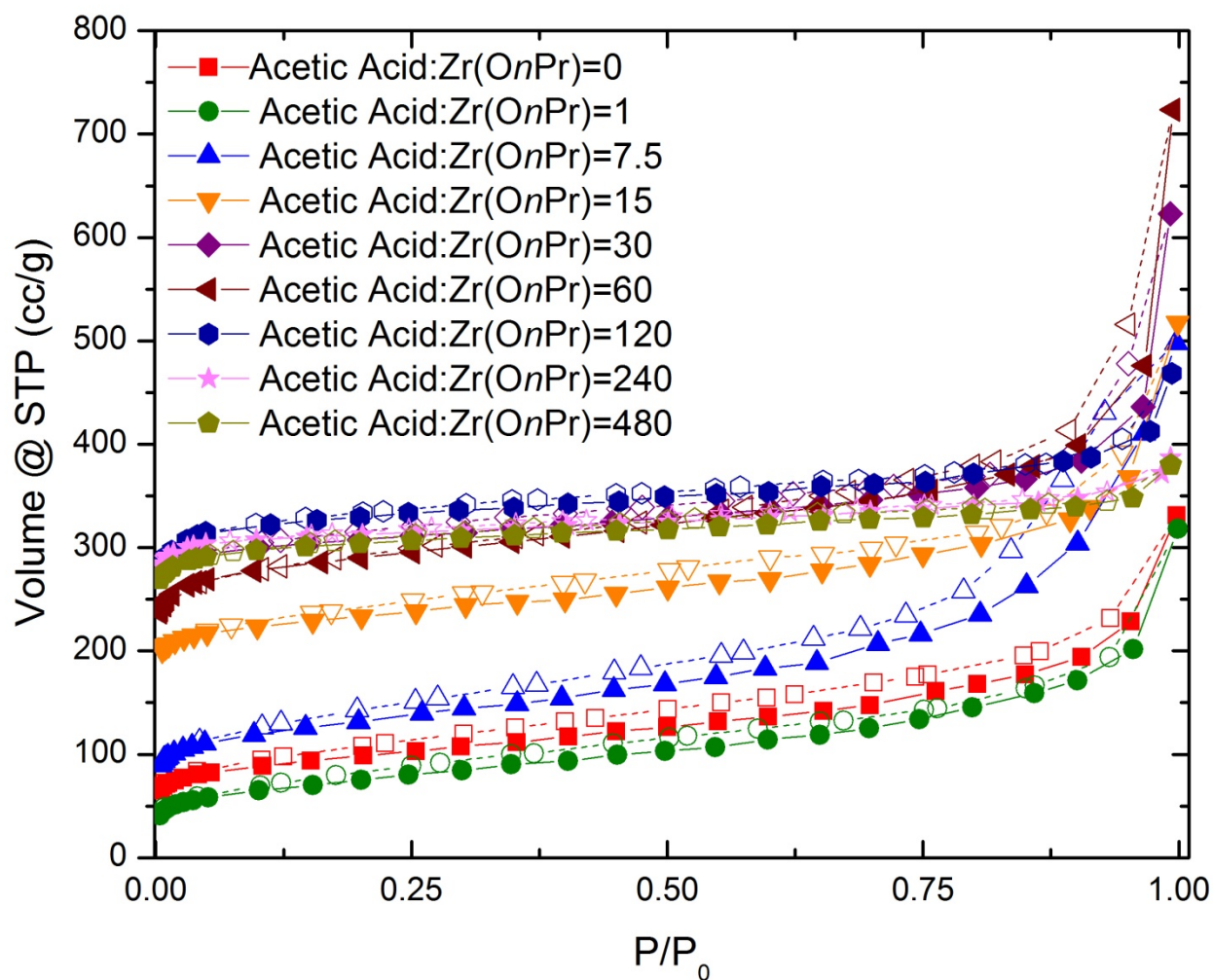


**Figure S12:** Relationship between acetic acid:Zr(OnPr) ratio, pH, and BET surface area at low acetic acid:Zr(OnPr) ratios. The closed points represent crystalline materials and the open points non-crystalline materials.

