Electronic Supplementary Material (ESI) for Chemical Communications

Fast and High Yield Post-Synthetic Modification of Metal-Organic Frameworks by Vapor Diffusion

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SUPPORTING INFORMATION

General Considerations

All reagents were used as purchased from commercial suppliers (Sigma-Aldrich, Merck) without further purification, solvents were dried over activated molecular sieves (0.3 nm). The synthesis and activation of MOF-5 derivatives (IRMOF-3 and NH_2-MIXMOF-5) were carried out in dry atmosphere under Ar atmosphere to preserve the crystallinity of the materials. Vapor-phase post-synthetic modification (VP-PSM) reactions were performed using standard Schlenk techniques. NMR spectra were recorded on a Bruker AM spectrometer (^{1}H: 300 MHz) at room temperature. BET surface area analysis was performed on a Micromeretics Tristar II 3020 equipped with a VacPrep 061 degassing station, PXRD analysis was performed at room temperature on a Philips X'pert PRO diffractometer at 40 kV, 20 mA with CuKα (λ = 1.540 Å) radiation, scan speed 0.003 s/step, step size 0.01° and a 2θ range of 2-60°. TGA was performed in nitrogen atmosphere with a Mettler Toledo TGA/SDTA851^e equipped with a TSO800GC1 gas control and a TSO801RO sample robot.

MOFs Syntheses and activation

IRMOF-3

IRMOF-3 was prepared by a slightly modified procedure from that reported in the literature.[1] 2-Aminoterephtalic acid (0.3 g, 1.66 mmol) and $Zn(NO_3)_2{\cdot}4H_2O$ (1.2 g, 4.59 mmol) were dissolved in dry DMF (30 ml), and the clear solution was divided and transferred into seven 20 mL scintillation vials. The vessels were placed on a sand bath and heated into a programmable oven to 105 °C using a gradient of 2.0 °C/min. The temperature was held for 24 h and then the oven was slowly cooled to room temperature at a rate of 0.1 °C/min. The solvent was decanted, and the amber/brown cubic crystals washed three times with dry DMF. The material was rinsed and then soaked in dry $CHCl_3$ for 3 days, replacing the solvent each day with fresh one. Afterwards the solvent was decanted, and the crystals soaked and stored in dry toluene as previously reported.[2]

NH_2-MIXMOF-5

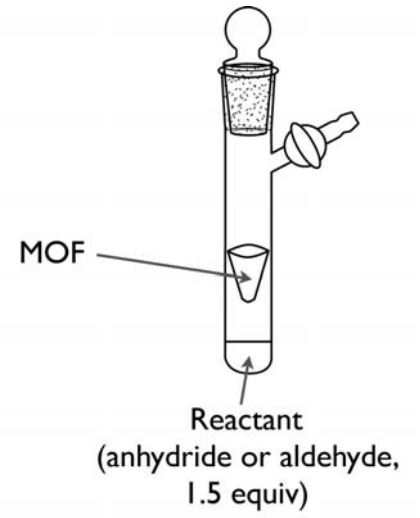
2-Aminoterephtalic acid (18 mg, 0.100 mmol), terephtalic acid (50 mg, 0.300 mmol) and $Zn(NO_3)_2{\cdot}4H_2O$ (314 mg, 1.20 mmol) were dissolved in dry DMF (20 ml) inside a screw-capped 100 mL PFA reagent bottle. The vessel was placed into a programmable oven and heated to 110 °C in a sand bath using a gradient of 2.0 °C/min. The temperature was held for 24 h and then the oven was slowly cooled to room temperature at a rate of 0.1 °C/min. The solvent was decanted, and the light yellow cubic crystals washed three times with dry DMF. Anologously to IRMOF-3, the activation was performed by rinsing and then soaking the crystals in dry $CHCl_3$ for 3 days, replacing the solvent each day with fresh one. Afterwards the solvent was decanted and the crystals were soaked and stored in dry toluene. NMR spectroscopy after digestion (see below) showed 12% of amino functionalizations.
^{1}H NMR (300 MHz, d^6-DMSO), terephtalic acid (88%) ™: 8.04 (s, 4H); 2-aminoterephtalic acid (12%) ™: 7.77 (d, 1H, *J* = 8.3 Hz), 7.37 (d, 1H, *J* = 1.5 Hz), 7.02 (d, 1H *J* = 8.4 Hz).

