

Post-synthetic modification of zirconium metal-organic frameworks by catalyst-free aza-Michael additions

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1. General experimental details

All reagents and solvents were purchased from commercial sources and used without further purification.

Powder X-ray diffraction (PXRD) patterns for all samples were recorded on a Bruker AXS D8 Advance diffractometer with copper K_{α} radiation ($\lambda = 1.5406 \text{ \AA}$) at 298 K. The beam slit was set to 1 mm, detector slit set to 0.2 mm and anti-scattering slit set to 1 mm. Samples were dried in ambient conditions and ground using a pestle and mortar. The powders were packed onto a flat plate and measured with a 2θ range of $5 - 60^{\circ}$. The step size was 0.024° with the scan speed set to 0.3 s per step.

^1H NMR spectra were recorded on the digested MOFs at 298 K on a Bruker Avance 300 MHz Ultrashield NMR spectrometer. All ^1H NMR spectra were referenced to the residual *protio* peaks at δ 2.50 ppm for $\text{DMSO-}d_6$. Samples were dried at 100°C for 15 minutes prior to digestion. A typical MOF digestion was carried out by adding 10 mg of a crystalline sample into 0.4 mL of $\text{DMSO-}d_6$ and 0.2 mL of a stock solution of NH_4F in D_2O (4.14 M). The mixture was sonicated until the solid had completely dissolved. In some cases, a trace amount of white solid precipitated out of the solution. This was removed by filtration prior to ^1H NMR analysis.

Mass spectra was recorded on $\text{NH}_4\text{F}/\text{H}_2\text{O}$ -digested MOF solutions diluted in EtOH, using a Bruker microTOF electrospray ionisation time-of-flight (ESI-TOF) mass spectrometer. FTIR spectra were recorded on solid samples mounted on a diamond/gem platform using a PerkinElmer Spectrum 100 spectrometer. Thermogravimetric analyses were carried out on the solid samples using a Setaram Setsys Evolution 16/18 thermogravimetric analyser. The samples were heated from 30°C to 600°C at a rate of 20 K/min under a flow of argon gas (20 mL/min).

Gas sorption measurements were carried out on MeOH-rinsed samples. In a typical measurement, approximately 20 mg the sample was transferred into a pre-weighed sample tube. The sample was then heated at 120°C for 12 hours on a BELSORP Mini-II (BEL Japan) gas sorption analyser. The sample tube was re-weighed to obtain a consistent mass of the activated sample prior to the gas adsorption measurement. To determine the specific surface area, the N_2 sorption isotherm was recorded at 77 K, with the temperature kept constant using a liquid nitrogen bath. The specific surface area was calculated based on the Brunauer-Emmett-Teller (BET) method in the p/p_0 range of 0.05 – 0.10. CO_2 and N_2 adsorption isotherms were also recorded at 273 K.

2. Synthesis of UiO-66-NH₂

The synthesis was modified from a procedure reported by Garibay and Cohen.^{S1} In a typical reaction, H₂bdc-NH₂ (190 mg, 1.05 mmol), ZrCl₄ (243 mg, 1.05 mmol) and DMF (12 mL) were loaded into a Teflon-lined autoclave. The solution was stirred until the reactants had completely dissolved. The autoclave was placed in an oven and heated at 120 °C for 24 h. After cooling to room temperature, the resulting yellow powder was rinsed and intermittently centrifuged with MeOH (6000 rpm for 15 min) to remove unreacted H₂bdc-NH₂ and residual DMF from the pores. The washing procedure was repeated over 3 days with the solvent replaced every 24 h. Finally, the UiO-66-NH₂ powder was dried under vacuum at 120 °C for 12 h. Prior to post-synthetic modification reactions, UiO-66-NH₂ was washed with H₂O by centrifugation over 3 days with the solvent replaced every 24 h. The powder was then left to dry under ambient conditions.

3. Synthesis of UiO-66-AN, 1

UiO-66-NH₂ (117 mg, ca. 0.4 mmol eq. of NH₂) and acrylonitrile (0.10 mL, 1.6 mmol, 4 eq.) were added to a Teflon-lined autoclave containing 7 mL H₂O. The autoclave was sealed and heated at 120 °C for 48 h. Upon cooling to ambient temperature, the autoclave was opened and the resulting yellow powder was rinsed and intermittently centrifuged with H₂O. The washing procedure was repeated over 3 days with the solvent replaced every 24 h. The product was left to dry under ambient conditions. The ¹H NMR spectrum of digested UiO-66-AN is shown in Figure S1 and the FTIR spectrum of UiO-66-AN is shown in Figure S2. The PXRD pattern for UiO-66-AN is shown in Figure S3 in comparison with simulated and experimental patterns for UiO-66-NH₂.

