

Supporting information

Synthesis and Characterization of Amine Functionalized Mixed Ligand Metal-organic Frameworks of UiO-66 topology

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A) Synthesis details and powder X-ray diffractions patterns (3-50°) of the mixed linker –MOFs prepared at 100 °C with M:L ration 1:1 and without addition of HCl.

Table S1. Synthesis of the Mixed ligand MOFs					
MOFs	Reagent amount				
	ZrCl ₄ (g)	BDC (g)	ABDC (g)	H ₂ O (ml)	DMF (ml)
UiO-66	1	0.712	0	0.10	110
UiO-66-NH ₂ -25	1	0.5346	0.1943	0.10	110
UiO-66-NH ₂ -50	1	0.3564	0.3886	0.10	110
UiO-66-NH ₂ -75	1	0.1782	0.5830	0.10	110
UiO-66-NH ₂	1	0	0.7773	0.10	110

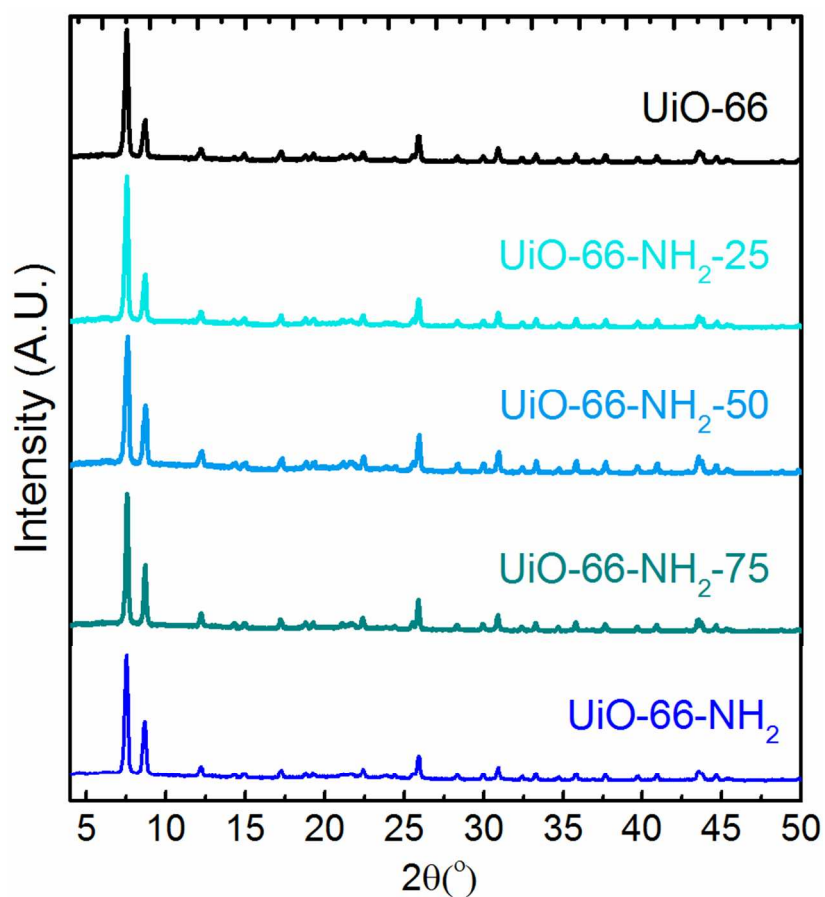


Figure S1: Comparison of the powder X-ray diffraction patterns of the as synthesized mixed linker –MOF series in the 4-50°, 2θ range.

B) PXRD and TGA-DSC of the undissolved solid obtained after MOF digestion.