NH_2-UiO-66

The preparation of NH_2-UiO-66 was performed according to the original procedure:[3] 2-Aminoterephtalic acid (252 mg, 1.392 mmol) and anhydrous $ZrCl_4$ (324 mg, 1.392 mmol) were dissolved in 16 ml DMF, transferred in a Teflon lined autoclave and heated at 120°C for 24 h. After slow cooling overnight, the yellowish microcrystalline material was isolated by centrifugation, rinsed three times with DMF followed by three additional washings with methanol and then dried overnight in a vacuum oven at 70°C.

Vapor-phase postsynthetic modification

The set up was prepared as following: a conical paper filter was introduced in a 10 mL Schlenk tube, the filter avoiding direct contact with the bottom of the vessel, containing the reactant. The system was evacuated in HV and strong heating and flushed three times with argon and prepared for the reaction (Scheme S1).



Scheme S1 General set-up for the vapor-phase postsynthetic modifications experiments

SI-IRMOF-3
Crystals of IRMOF-3 (100 mg, 0.122 mmol, 1 eq) were dried under a stream of argon and transferred inside the conical filter paper of the Schlenk tube with positive argon pressure. Salicylaldehyde (20 µL, 0.184 mmol, 1.5 eq) was introduced with the help of a syringe on the bottom of the vessel avoiding any direct contact with the MOF. The system was heated overnight at 100 °C under static vacuum. The red crystals were washed three times and then soaked in toluene overnight to remove the excess aldehyde. The product was stored in fresh toluene.

SI-MIXMOF-5
As for IRMOF-3, the material was dried under argon and then evacuated at 150°C overnight. The MOF (100 mg, 0.129 mmol, 1 eq), was moved inside the conical filter and salicylaldehyde (21 µL, 0.193 mmol, 1.5 eq) added on the bottom of the Schlenk tube. The system was heated at 100°C overnight under static vacuum. The orange crystals were then washed three times and soaked in toluene overnight. The product was stored in fresh toluene.

SI-UiO-66
The oven dried microcrystalline powder (100 mg, 0.351 mmol, 1 eq) was evacuated at 150°C overnight and then transferred inside the conical filter paper. In a typical experiment, salycilaldehyde (56 µL, 0. 526 mmol, 1.5 eq) was added with a syringe on the bottom of the Schlenk tube and the system was heated under static vacuum at 120°C overnight. The obtained bright yellow solid was then washed three times and soaked in dichloromethane overnight, collected by centrifugation and dried in a vacuum oven at 70°C.

AMX-UiO-66 (X = 2, 5, Mal)
The whitish compounds AMX-UiO-66 were prepared similarly to SI-UiO-66 by replacing the aldehyde with the corresponding anhydrides.

Characterisation of functionalised MOFs

Digestion and ^{1}H-NMR
SI-IRMOF-3 and SI-MIXMOF-5: The evacuated functionalized material (6 mg) was digested in d^{6}-DMSO (500 µL) and diluted DCl (100 µL prepared by adding 23 µL of 35% DCl in D_2O diluted with 1 mL of d^{6}-DMSO) by sonication. After complete dissolution of the MOF, the clear solution was analysed by ^{1}H-NMR.
SI-UiO-66 and AMX-UiO-66: The material (6 mg) was digested with d^{6}-DMSO (570 µL) and 48% HF (30 µL) by sonication. Upon complete dissolution of the functionalized MOF, the solution was analyzed by ^{1}H-NMR.