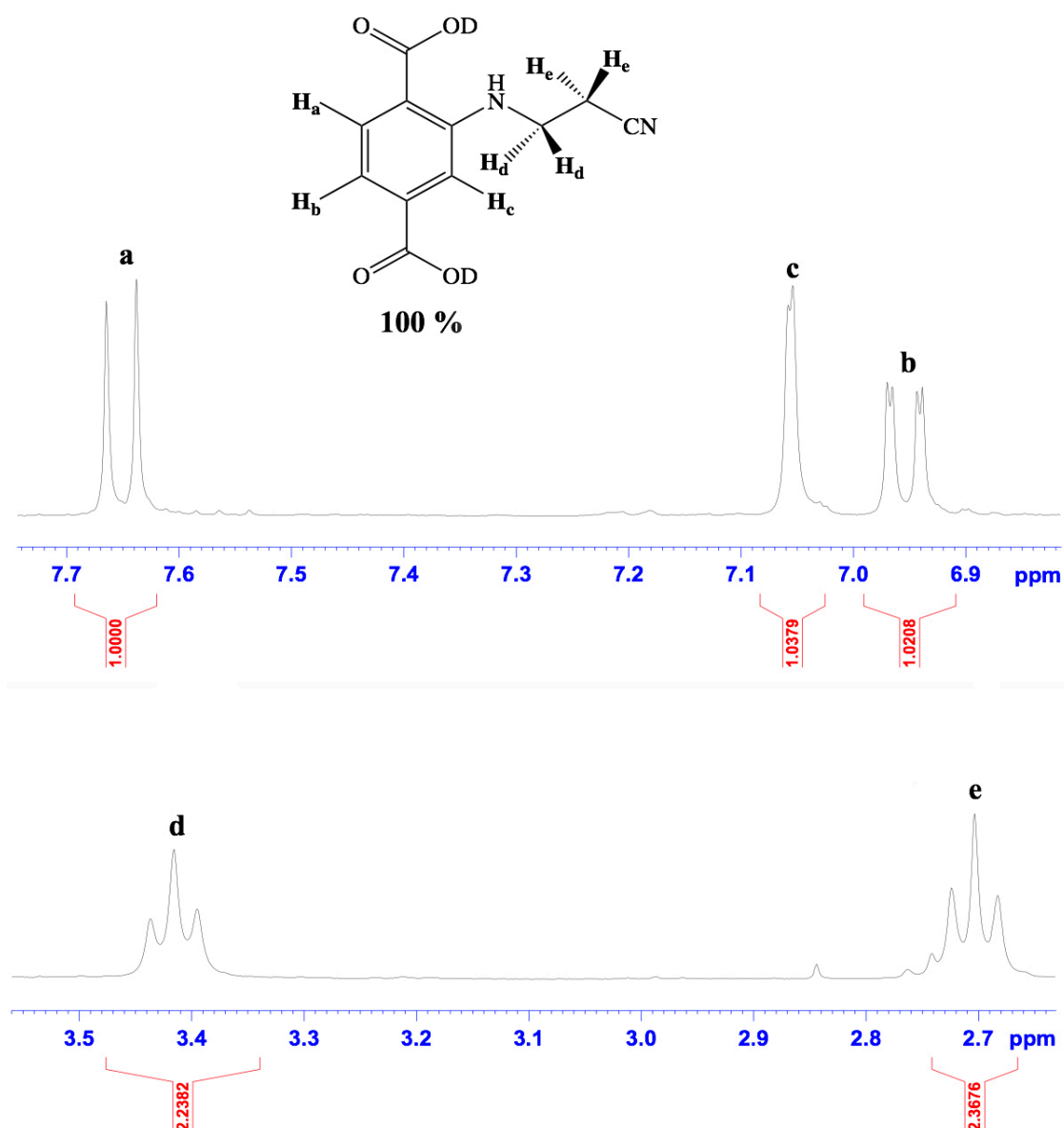


Figure S1. The ¹H NMR spectrum of UiO-66-AN **1** following digestion in NH₄F/D₂O and DMSO-*d*₆ showing the aromatic and aliphatic regions.

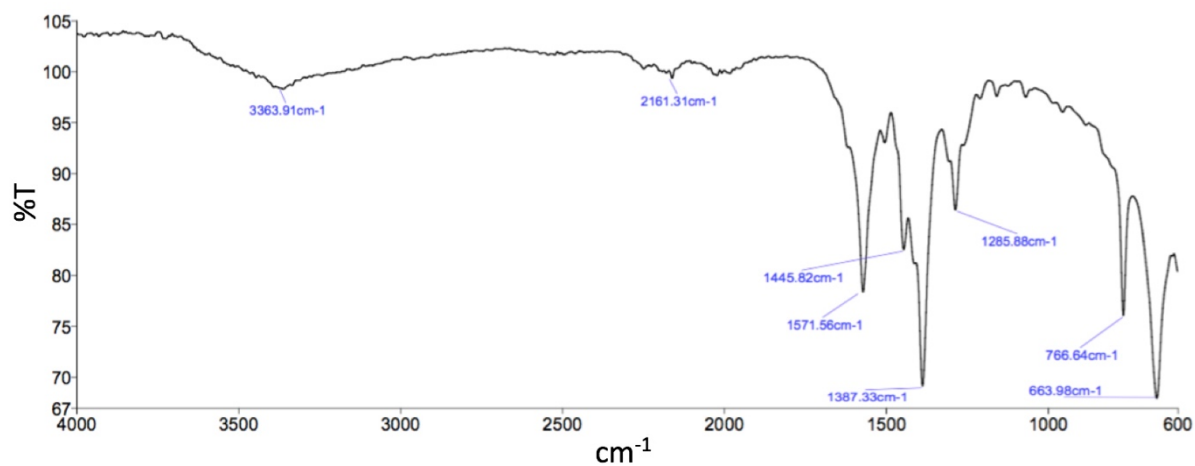


Figure S2. The FT-IR spectrum of UiO-66-AN **1**.

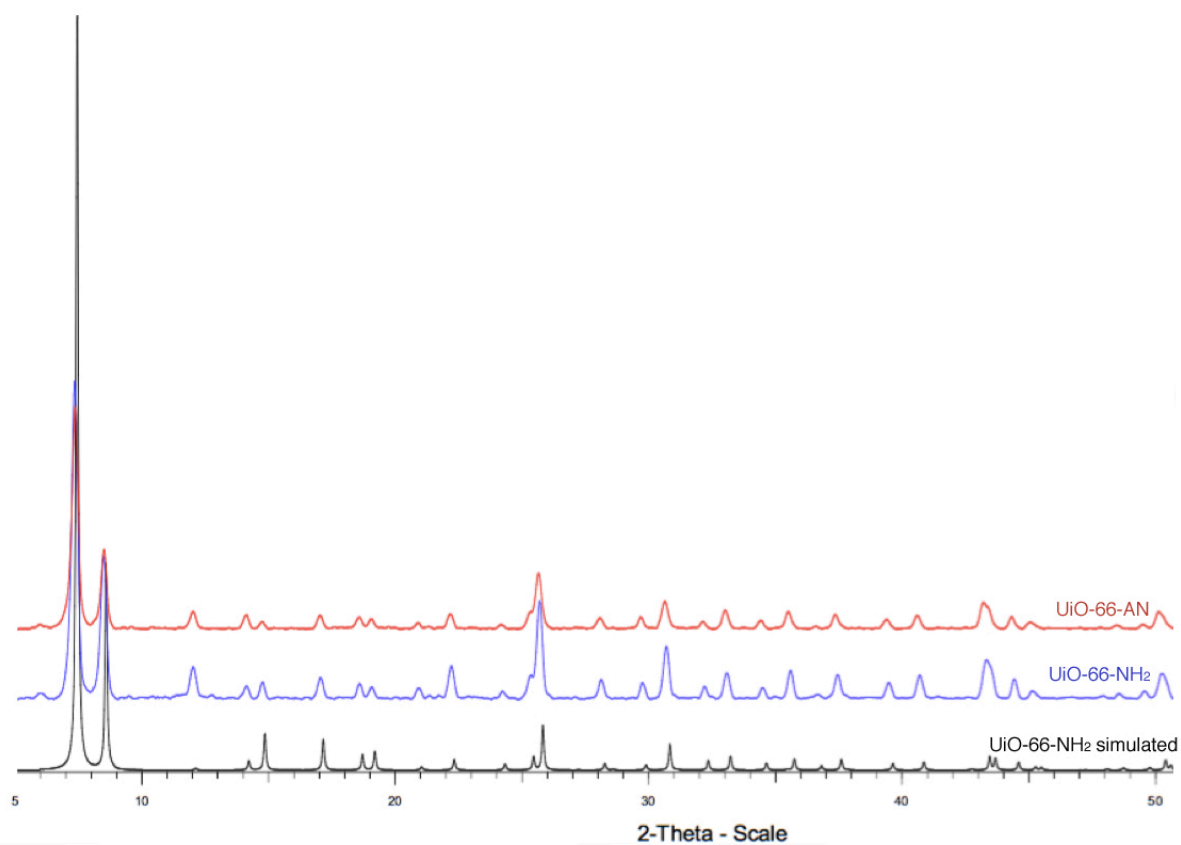


Figure S3. The PXRD pattern for UiO-66-AN **1** in comparison with simulated and experimental PXRD patterns for UiO-66-NH₂.

