Electronic Supporting Information

Microwave Assisted Activation and Modulator Removal in Zirconium MOFs for Buffer-Free CWA Hydrolysis

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Instrumentation

^{1}H and ^{31}P NMR spectroscopy was conducted using a JEOL 400MHz spectrometer with an auto-sampler. PXRD patterns were collected on zero-background sample holder using a Rigaku Miniflex 600 desktop XRD. A Netzsch STA 409 PC25 instrument and an aluminium crucible was employed for all thermogravimetric analyses. A CEM Explorer Microwave Reactor with dynamic power cycling was used for all MOF activation steps.

Experimental

MOF-808 (AcOH)

MOF-808 (AcOH) was synthesised using a slightly modified procedure reported in (1). In a 250ml vessel, $ZrCl_4$, 1281mg (5.5mmol) was dissolved in 60ml of N,N dimethylformamide and sonicated for 10 minutes. 1,3,5 benzenetricarboxylic acid (H_3BTC), 1115mg (5.5mol) was then added and the solution was sonicated for a further 10 minutes. Finally, 31ml (54mmol) acetic acid was added to the solution which was sonicated for another 10 minutes. The solution was sealed in a glass vial and placed in a preheated oven where it was heated at 130^{o}C for 24 hours. The vial was removed from the oven and allowed to cool to room temperature. A white solid was observed. The solid was vacuum filtered, washed with DMF (3 x 20ml) and acetone (3 x 20ml). The filtrate was dried under vacuum for 24 hours to yield a white microcrystalline powder of nMOF-808.

200mg of as synthesised nMOF-808. was suspended in 7ml of distilled water in an 11ml microwave vessel. The vessel was placed in a microwave reactor where it was activated at 150^{o}C for 20 minutes with heavy stirring. After cooling to room temperature, the MOF was vacuum filtered, washed with H_2O (3 x 10ml) and acetone (3 x 10ml) to yield the white microcrystalline powder of aMOF-808. $(Zr_6O_4(OH)_4(BTC)_2(CH_3COO)_{0.5}(H_2O)_{5.5} \cdot (H_2O)_{1.3})$. CHN analysis Calculated: C, 18.32; H, 2.02; N, 0.00 Found: C, 18.75; H, 2.03; N, 0.00.

For TGA analysis, each sample was annealed at 100^{o}C for 24 hours before analysis.

nMOF-808 and aMOF-808 were digested in a mixture of D_2SO_4/DMSO. A ^{1}H NMR spectrum was obtained of both materials to investigate the ratio of acetic acid that remained after the activation procedure.

DUT-84

DUT-84 was synthesised using a slightly modified procedure reported in (2). In a 250ml vessel, $ZrCl_4$, 570mg (3.05mmol) was dissolved in 120ml of N,N dimethylformamide and sonicated for 10 minutes.

2,6 napthalenedicarboxylic acid (H_2NDC), 500mg (2.78mmol) was then added and the solution was sonicated for a further 10 minutes. Finally, acetic acid, 50ml (794mmol) was added to the solution which was sonicated for another 10 minutes. The solution was sealed in a glass vial and placed in a preheated oven where it was heated at 120^{o}C for 24 hours. The vial was removed from the oven and allowed to cool to room temperature. A white solid was observed. The solid was vacuum filtered, washed with DMF (3 x 20ml) and acetone (3 x 20ml). The filtrate was dried under vacuum for 24 hours to yield a white microcrystalline powder of nDUT-84.

200mg of nDUT-84 was suspended in 7ml of distilled water in an 11ml microwave vessel. The vessel was placed in a microwave reactor where it was activated at 150^{o}C for 20 minutes with heavy stirring. After cooling to room temperature, the MOF was vacuum filtered, washed with H_2O (3 x 10ml) and acetone (3 x 10ml) to yield the white microcrystalline powder of aDUT-84. ($Zr_6O_8(NDC)_3(C_2H_3O_2)(H_2O)_5$). CHN analysis Calculated C, 31.11; H, 2.13; N, 0.00 Found C, 35.49; H, 2.87; N 0.00.

For TGA analysis, each sample was annealed at 100^{o}C for 24 hours before analysis.

nDUT-84 and aDUT-84 were digested in a mixture of D_2SO_4/DMSO. A ^{1}H NMR spectrum was obtained of both materials to investigate the ratio of acetic acid that remained after the activation procedure.

UiO-66 (AcOH)

Defective UiO-66 (AcOH) was synthesised using a slightly modified procedure (3). In a 250ml vessel, $ZrCl_4$, 862mg (4.62mmol) was dissolved in 100ml of N,N dimethylformamide and sonicated for 10 minutes. 1,4 benzenedicarboxylic acid (H_2BDC), 615mg (3.70mmol) was then added and the solution was sonicated for a further 10 minutes. Finally, acetic acid, 22ml (349.4mmol) and conc. HCl, 0.2ml, (2.3mmol) was added to the solution which was sonicated for another 10 minutes. The solution was sealed in a glass vial and placed in a preheated oven where it was heated at 120^{o}C for 24 hours. The vial was removed from the oven and allowed to cool to room temperature. A white solid was observed. The solid was vacuum filtered, washed with DMF (3 x 20ml) and acetone (3 x 20ml). The filtrate was dried under vacuum for 24 hours to yield a white microcrystalline powder of nUiO-66.

200mg of nUiO-66 was suspended in 7ml of distilled water in an 11ml microwave vessel. The vessel was placed in a microwave reactor where it was activated at 150^{o}C for 20 minutes with heavy stirring. After cooling to room temperature, the MOF was vacuum filtered, washed with H_2O (3 x 10ml) and acetone (3 x 10ml) to yield the white microcrystalline powder of aUiO-66. ($Zr_6O_6(BDC)_5(CH_3COO)_{0.6}(H_2O)_{1.4} \cdot (H_2O)_6$). CHN analysis Calculated C, 31.11; H, 2.13; N, 0.00 Found C, 24.68; H 3.13; N 0.00.