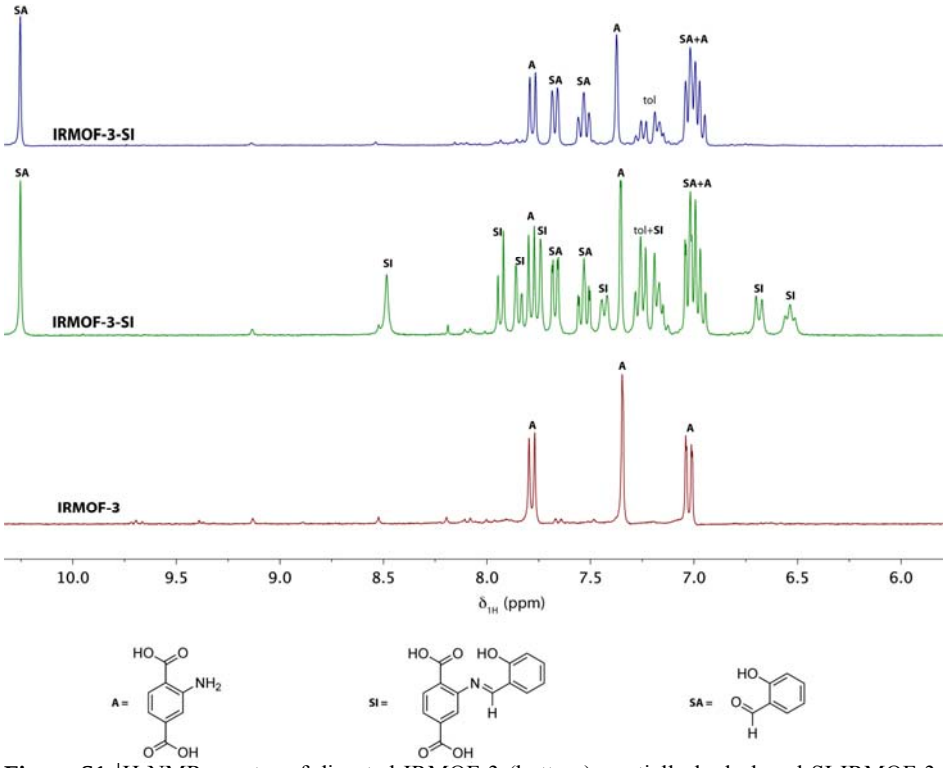
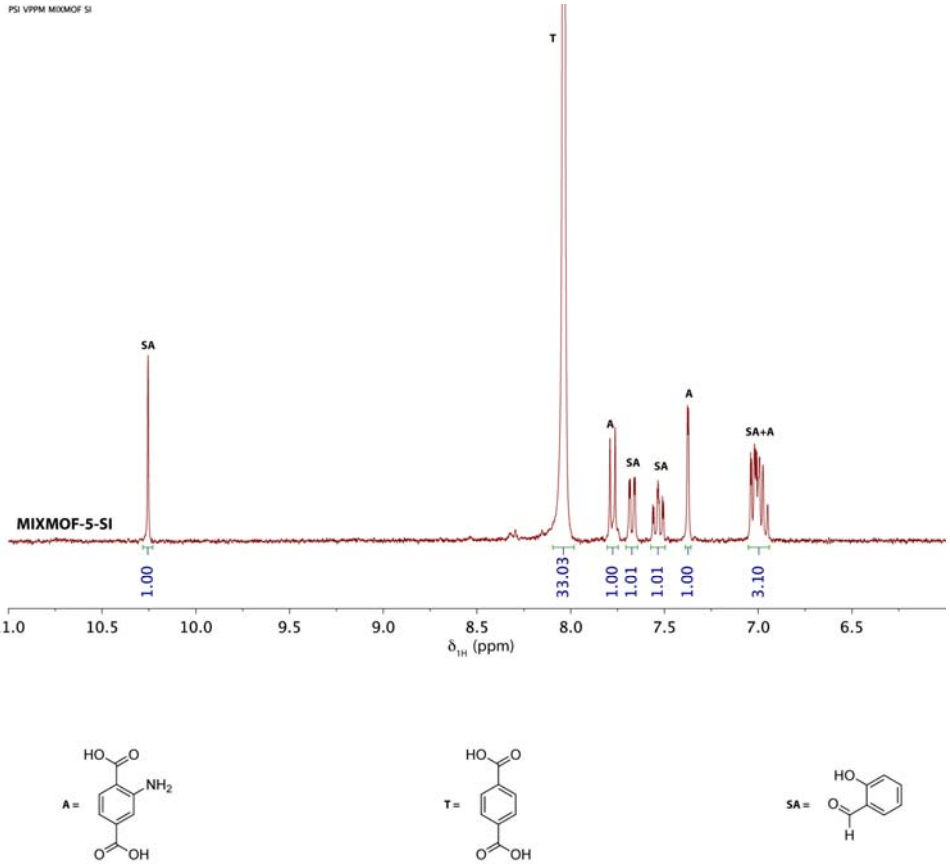