**Table S4:** BET surface areas for synthesis procedures with varying acetic acid:Zr(*On*Pr) ratios

Acetic Acid:Zr( <i>On</i> Pr) <sup>a</sup>	BET Surface Area (m <sup>2</sup> /g)	Total Pore Volume <sup>b</sup> (cm <sup>3</sup> /g)
0	281	0.19
1	282	0.19
7.5	501	0.31
15	848	0.42
30	1155	0.51
60	1189	0.52
120	1326	0.55
240	1289	0.52
480	1220	0.52

<sup>a</sup>Average of two samples; <sup>b</sup>Measured at P/P<sub>0</sub>=0.6

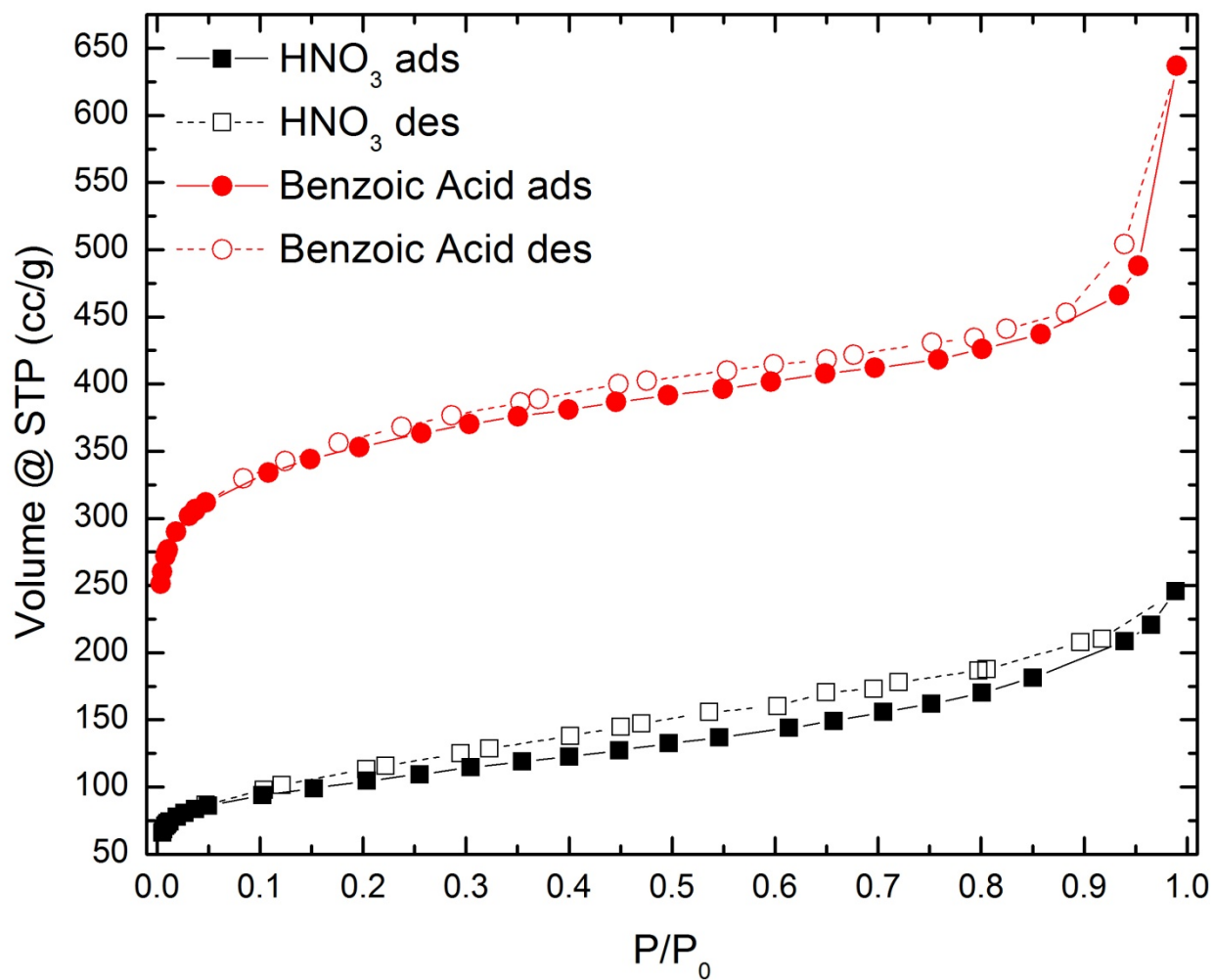


**Figure S13:** Nitrogen sorption at 77K isotherms of synthesis procedures with varying ratios of acetic acid:Zr(*On*Pr). Closed symbols are adsorption curves and open symbols are desorption curves.