For TGA analysis, each sample was annealed at 100^{o}C for 24 hours before analysis.

nUiO-66 and aUiO-66 were digested in a mixture of D_2SO_4/DMSO. A ^{1}H NMR spectrum was obtained of both materials to investigate the ratio of acetic acid that remained after the activation procedure.

DMNP and VM hydrolysis procedure

The following procedure was used to probe the hydrolysis rates of the as-synthesised MOFs and their activated counterparts. An NMR tube was charged with DMNP, 20 μL (0.09 mmol). The MOF catalyst (0.11 μmol, 1.25 mol%) was then added to the tube. 0.1 ml of D_2O along with 0.5ml of 0.1 M *N*-ethyl morpholine aqueous buffer was then added to the tube. The tube was inverted 3 times and immediately loaded into an NMR auto-sampler and the first spectrum was obtained within 3 minutes of the reaction commencing. The sample was then cycled on the auto-sampler to collect subsequent data points. For VM, the same procedure and the same ratios were used, the only difference was that the testing was conducted in the absence of any buffer.

NMR Digestion Data

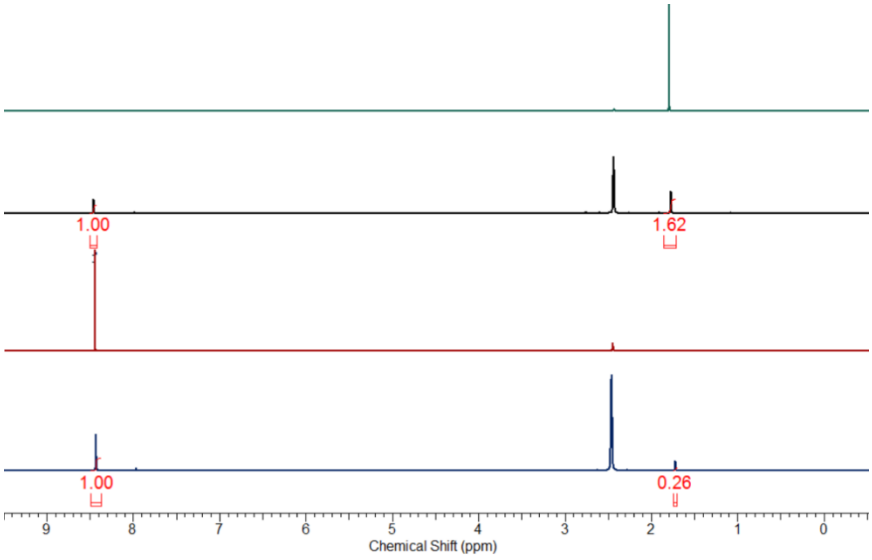

Fig. S1. A proton NMR (in DMSO/D_2SO_4) overlay showing acetic acid (green), as-synthesised (Washed with H2O) digested nMOF 808 (black), free H_3BTC ligand (red) and the digested *activated* aMOF-808 (blue).

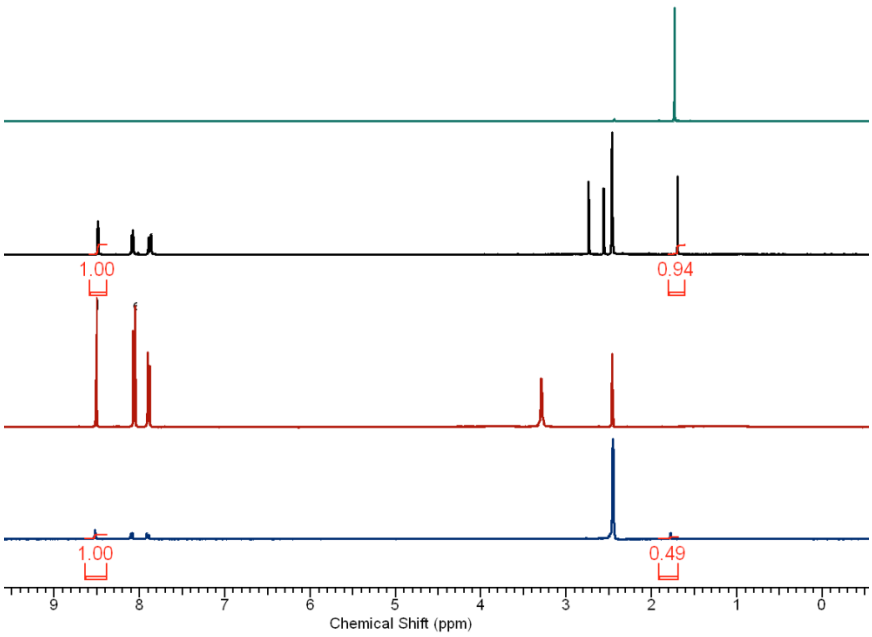

Fig. S2. A proton NMR (in DMSO/D_2SO_4) overlay showing acetic acid (green), as-synthesised (Washed with H2O) digested nDUT-84 (black), free H_2NDC ligand (red) and the digested *activated* aDUT-84 (blue).