Figure S1 ^{1}H-NMR spectra of digested IRMOF-3 (bottom), partially hydrolyzed SI-IRMOF-3 (middle, showing imine formation)



and completely hydrolyzed SI-IRMOF-3 (top).

Figure S2 ^{1}H-NMR spectrum of digested SI-MIXMOF.

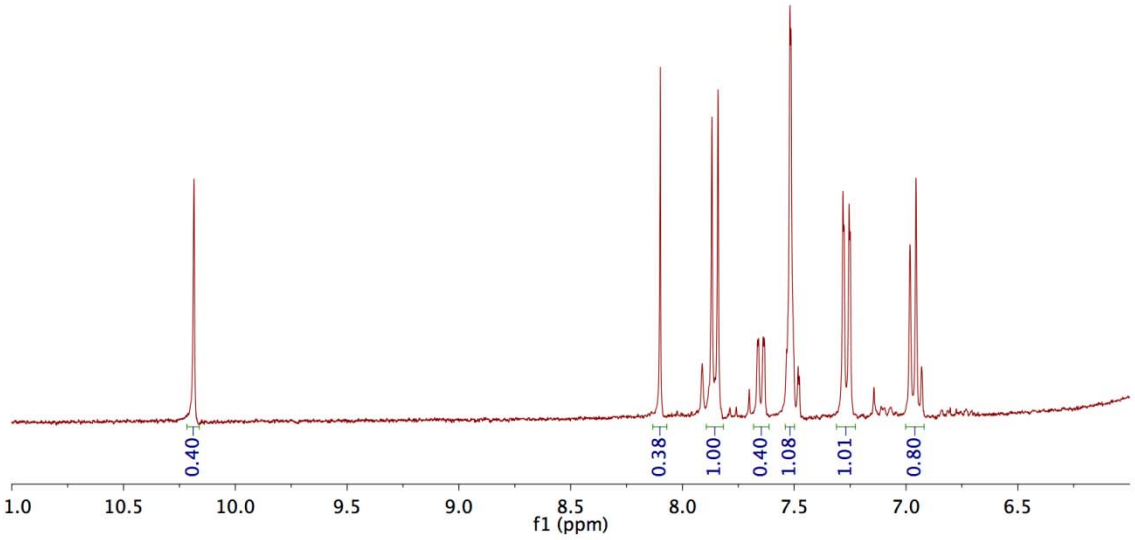


Figure S3 ^{1}H-NMR spectrum of digested SI-UiO-66.

PXRD

Approximately 10 mg of dry functionalised material were suspended in $CHCl_3$ and dispersed as a homogeneous layer on a thin glass slide prior the measurements.