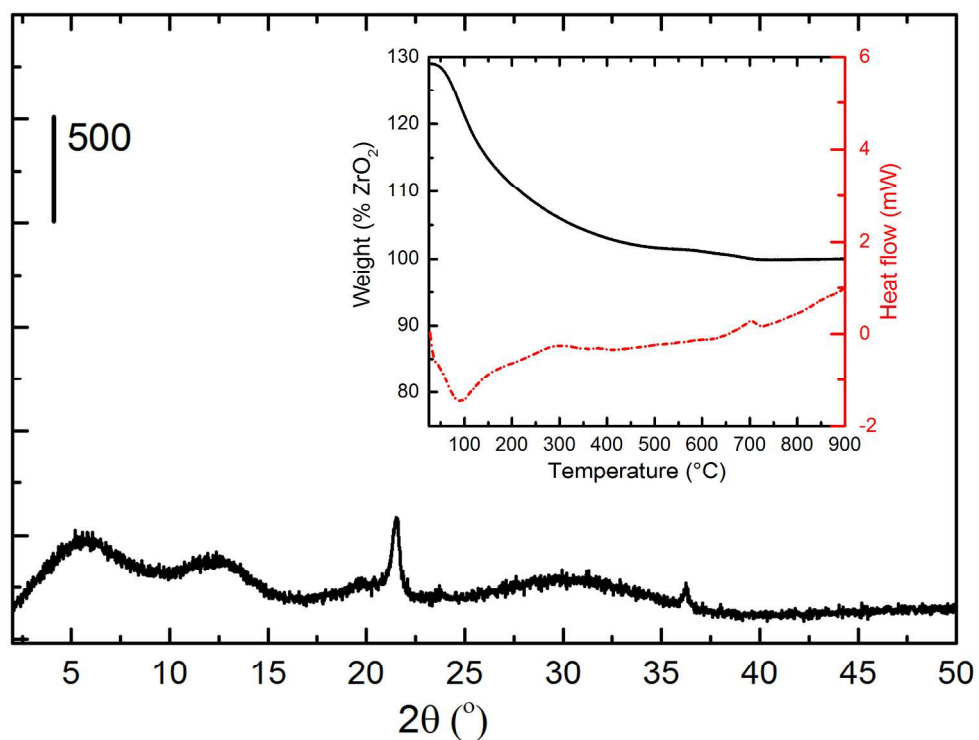


Figure S2. The PXRD and TG-DSC of the undissolved solid obtained after the digestion of UiO-66-NH₂ MOF sample in 1M NaOH. PXRD clearly shows no sign of residual MOF while TG-DSC results show no weight loss and exothermic heat signal expected for the burning of ligand/organic residue. In the diffraction pattern a peak at 21.41, 2θ is due to the plastic foil used to cover the sample while collecting the data.

C) Diffuse Reflectance UV-visible spectra of as synthesized mixed linker–MOFs series.

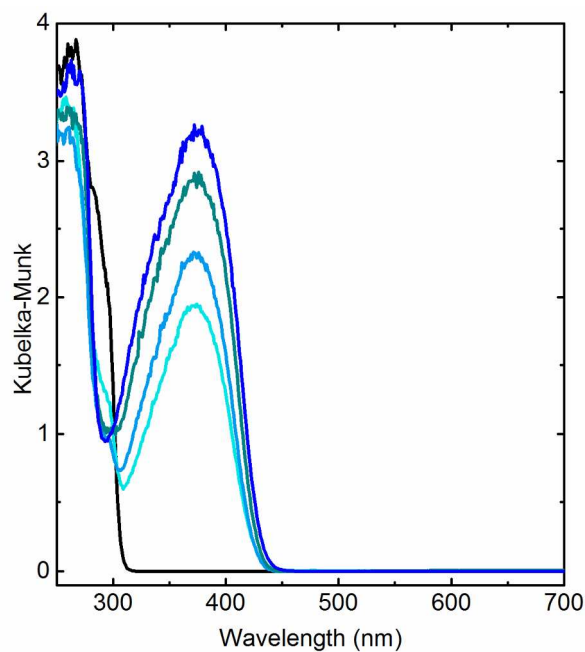


Figure S3. Diffuse reflectance Uv-visible spectra of samples containing DMF: UiO-66, UiO-66-NH₂-25, UiO-66-NH₂-50, UiO-66-NH₂-75, and UiO-66-NH₂.

D) UV-visible absorbance spectra of ABDC standard solution in 1M NaOH .