4. Synthesis of UiO-66-AA, 2

UiO-66-NH₂ (117 mg, ca. 0.4 mmol eq. of NH₂) and acrylic acid (0.11 mL, 1.6 mmol, 4 eq.) were added to a Teflon-lined autoclave containing 7 mL H₂O. The autoclave was sealed and heated at 120 °C for 48 h. Upon cooling to ambient temperature, the autoclave was opened and the resulting brown powder was rinsed and intermittently centrifuged with H₂O. The washing procedure was repeated over 3 days with the solvent replaced every 24 h. The product was left to dry under ambient conditions. The ¹H NMR spectrum of digested UiO-66-AA is shown in Figure S4 and the PXRD pattern for UiO-66-AN is shown in Figure S5 in comparison with the experimental pattern for UiO-66-NH₂.

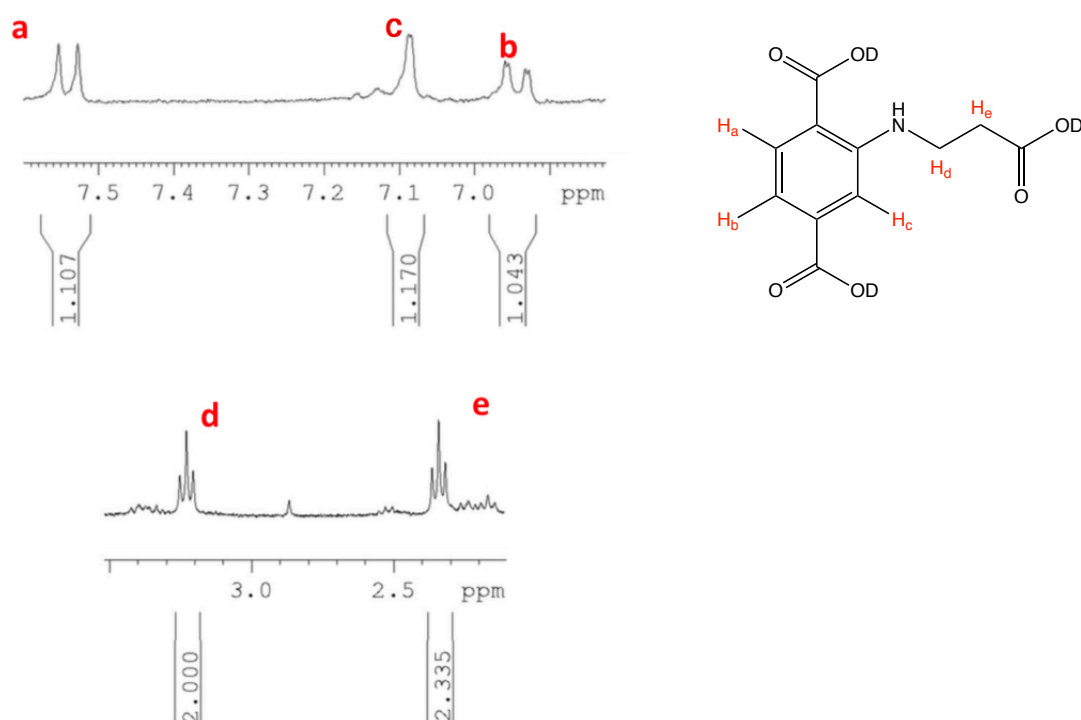


Figure S4. The ¹H NMR spectrum of UiO-66-AA 2 following digestion in NH₄F/D₂O and DMSO-*d*₆ showing the aromatic and aliphatic regions.

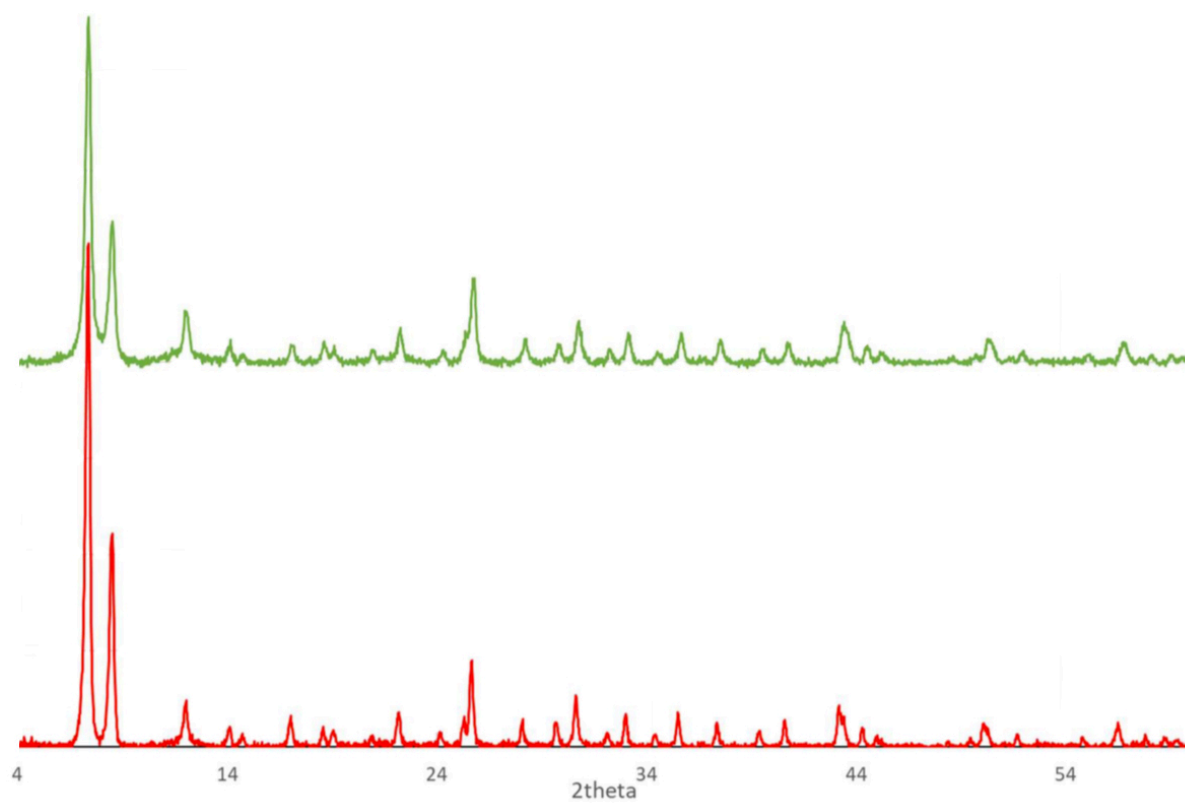


Figure S5. The PXRD pattern for UiO-66-AA **2** (green) in comparison with the experimental PXRD pattern for UiO-66-NH₂ (red).