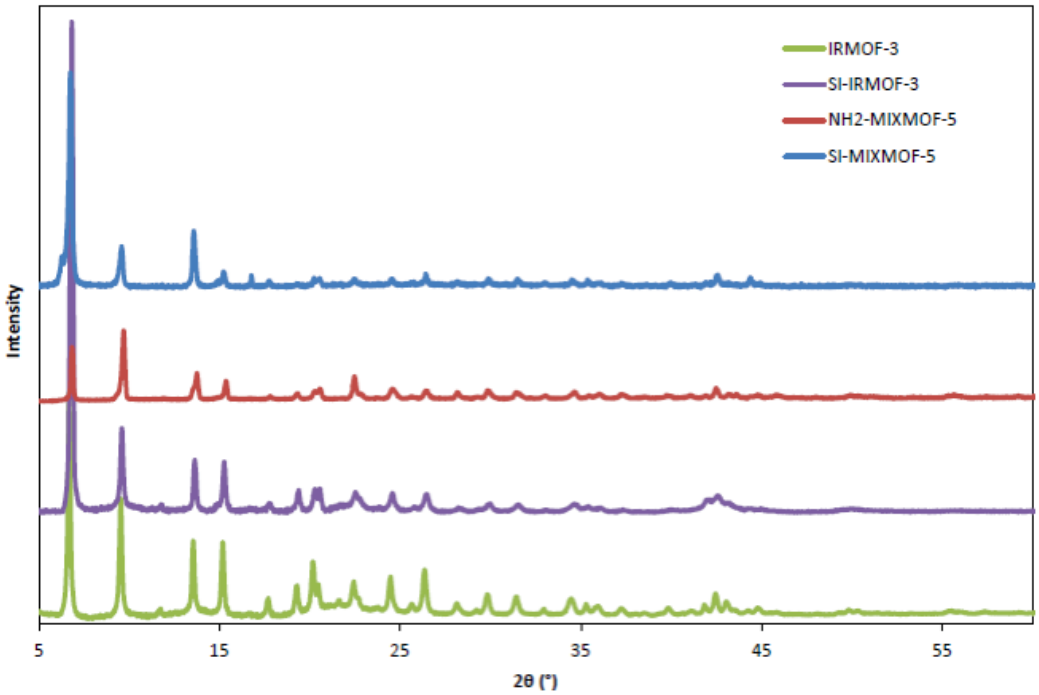


Figure S4 PXRD spectra of IRMOF-3, SI-IRMOF-3, NH_2-MIXMOF-5 and SI-MIXMOF-5.