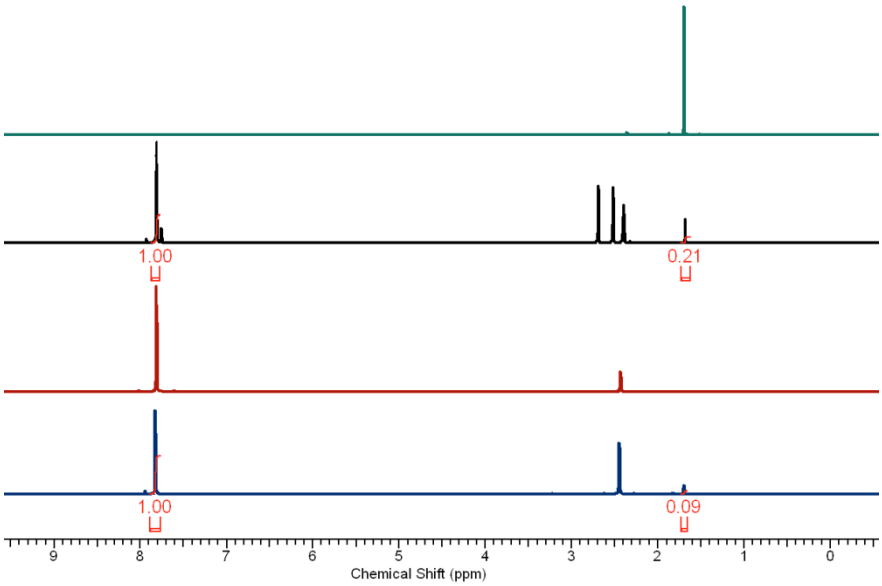

Fig. S3. A proton NMR (in DMSO/D_2SO_4) overlay showing acetic acid (green), as-synthesised (Washed with H2O) digested nUiO-66 (black), free H_2BDC ligand (red) and the digested *activated* aUiO-66 (blue).

Thermal Gravimetric Analysis Data

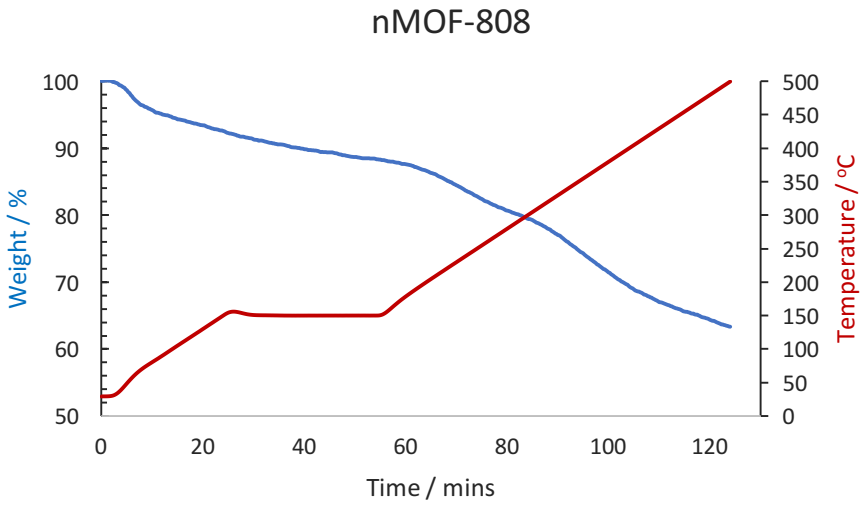

Fig. S4. TGA trace for nMOF-808, heating rate: 5 °C min^{-1} in N_2, 30 min isotherm at 150°C.

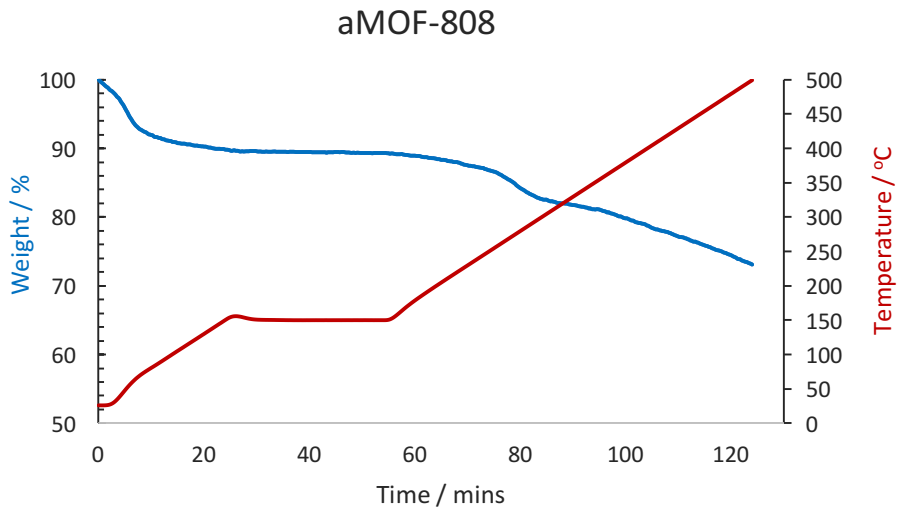

Fig. S5. TGA trace for aMOF-808, heating rate: 5 °C min^{-1} in N_2, 30 min isotherm at 150°C.