5. Synthesis of UiO-66-MA, 3

UiO-66-NH₂ (117 mg, ca. 0.4 mmol eq. of NH₂) and methyl acrylate (0.14 mL, 1.6 mmol, 4 eq.) were added to a Teflon-lined autoclave containing 7 mL H₂O. The autoclave was sealed and heated at 120 °C for 48 h. Upon cooling to ambient temperature, the autoclave was opened and the resulting yellow powder was rinsed and intermittently centrifuged with H₂O. The washing procedure was repeated over 3 days with the solvent replaced every 24 h. The product was left to dry under ambient conditions. The ¹H NMR spectrum of digested UiO-66-MA is shown in Figure S6 and the FTIR spectrum of UiO-66-MA is shown in Figure S7. The PXRD pattern for UiO-66-MA is shown in Figure S8 in comparison with simulated and experimental patterns for UiO-66-NH₂.

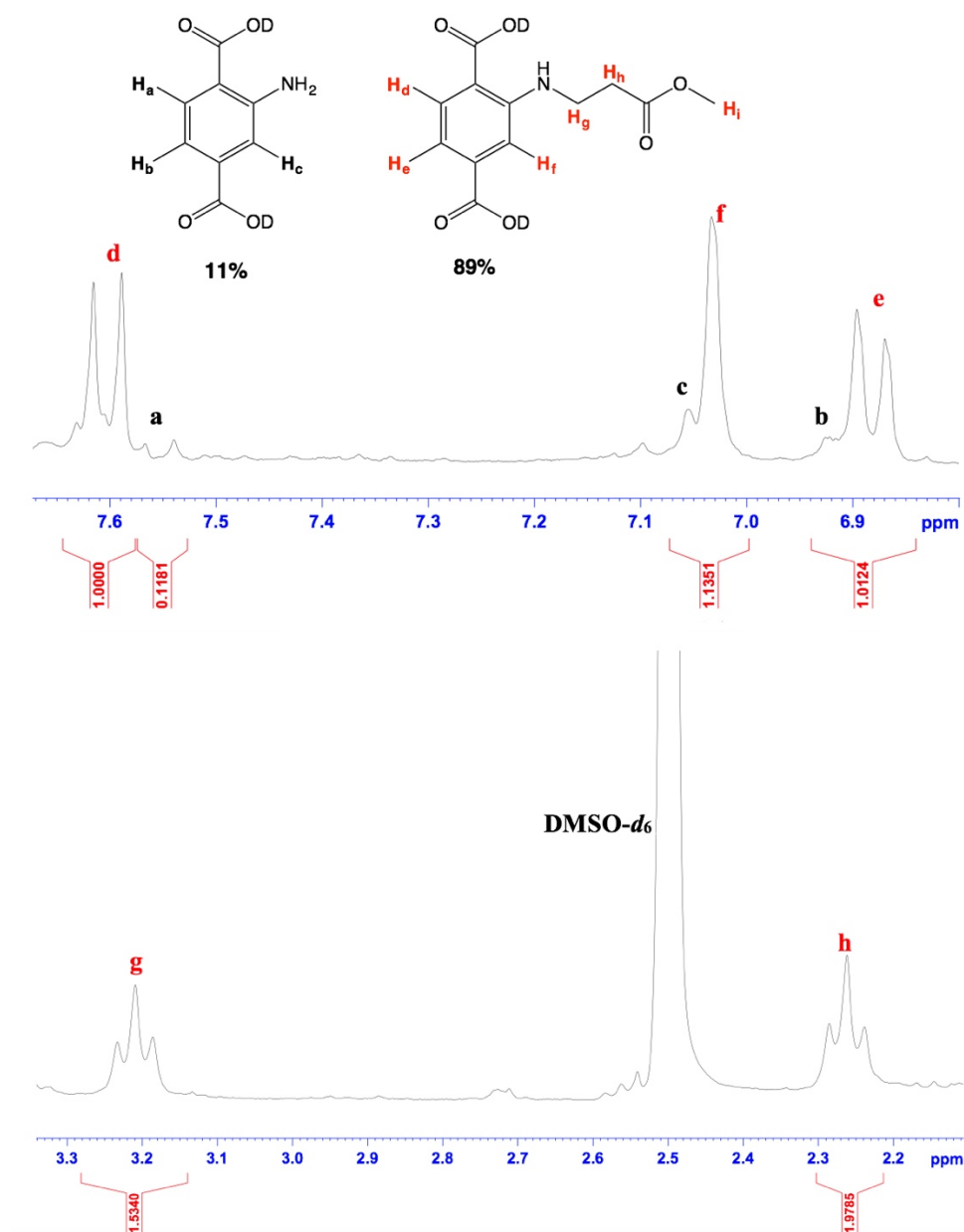


Figure S6. The ¹H NMR spectrum of UiO-66-MA **3** following digestion in NH₄F/D₂O and DMSO-*d*₆ showing the aromatic and aliphatic regions.

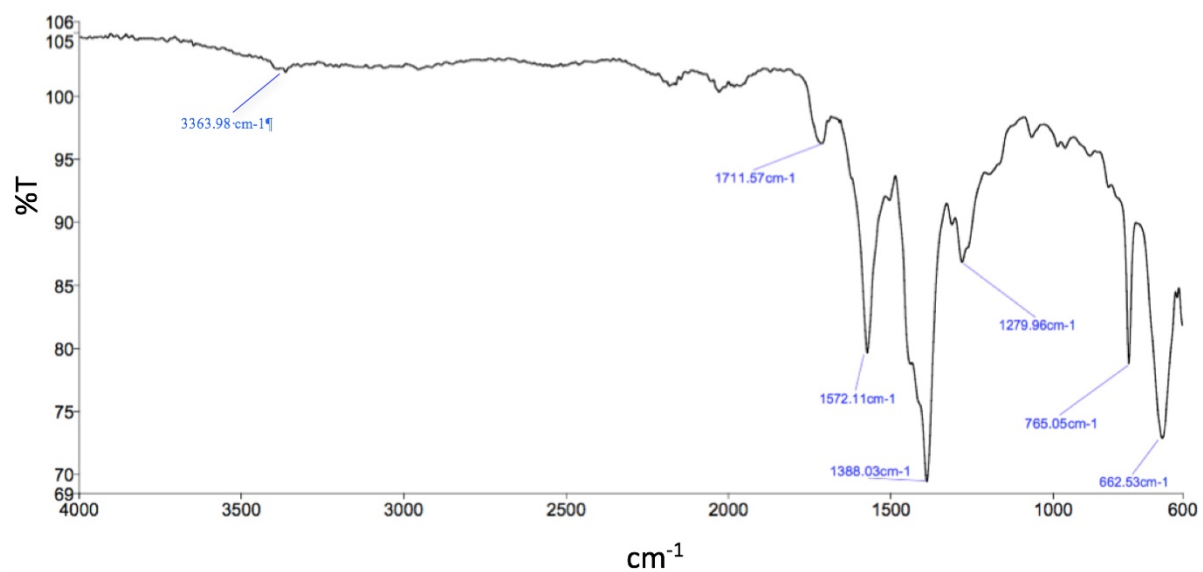


Figure S7. The FT-IR spectrum of UiO-66-MA **3**.