**Table S5:** BET surface areas for synthesis procedures with substituted acids

Acid	BET Surface Area (m <sup>2</sup> /g)	Total Pore Volume <sup>a</sup> (cm <sup>3</sup> /g)
HNO <sub>3</sub>	358	0.22
Benzoic Acid	1307	0.62

<sup>a</sup>Measured at P/P<sub>0</sub>=0.6



**Figure S14:** Nitrogen sorption at 77K isotherms of UiO-66(Zr(OnPr)) when acetic acid is exchanged with HNO<sub>3</sub> (squares) and benzoic acid (red).



**5. Scanning Transmission Electron Microscopy-Energy Dispersive Spectroscopy (STEM-EDS):** STEM-EDS is run using the FEI Tecnai F30 operated at 300keV. EDS spectra are acquired using the Oxford EDX 6763. The composition is measured at a specified point marked with a red circle and analyzed using TEM Imaging & Analysis (TIA) Software. The TEM used in this work is supported by funding DMR 0922776.

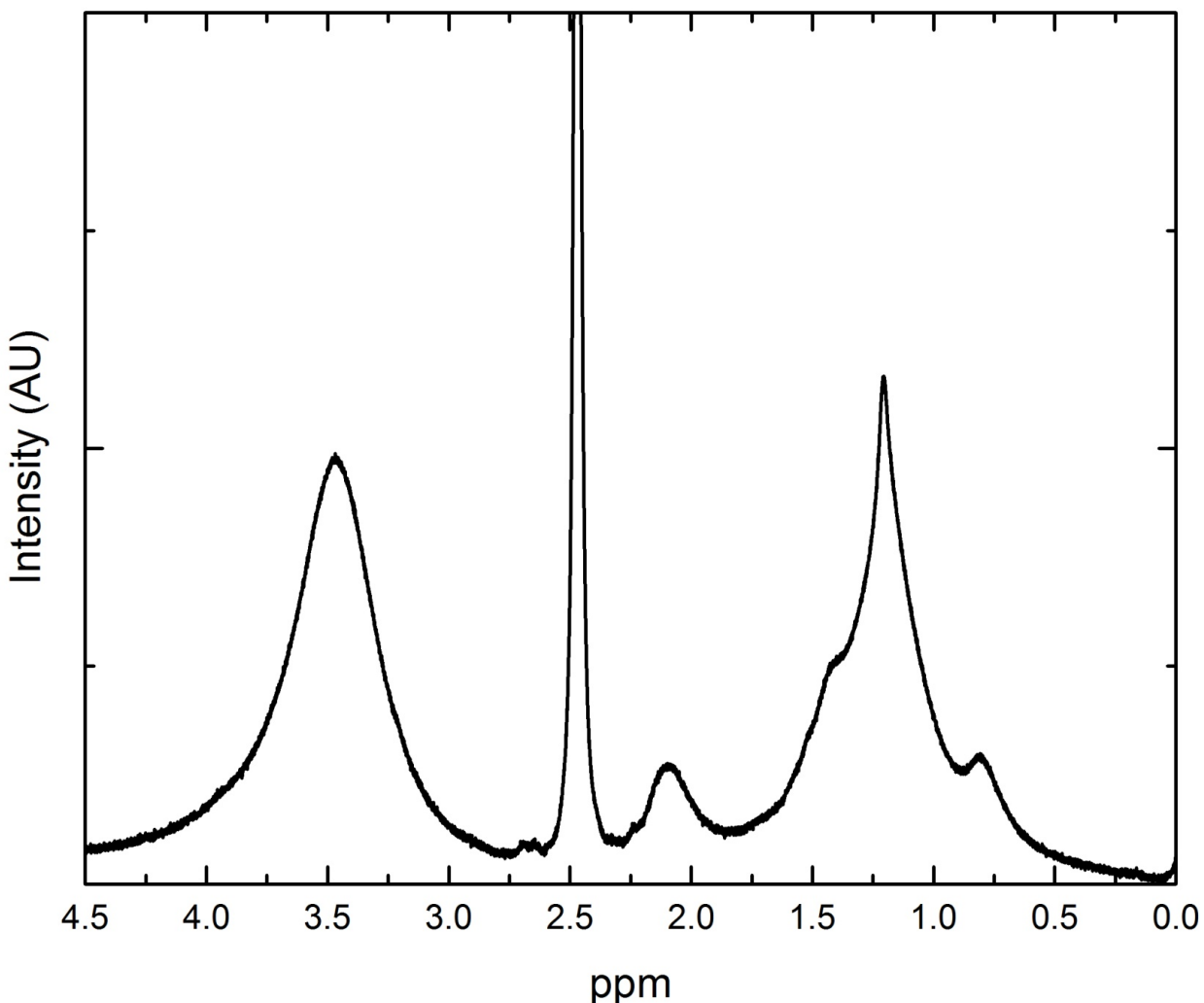
**Table S6:** EDS analysis of Au@UiO-66(Zr(OnPr))