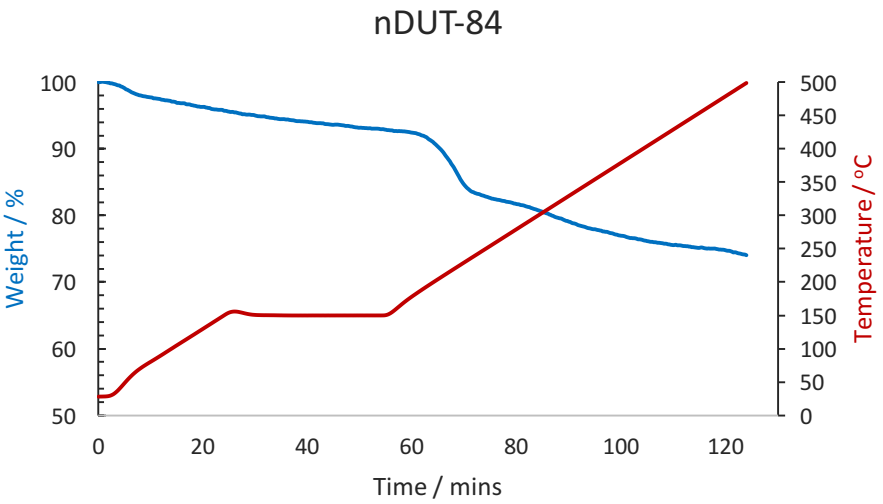

Fig. S6. TGA trace for nDUT-84, heating rate: 5 °C min^{-1} in N_2, 30 min isotherm at 150°C.

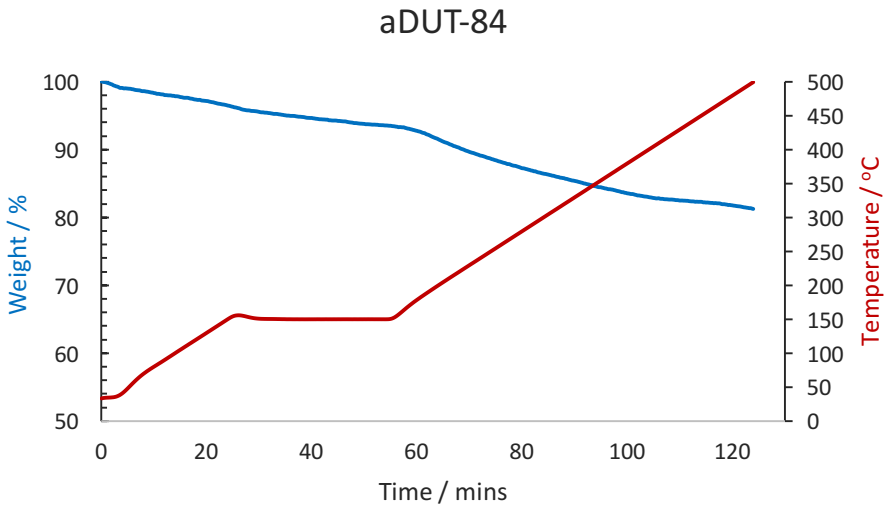

Fig. S7. TGA trace for aDUT-84, heating rate: 5 °C min^{-1} in N_2, 30 min isotherm at 150°C.

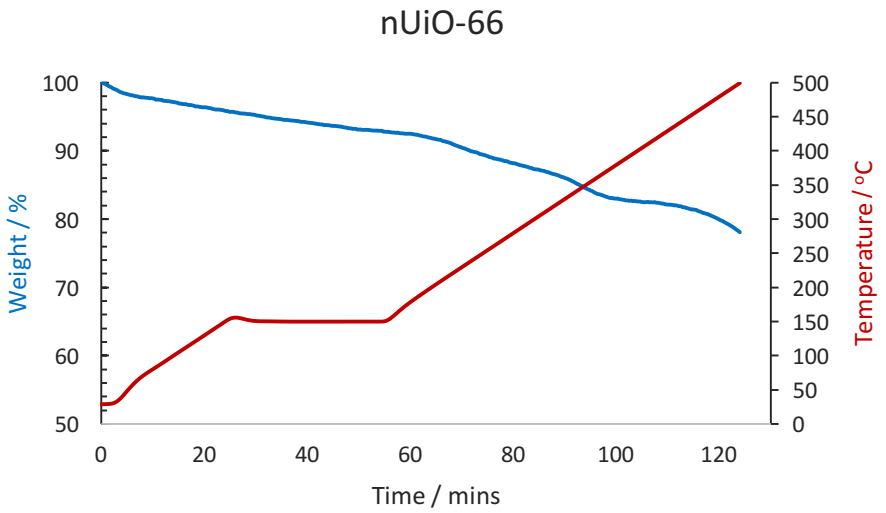

Fig. S8. TGA trace for nUiO-66, heating rate: 5 °C min^{-1} in N_2, 30 min isotherm at 150°C.

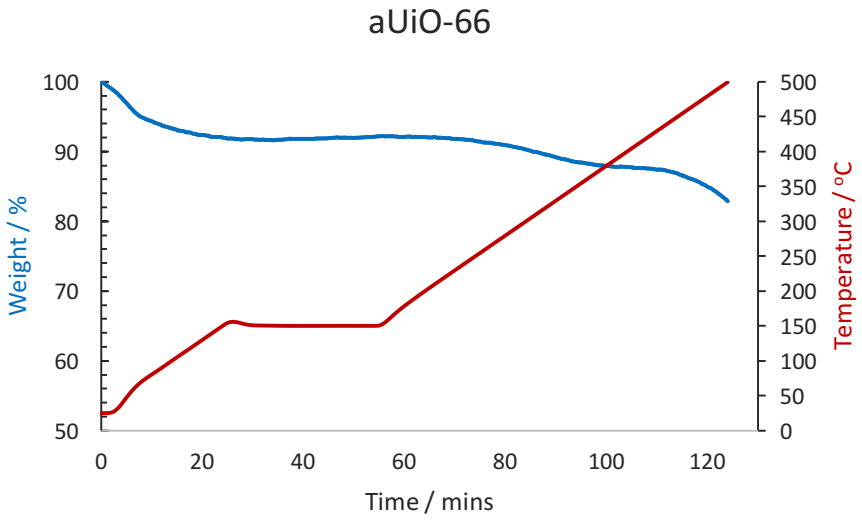

Fig. S9. TGA trace for aUiO-66, heating rate: 5 °C min^{-1} in N_2, 30 min isotherm at 150°C.