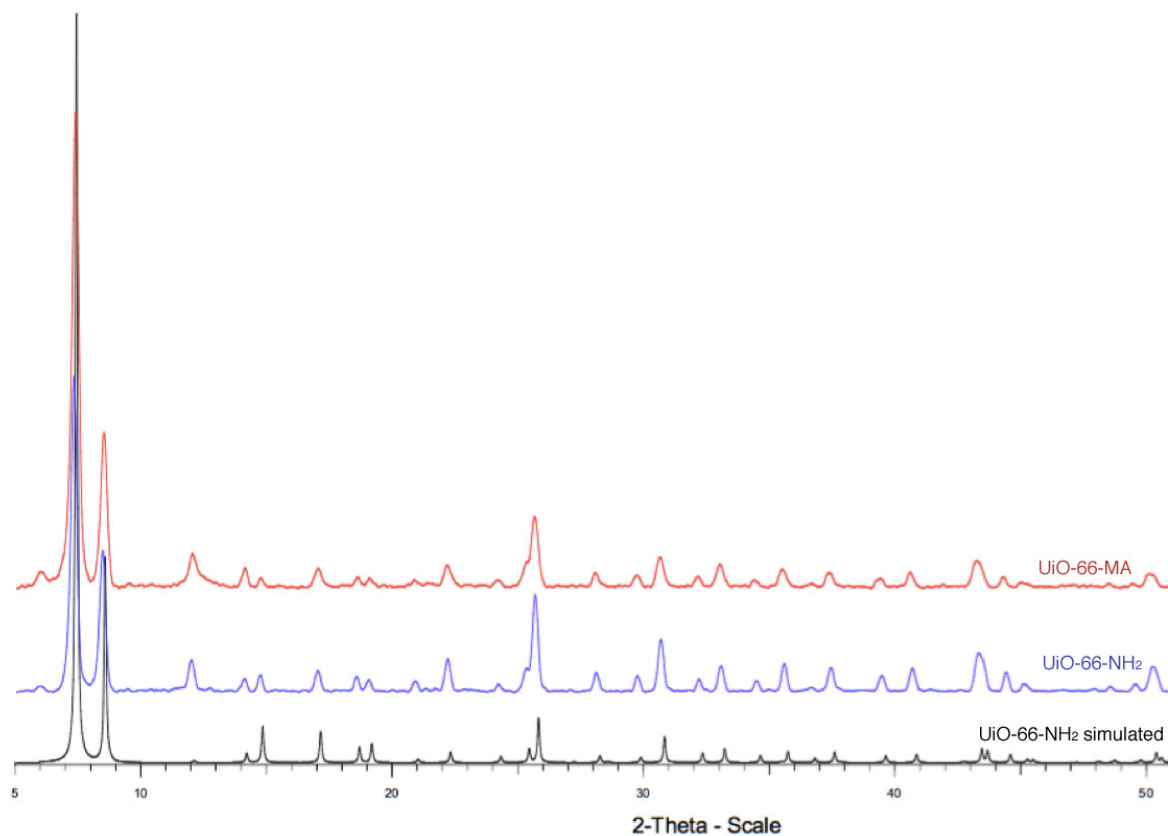


Figure S8. The PXRD pattern for UiO-66-MA **3** in comparison with simulated and experimental PXRD patterns for UiO-66-NH₂.

6. Synthesis of UiO-66-MVK, 4

UiO-66-NH₂ (117 mg, ca. 0.4 mmol eq. of NH₂) and methyl vinyl ketone (0.13 mL, 1.6 mmol, 4 eq.) were added to a Teflon-lined autoclave containing 7 mL H₂O. The autoclave was sealed and heated at 120 °C for 48 h. Upon cooling to ambient temperature, the autoclave was opened and the resulting yellow powder was rinsed and intermittently centrifuged with H₂O. The washing procedure was repeated over 3 days with the solvent replaced every 24 h. The PSM product was left to dry under ambient conditions. The ¹H NMR spectrum of digested UiO-66-MVK is shown in Figure S9 and the FTIR spectrum of UiO-66-MVK is shown in Figure S10. The PXRD pattern for UiO-66-MVK is shown in Figure S11 in comparison with simulated and experimental patterns for UiO-66-NH₂.

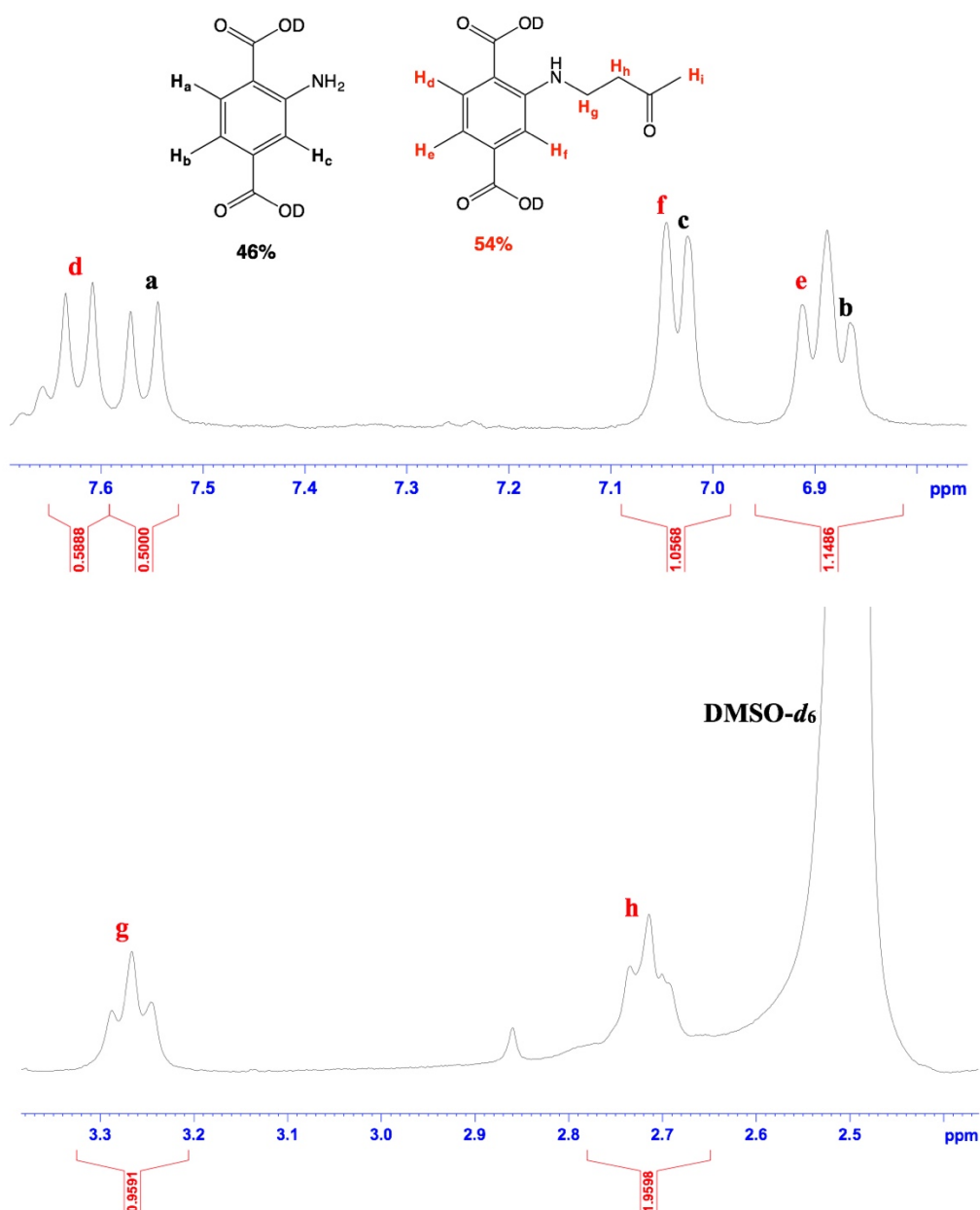


Figure S9. The ¹H NMR spectrum of UiO-66-MVK 4 following digestion in NH₄F/D₂O and DMSO-*d*₆ showing the aromatic and aliphatic regions.