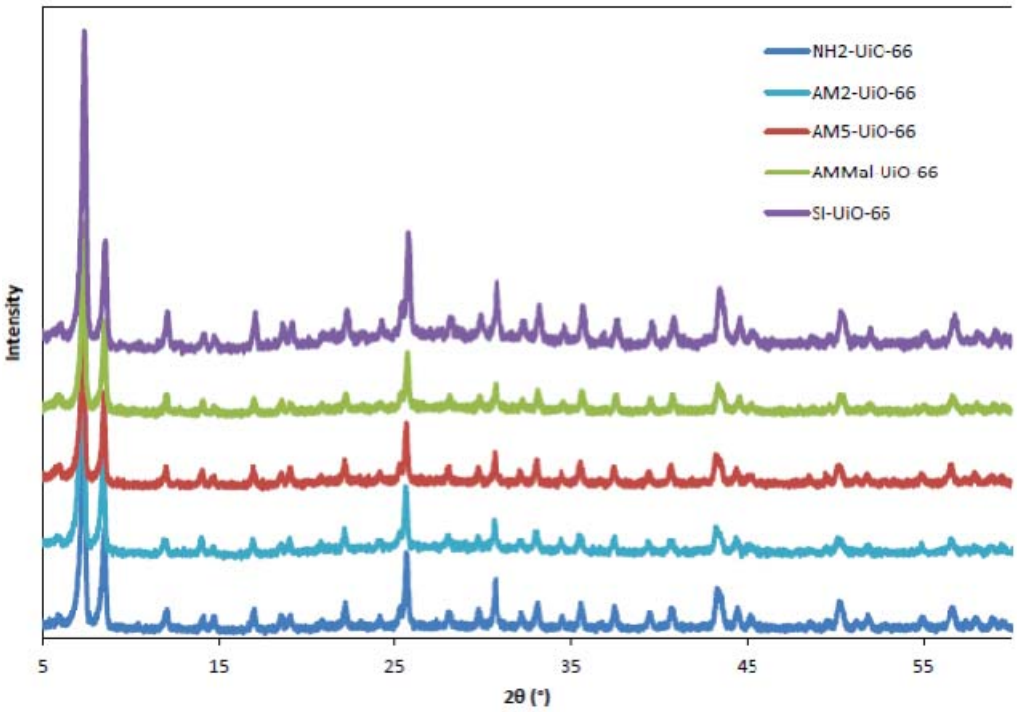


Figure S5 PXRD spectra of the post-synthetically modified NH_2-UiO-66.

BET and Langmuir surface areas

Approximately 100 mg of material was evacuated at 150°C overnight prior to measurement. The surface areas were calculated from N_2 adsorption/desorption isotherms at 77K on a Micromeretics Tristar II 3020 analyzer.

MOF	**BET surface area (m^2/g)**	**Langmuir surface area (m^2/g)**
IRMOF-3	2314	2657
SI-IRMOF-3	362	561
NH_2-MIXMOF-5	3121	3564
SI-MIXMOF-5	2871	3268

Table S1 BET and Langmuir surface areas of the IRMOF-3 and MIXMOF series.

MOF	**BET surface area (m^2/g)**	**Langmuir surface area (m^2/g)**
NH_2-UiO-66	1128	1284
SI-UiO-66	782	885
AM2-UiO-66	707	802
AM5-UiO-66	652	727
AMMal-UiO-66	673	824

Table S2 BET and Langmuir surface areas of the UiO-66 series.

TGA analysis

IRMOF-3 and NH_2-MIXMOF-5: the samples were freshly prepared prior to every measurement by drying them under a stream of nitrogen. Approximately 10 mg of the solvated materials were used for the measurements running from room temperature to 700°C with a gradient of 5°C/min in a nitrogen atmosphere.

NH_2-UiO-66: Approximately 10 mg of the activated materials were used for the measurements. Analysis was performed in nitrogen atmosphere running from room temperature to 800°C with a gradient of 5°C/min using an autosampler.