PXRD Data

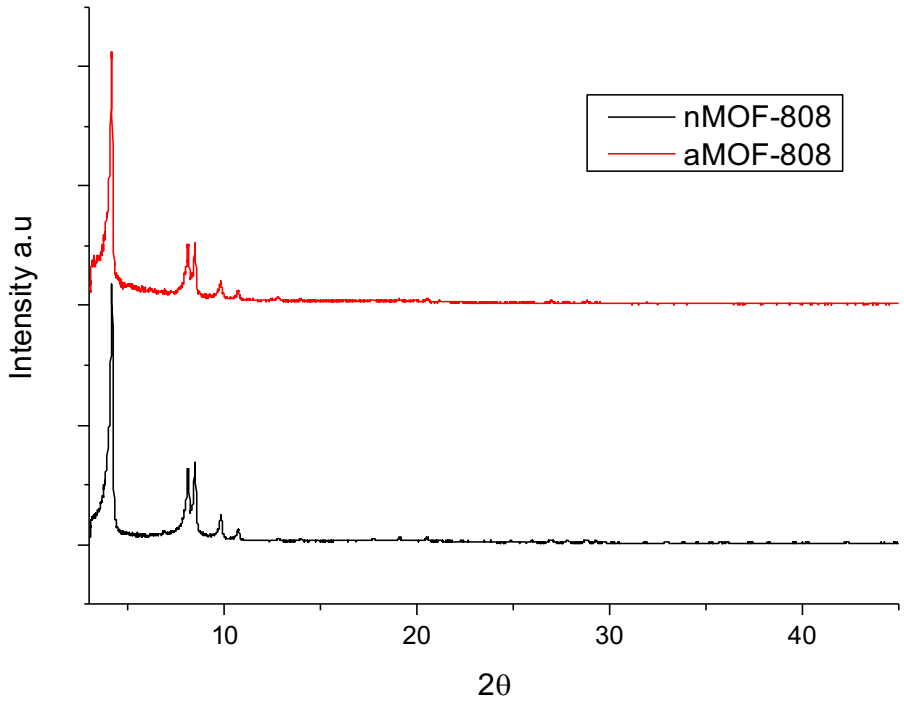

Fig. S10. A PXRD overlay showing nMOF 808 (black) and aMOF-808 (red).

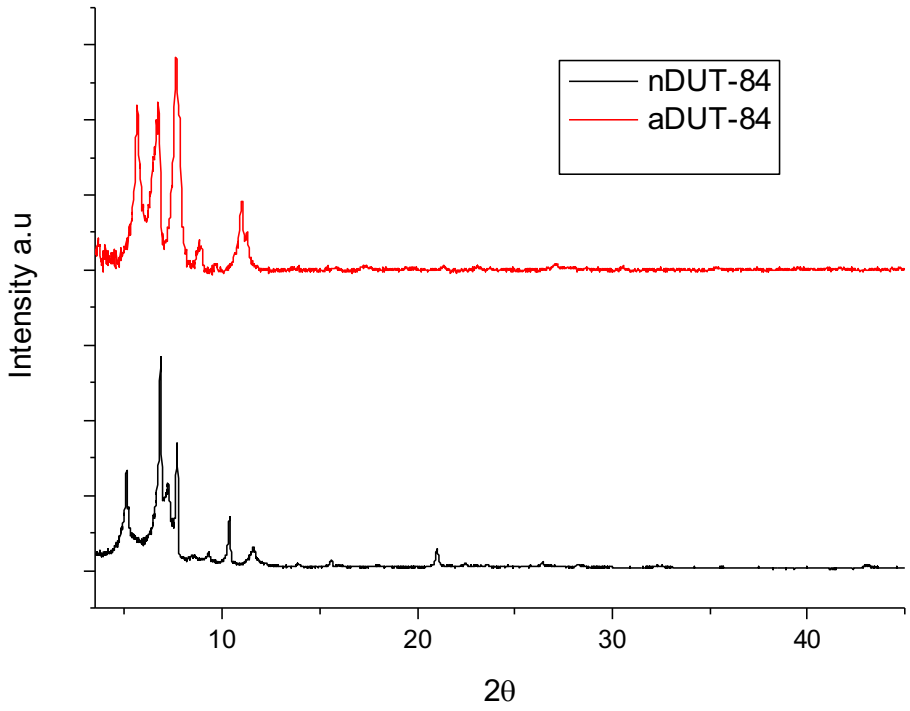

Fig. S11. A PXRD overlay showing nDUT-84 (black) and aDUT-84 (red), the authors reported the same phase upon utilising their own activation procedure.[3]