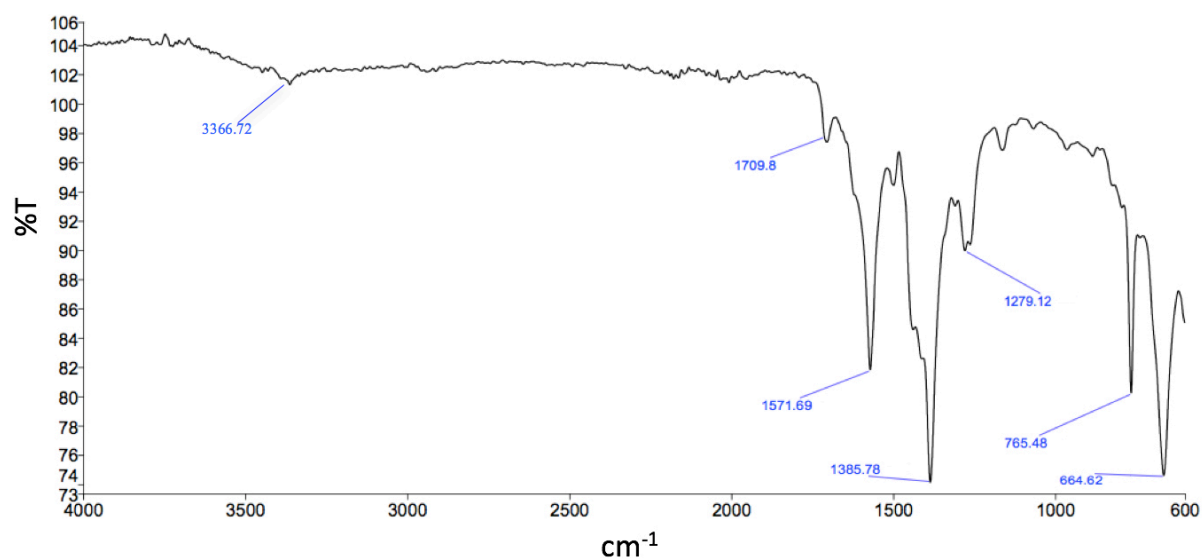


Figure S10. The FT-IR spectrum of UiO-66-MVK **4**.

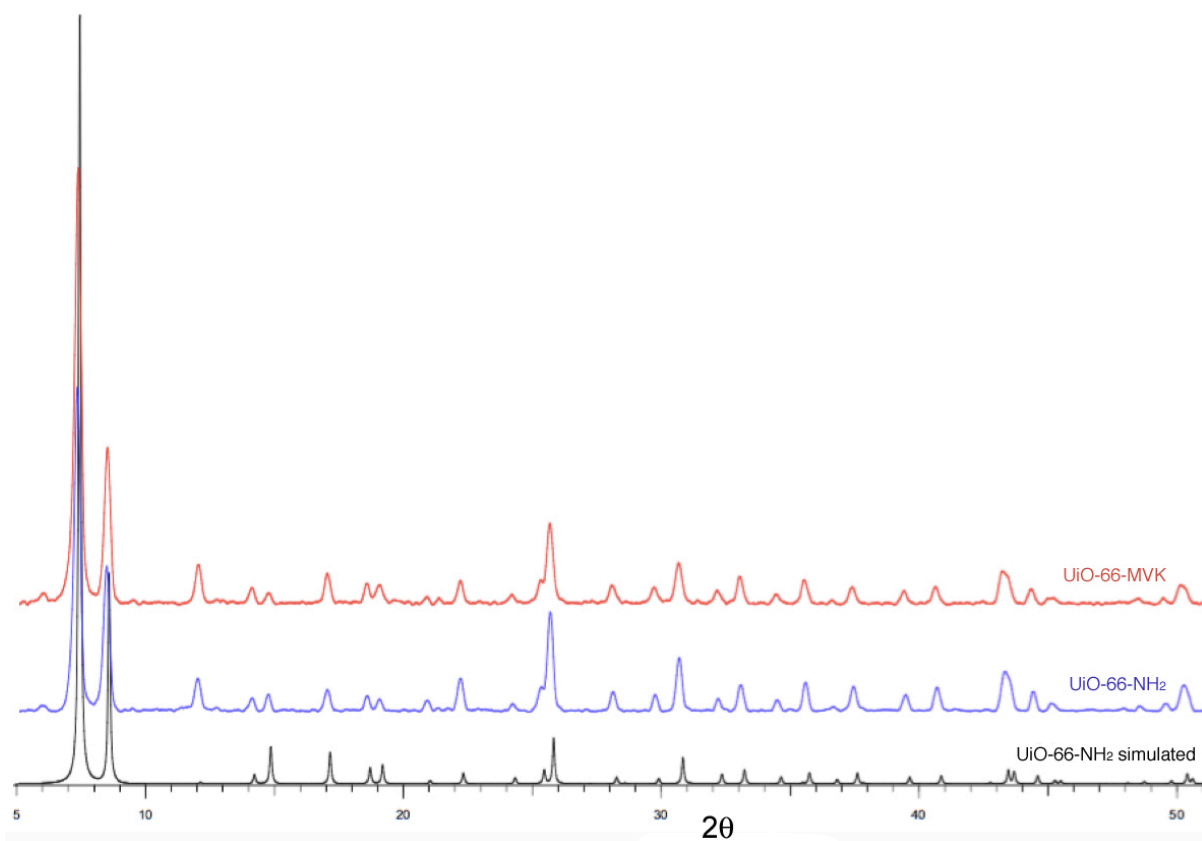


Figure S11. The PXRD pattern for UiO-66-MVK **4** in comparison with simulated and experimental PXRD patterns for UiO-66-NH₂.

7. Synthesis of UiO-66-TZ, 5

UiO-66-AN was prepared as described above, then washed with *n*-butanol over 3 days with the solvent replaced every 24 h. This sample (69 mg, ca. 0.2 mmol eq. of CN) was suspended in *n*-BuOH (10 mL) in a round bottom flask, followed by the addition of NaN₃ (16 mg, 0.24 mmol, 1.2 eq.) and ZnCl₂ (27 mg, 0.2 mmol, 1 eq.). The reaction mixture was stirred vigorously and heated under reflux for 24 h. The reaction was quenched by cooling the reaction mixture to ambient temperature and the product was separated by filtration then washed with fresh *n*-butanol. This washing procedure was repeated over 3 days with the solvent replaced every 24 h. The sample was then left to dry under ambient conditions. The ¹H NMR spectrum of digested UiO-66-TZ is shown in Figure S12 and the PXRD pattern is shown in Figure S13.