<b>Element</b>	<b>Weight Percentage</b>
C(K)	39.95
O(K)	7.89
Cu(K)	11.03
Zr(K)	14.88
Au(L)	26.22

Table S6 shows the compositional makeup measured at the red dot on Figure 3b. The copper signal comes from the lacy carbon copper grid.

## 6. AuNP Analysis

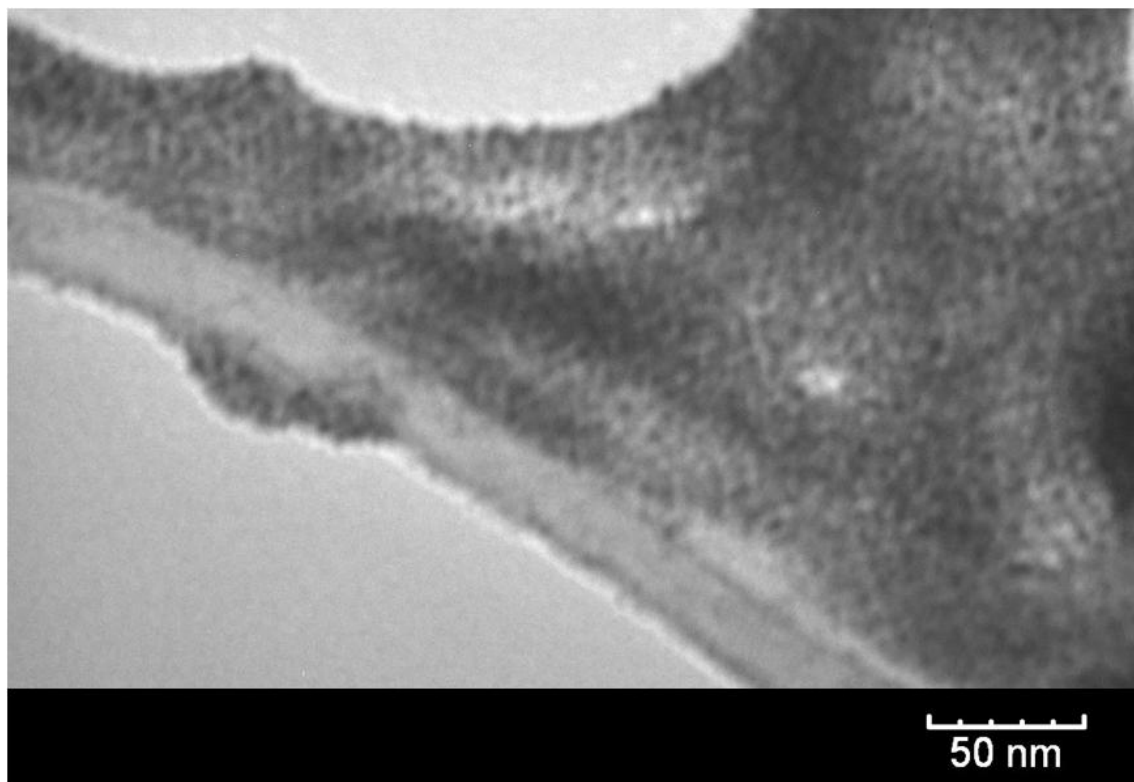
6.1. Proton Nuclear Magnetic Resonance ( $^1\text{H}$  NMR):  $^1\text{H}$  NMR is measured on a Varian Mercury Vx 300. The samples are prepared by suspending approximately 10mg of AuNPs in 1mL of dimethyl sulfoxide- $d_6$ .