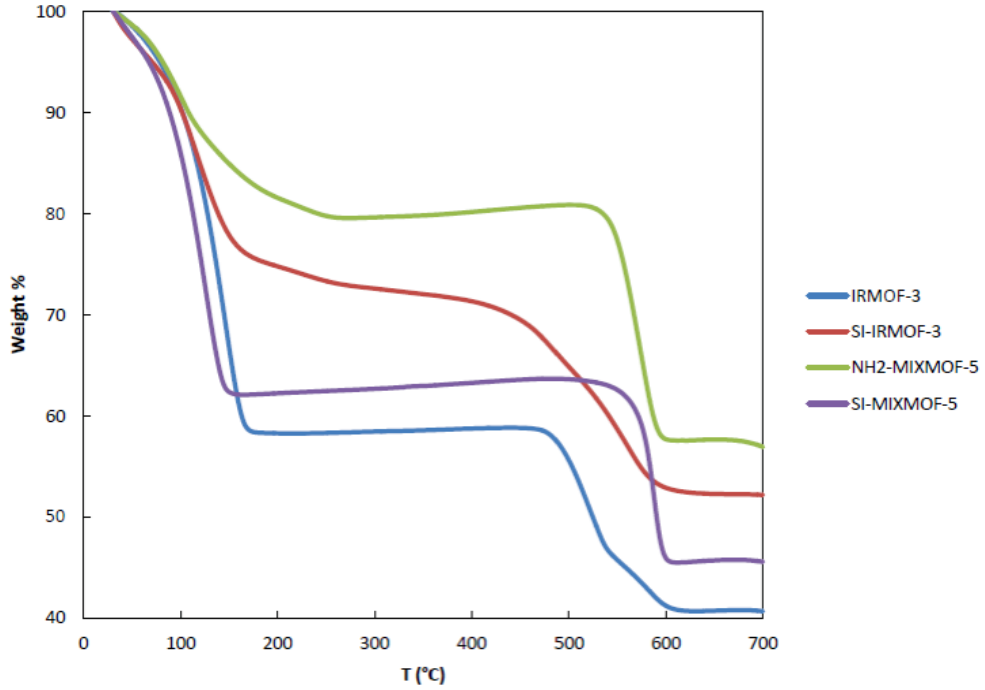


Figure S6 TGA of the solvated IRMOF-3, SI-IRMOF-3, NH_2-MIXMOF and SI-MIXMOF. Toluene loss is observed in the range of 30-200°C (weight loss dependant on degree of solvation).

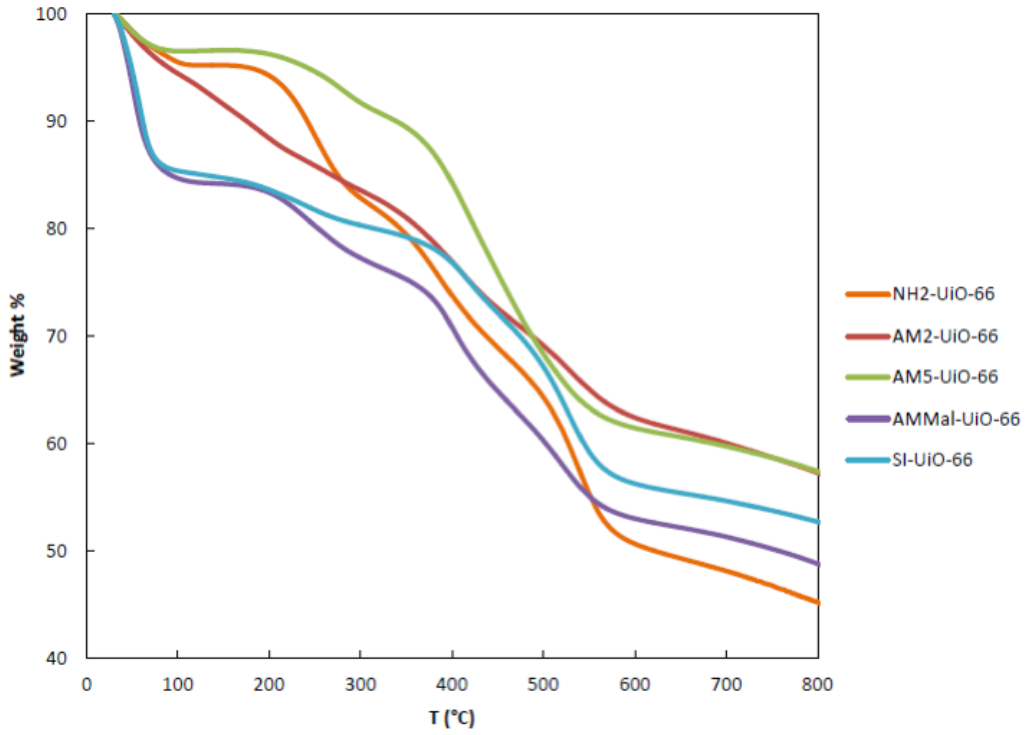


Figure S7 TGA curves of the UiO-66 series.

References

1 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469-472.

2 M. J. Ingleson, J. Perez Barrio, J.-B. Guilbaud, Y. Z. Khimyak, M. J. Rosseinsky, J. P. Barrio, Y. Z. K. M. J. Rosseinsky, *Chem. Commun.* **2008**, 2680-2682.

3 S. J. Garibay, S. M. Cohen, *Chem. Commun.* **2010**, *46*, 7700-7702.