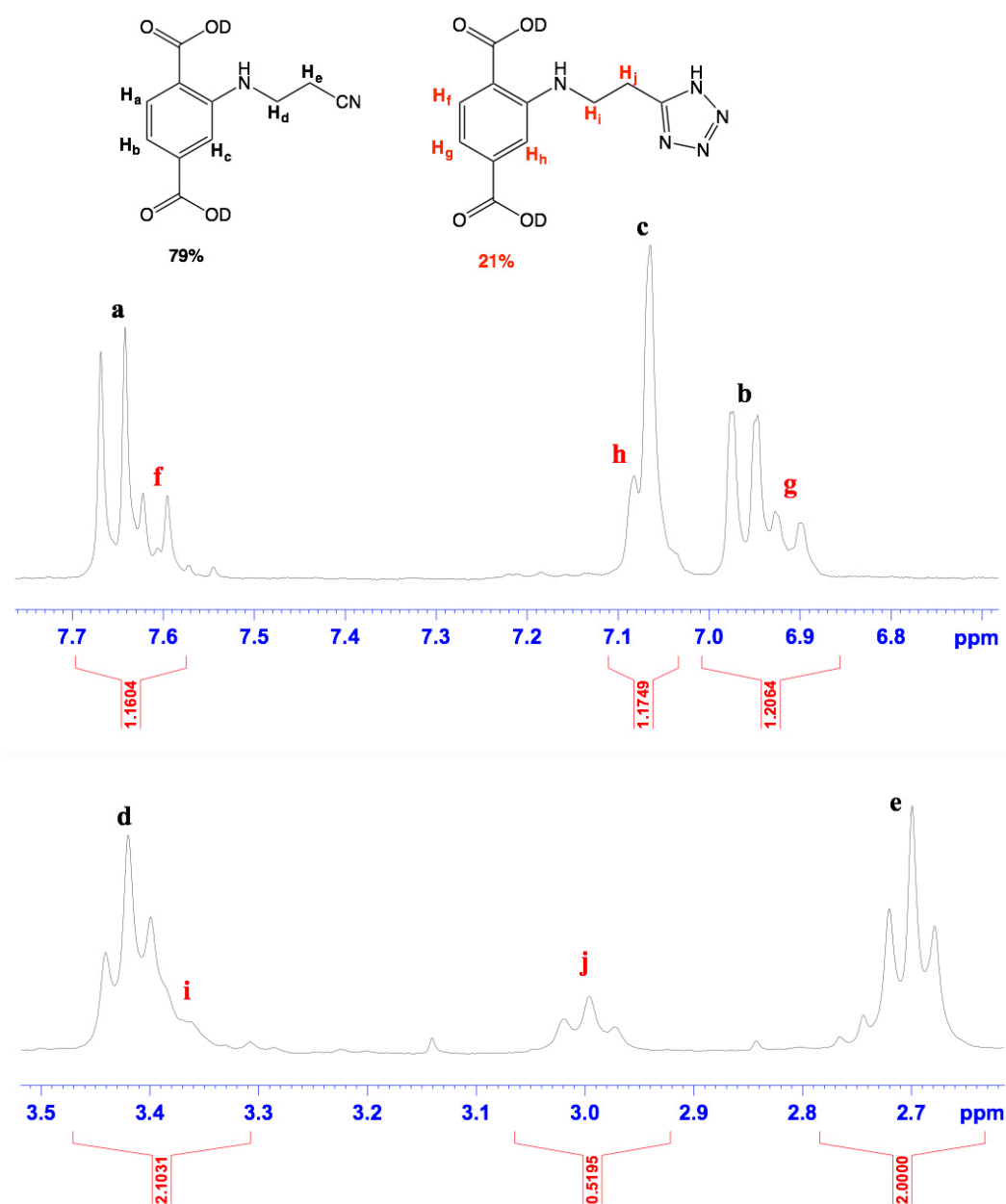


Figure S12. The ¹H NMR spectrum of UiO-66-TZ 5 following digestion in NH₄F/D₂O and DMSO-*d*₆ showing the aromatic and aliphatic regions.

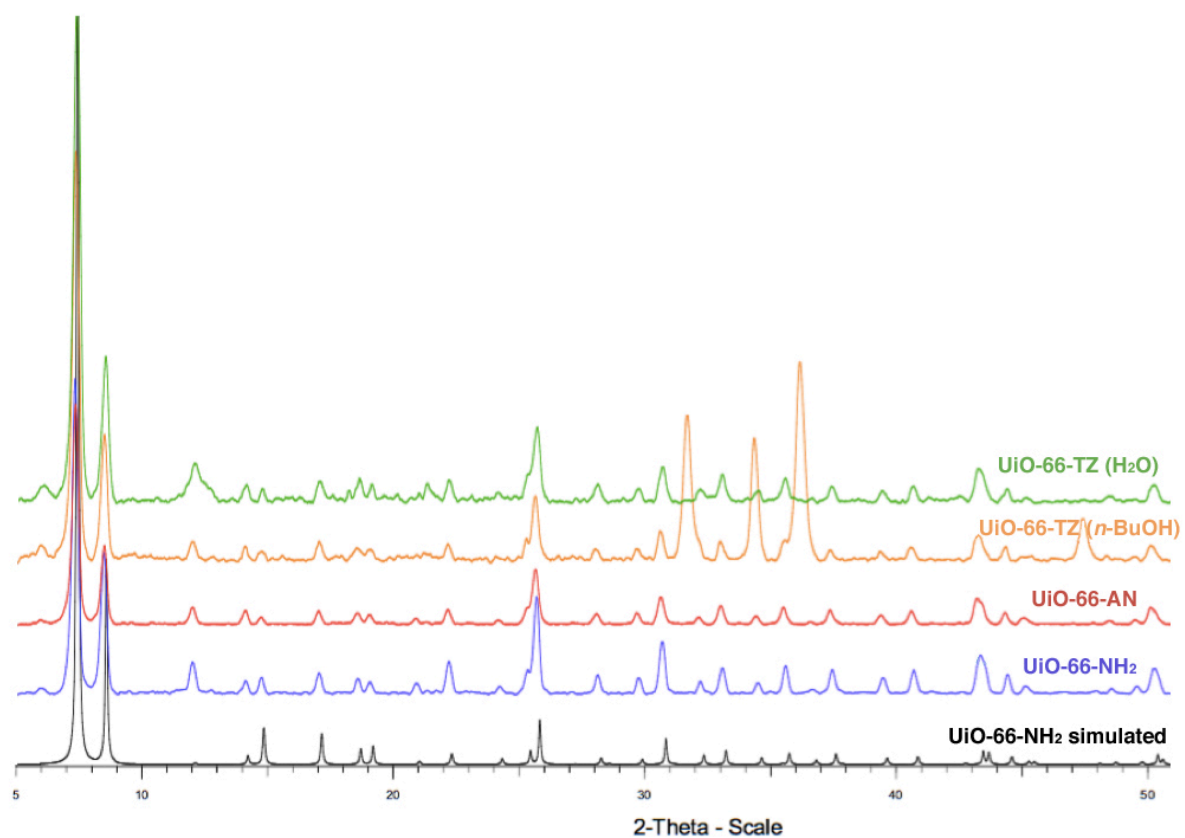


Figure S13. The PXRd pattern for UiO-66-TZ **5** after washing with water and *n*-butanol in comparison with simulated and experimental PXRd patterns for UiO-66-NH₂ and the PXRd pattern for UiO-66-AN **1**.