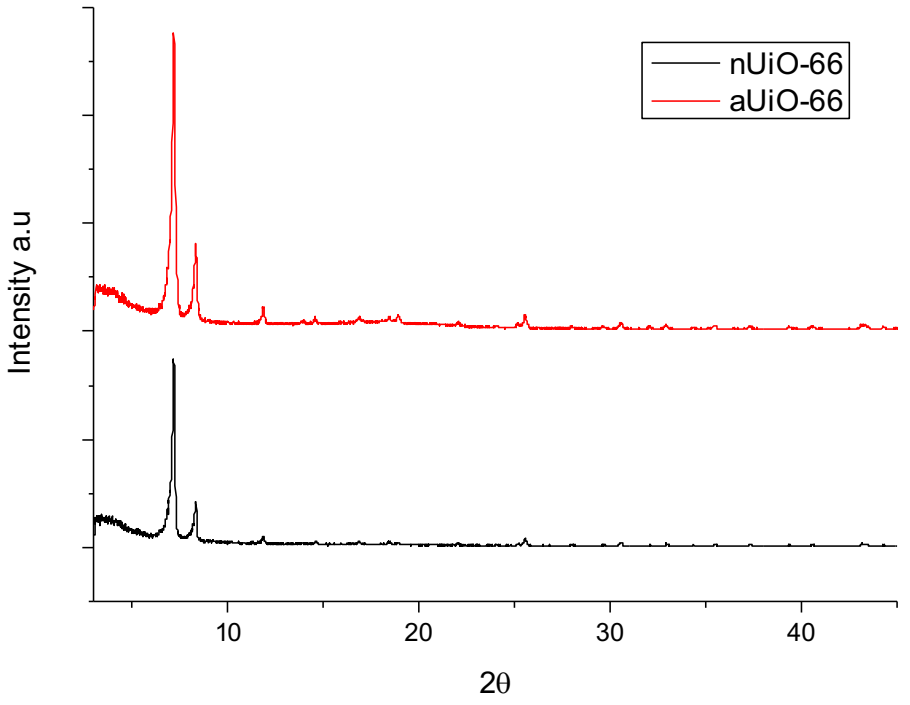

Fig. S12. A PXRD overlay showing nUiO-66 (black) and aUiO-66 (red).

First order DMNP residue plots

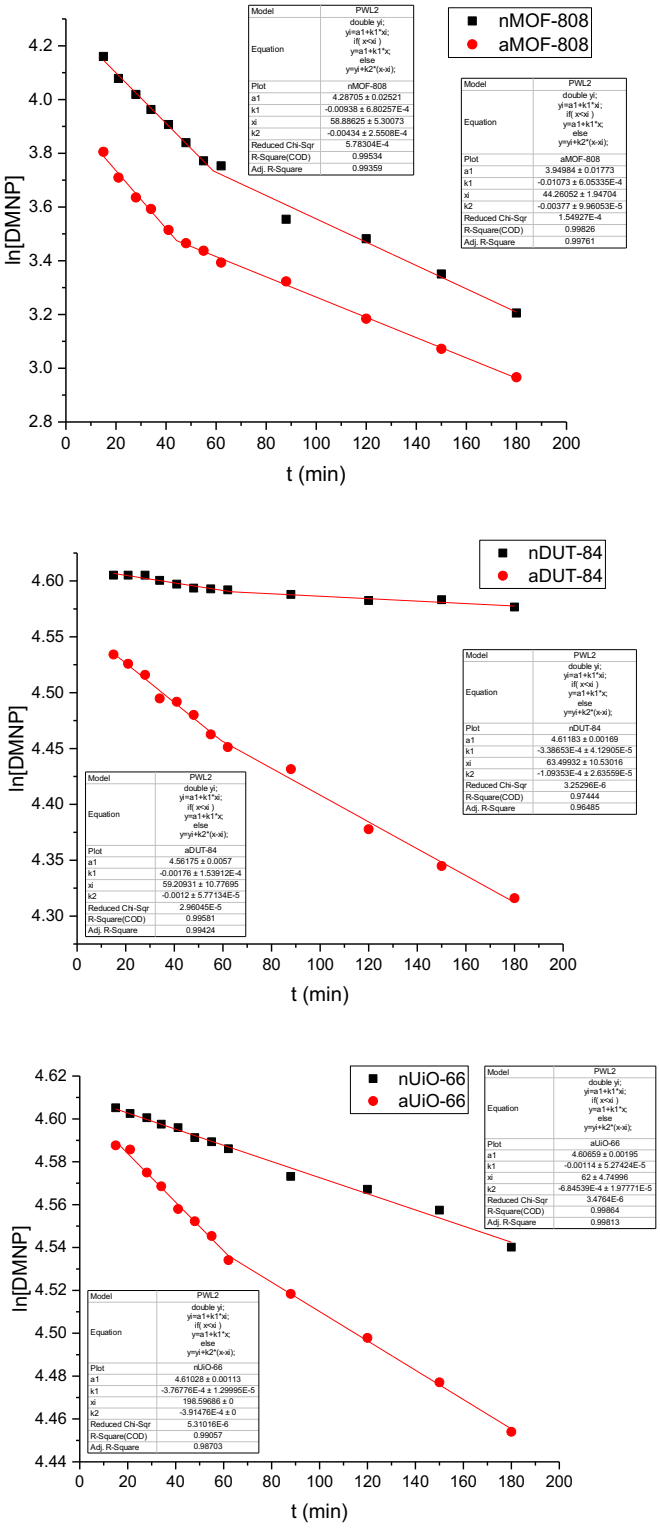

Fig. S13. Natural logarithms of concentrations corresponding to DMNP residues in the presence of the as-synthesised and activated MOF catalysts. The first order rate constants were calculated from a linear fit through the initial data points for each catalyst.

Rate constants, limiting pore diameter size and BET surface area

	k (s^{-1})	k standard error	Limiting pore diameter (Å)	BET ($m^2 g^{-1}$)
nMOF-808	0.0088	3.8×10^{-4}		
aMOF-808	0.0095	5.7×10^{-4}	**10**[1]	**1606**[1]
nDUT-84	0.0003	2×10^{-5}		
aDUT-84	0.0018	1.5×10^{-4}	**7.57**[2]	**637**[2]
nUiO-66	0.0004	1×10^{-5}		
aUiO-66	0.0012	4×10^{-5}	**5**[3]	**1525**[3]

Fig. S14. A table showing the first order rate constants with respect to DMNP in the presence of the MOF catalysts. The limiting pore diameter and BET surface area are also shown for comparison.