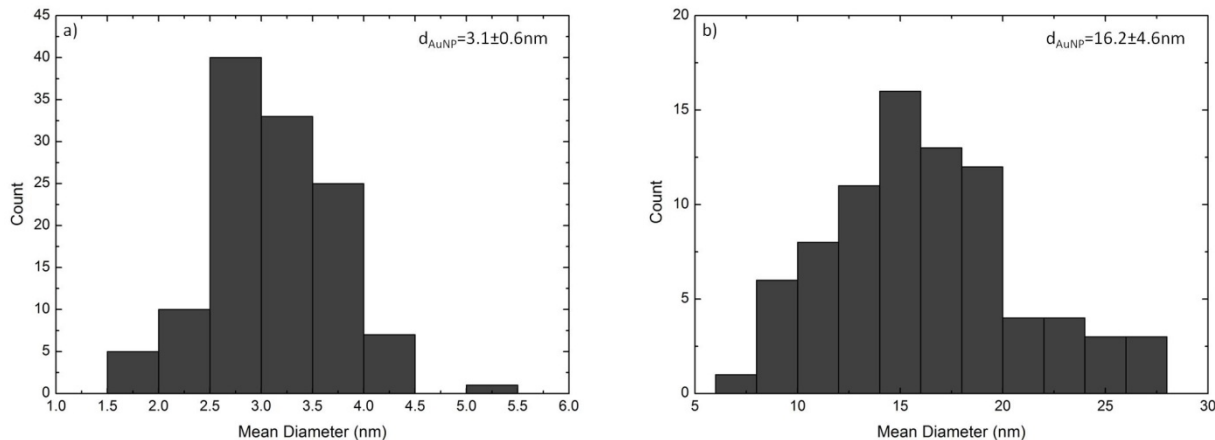
**Figure S15:**  $^1\text{H}$  NMR of AuNPs with a mixed monolayer of dodecanethiol and mercaptoundecanoic acid.

The broad peaks are characteristic of ligands bound to a surface. The  $T_2$  relaxation time accelerates when an organic is bound to a surface.<sup>4</sup> Therefore, the lack of coupling suggests that all of the ligands are bound to the AuNP surface. Additionally, the composition of the monolayer is confirmed by analyzing the characteristic peak positions. Dodecanethiol has a unique peak at 0.84ppm associated with  $-\text{CH}_3$  and 11-mercaptoundecanoic acid has a characteristic peak at 2.13ppm for  $-\text{CH}_2-\text{COOH}$ .

6.2. Transmission Electron Microscopy (TEM): The AuNPs are analyzed using the JEOL 100CX operated at 100keV. The samples are prepared by suspending a small sample in solution and drop-casting onto a lacy carbon coated copper grid. The average nanoparticle diameter was calculated from 121 nanoparticles from eight different sample spots.



**Figure S16:** TEM of as-synthesized AuNPs with a mixed monolayer of dodecanethiol and mercaptoundecanoic acid.



**Figure S17:** Mean diameter histograms of (a) as-synthesized AuNPs and (b) AuNPs after UiO-66(Zr(OnPr)) synthesis.

1. J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *Journal of the American Chemical Society*, 2008, **130**, 13850-13851.

2. M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *Journal of the Chemical Society-Chemical Communications*, 1994, 801-802.
3. M. J. Hostetler, A. C. Templeton and R. W. Murray, *Langmuir*, 1999, **15**, 3782-3789.
4. M. J. Hostetler, J. E. Wingate, C. J. Zhong, J. E. Harris, R. W. Vachet, M. R. Clark, J. D. Londono, S. J. Green, J. J. Stokes, G. D. Wignall, G. L. Glish, M. D. Porter, N. D. Evans and R. W. Murray, *Langmuir*, 1998, **14**, 17-30.