8. Thermogravimetric analyses

Thermogravimetric analyses for UiO-66-NH₂ and compounds **1** and **3-5** are shown in Figure S14.

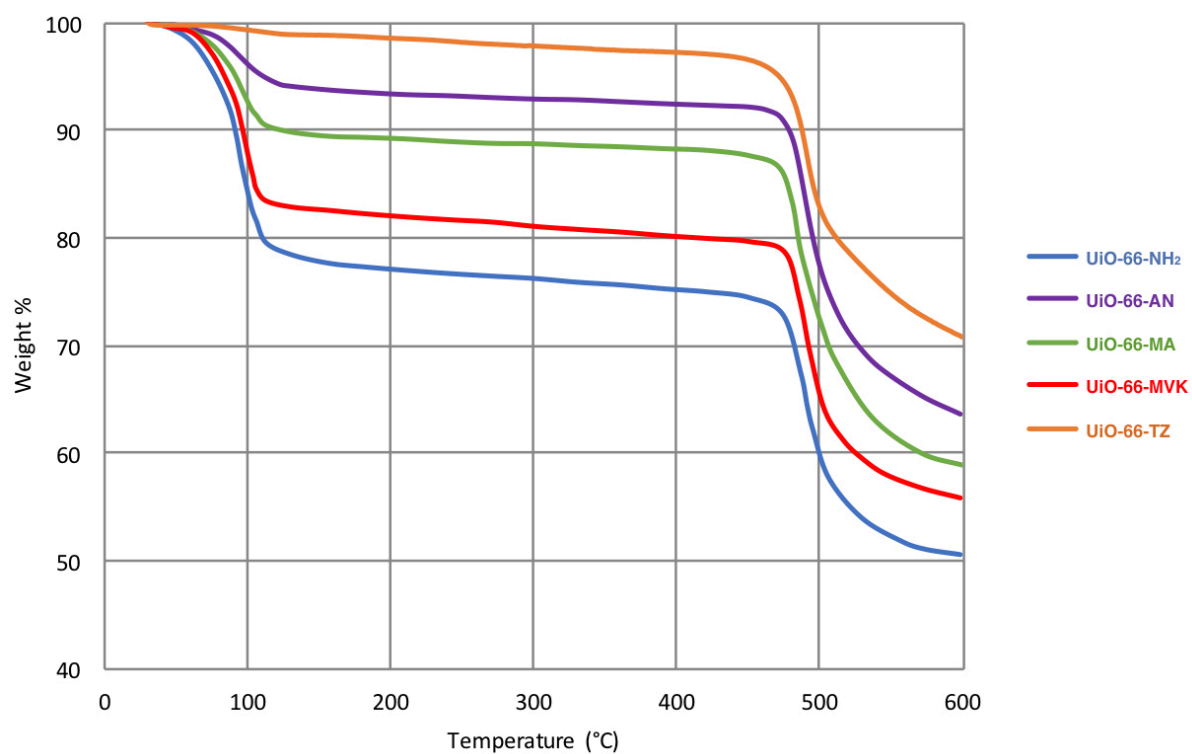


Figure S14. Thermogravimetric analyses for UiO-66-NH₂ and compounds **1** and **3-5**.

9. Nitrogen adsorption

Nitrogen sorption data at 273 K for UiO-66-NH₂ and compounds **1** and **3-5** are shown in Figure S15.

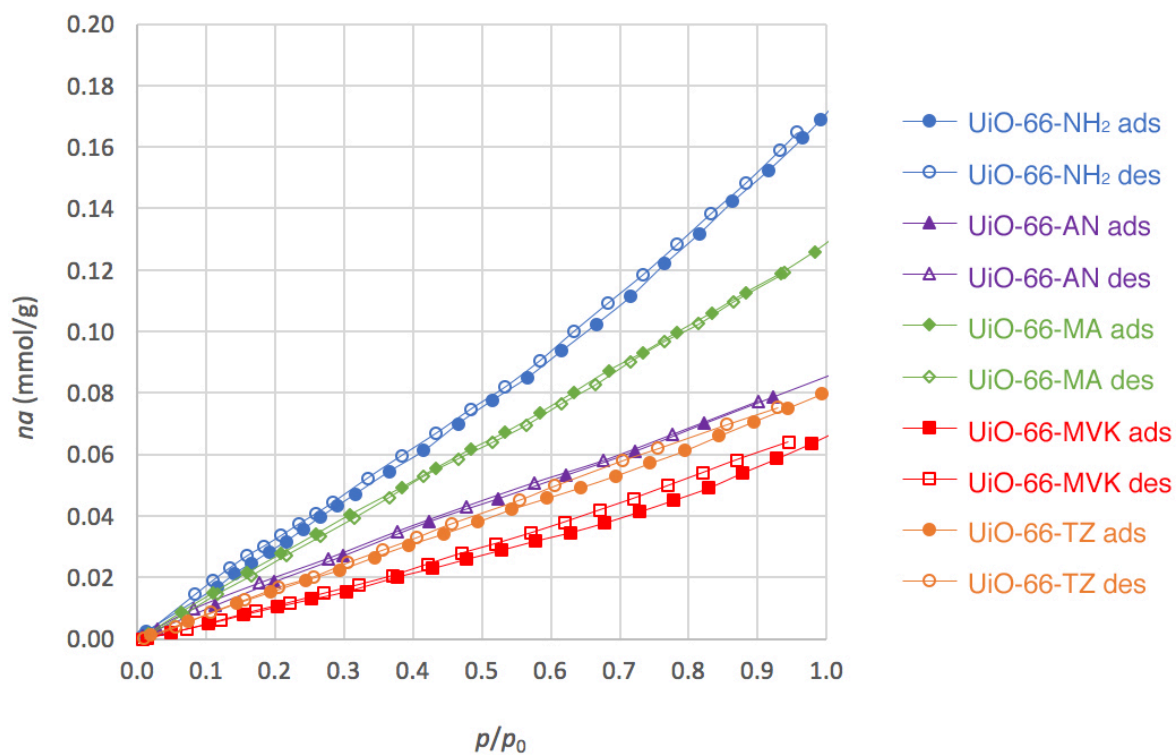


Figure S15. Nitrogen adsorption and desorption data for UiO-66-NH₂ and compounds **1** and **3-5** at 273 K.

10. References

- S1. S. J. Garibay and S. M. Cohen, *Chem. Commun.*, 2010, **46**, 7700.