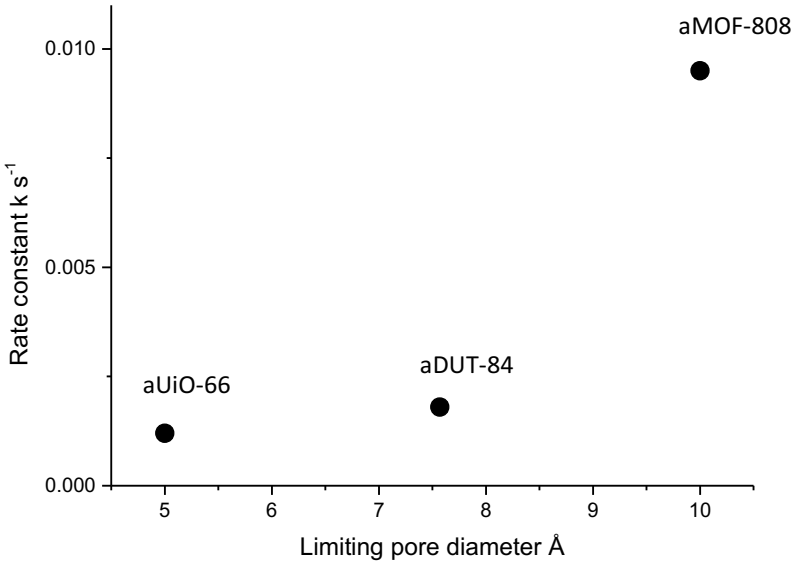

Fig. S15. A chart showing the relationship between the limiting pore diameter of the activated MOFs and the rate constant observed for DMNP hydrolysis in the presence of the activated material.

SEM Data

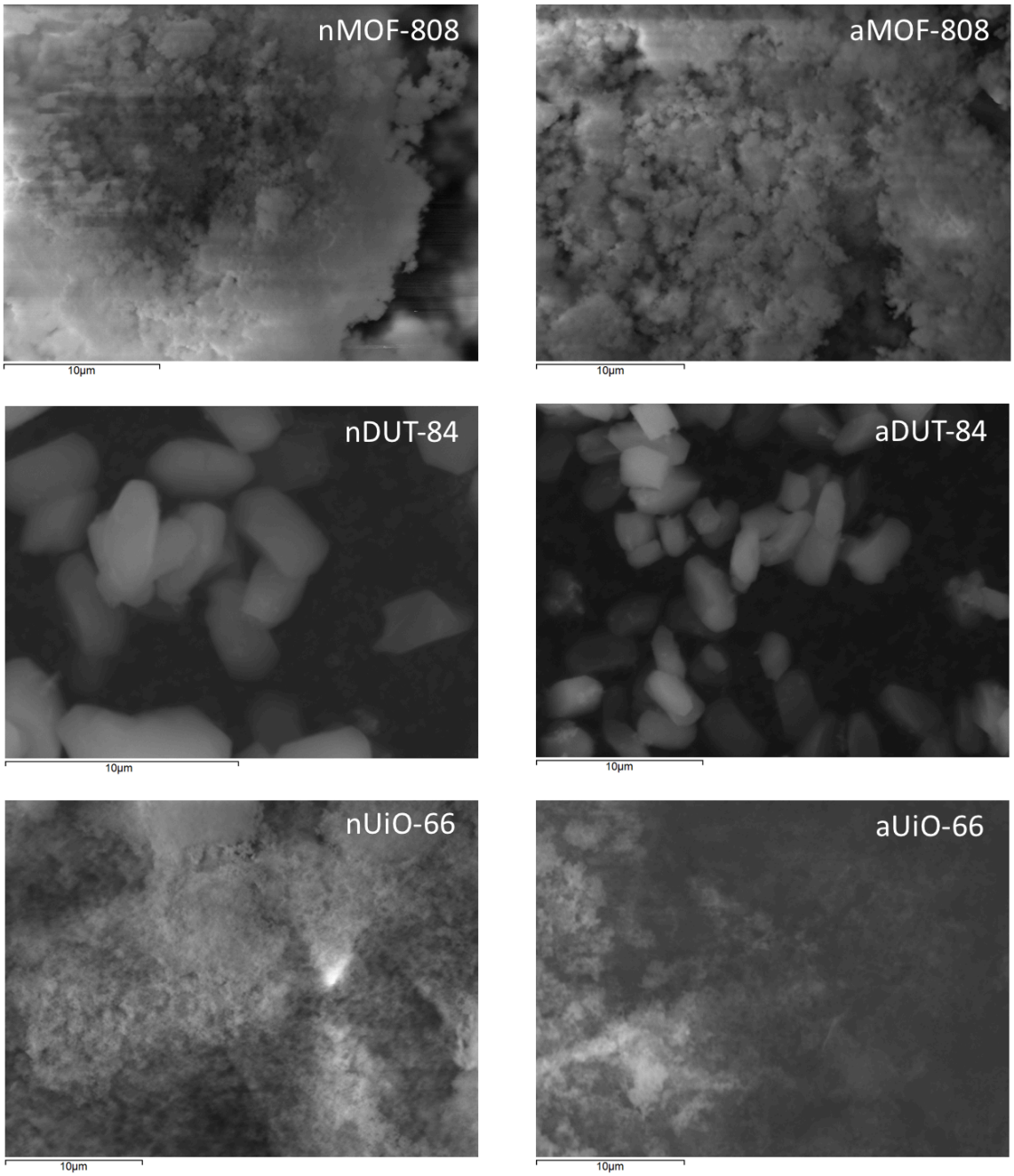

Fig. S16. Scanning electron microscope (SEM) images of MOF-808, DUT-84 and UiO-66 before and after activation.

NMR Hydrolysis Data

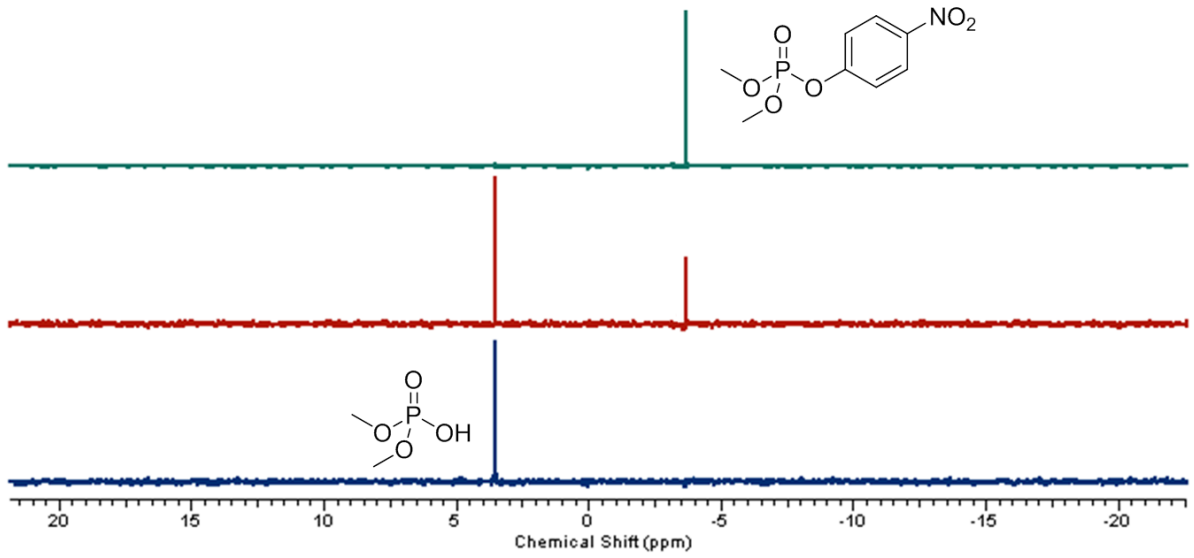

Fig. S17. A ^{31}P NMR overlay showing the different stages of methyl-paraoxon hydrolysis that were observed before catalyst addition (green), 30 mins after the addition of 1.25mol% aMOF-808 relative to substrate in 0.1M n-ethyl morpholine buffer (red), 24 hours after the addition of 1.25mol% aMOF-808 relative to substrate in 0.1M n-ethyl morpholine buffer (blue).

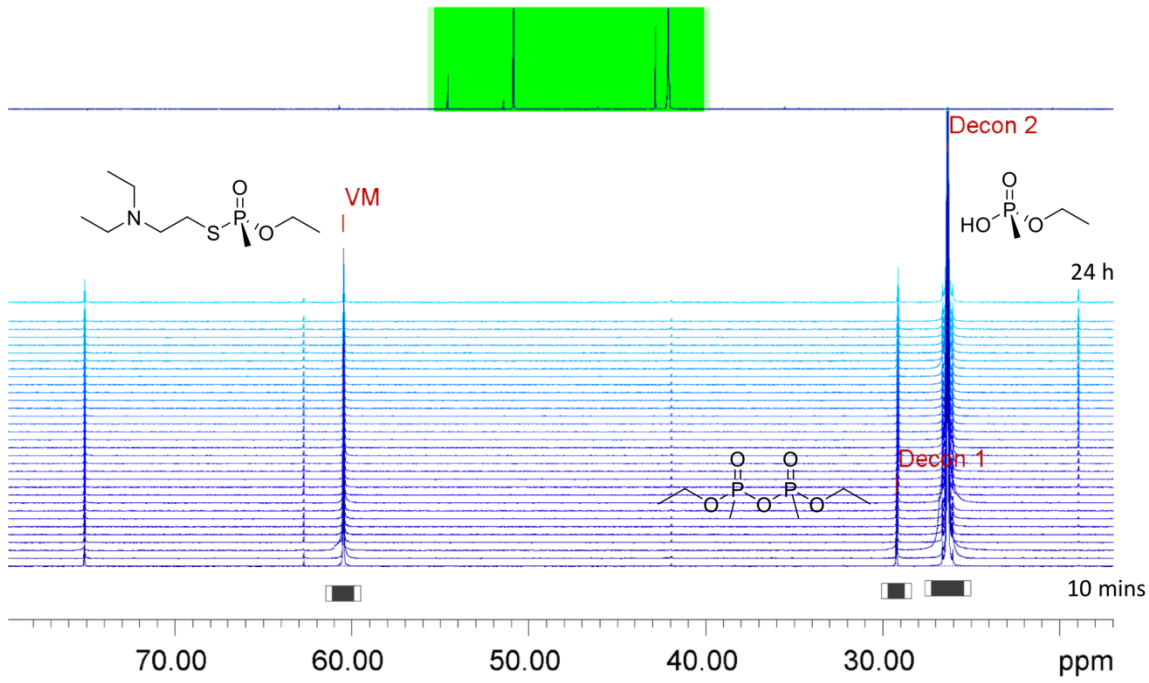

Fig. S18. A ^{31}P NMR overlay showing the different stages of VM hydrolysis in H_2O that were observed over 24 hours in the presence of 1.25mol% nMOF-808 relative to VM.

References

1 W. Liang, H. Chevreau, F. Ragon, P. D. Southon, V. K. Peterson and D. M. D'Alessandro, *CrystEngComm,* 2014, **16**, 6530-6533
2 V. Bon, I. Senkovska, M. S. Weiss and S. Kaskel, *CrystEngComm,* 2013, **15**, 9572-9577
3 G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, NOlsbye and K. P. Lillerud, *Chemistry of Materials,* 2016, **28**, 3749-3761