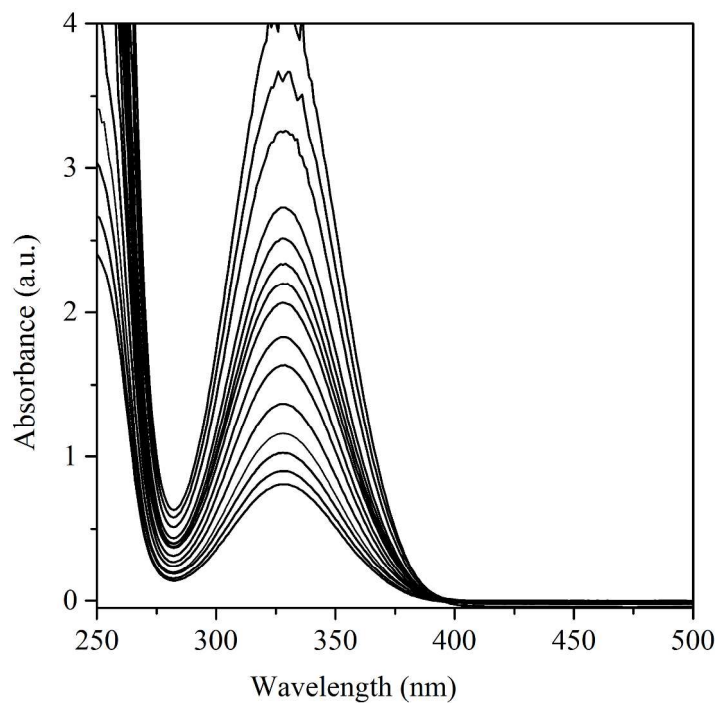


Figure S4: Absorbance spectra of the ABDC standard solutions in 1M aqueous NaOH solution. These spectra are used to obtain the calibration curve shown in figure 2 inset of the paper.

E) Quantitative analysis of ABDC linker in the mixed linker-MOFs series by UV-visible spectroscopy.

Table S2. The quantitative analyses of ABDC linker in the series of mixed linker-MOFs, Samples were digested in 35 ml of 1M NaOH-D₂O for 24h. Absorbance spectra of solutions were recorded after filtering out the white precipitate (most probably of zirconium hydroxide).

MOF	Sample Mass mg	Actual mass of MOF ^a mg	Calc. mass of ABDC ^b mg	Calc. [ABDC×10 ⁻⁴] ^c mol L ⁻¹	Exp. [ABDC×10 ⁻⁴] mol L ⁻¹	Exp. mol % of ABDC ^d
UiO-66-NH ₂	10.1	7.07	4.34	6.42	6.69	104
UiO-66-NH ₂ -75	10.4	7.28	3.39	5.02	4.70	70
UiO-66-NH ₂ -50	15.5	10.85	3.41	5.06	5.50	54
UiO-66-NH ₂ -25	20.0	14.0	2.23	3.31	4.0	30

^a Actual mass of MOF (65 weight % of the sample Mass) is the sample mass excluding solvent.

^b Theoretical mass of ABDC = $\frac{6x \cdot M.W. of ABDC}{Theo. M.W. of MOF} \times Actual mass of MOF$, where x and the theoretical molecular weight of MOF is derived from the idealized chemical formula: Zr₆(O)₄(OH)₄(ABDC)_{6x}(BDC)_{6-6x}, where x = 0.25, 0.5, 0.75, and 1, for UiO-66-NH₂-25, -50, -75, and UiO-66-NH₂ respectively.

^c Theoretical [ABDC] = $\frac{Theo. Mass of ABDC}{M.W. of ABDC \cdot 35 \cdot 10^{-3} L}$

^d mol% of ABDC = $\frac{Experimental[ABDC]}{Theoretical[ABDC]} \cdot x \cdot 100 \%$

F) Quantitative analysis of ABDC linker in the mixed linker-MOFs series by ¹H-NMR spectroscopy

The mol % of ABDC was calculated from the integrals by first integrating the BDC signal (Figure 3a) and defining the integral as 12 protons (3 molecules, since the number of protons represented by the BDC signal is 4). The 3 ABDC signals were then integrated relative to this number (Figure 3b). In order for the relative concentration of ABDC to be represented by one number, the average of the three integrals (representing 1 proton each) was used. Finally, the following three formulae were applied to calculate the ABDC content of the samples:

$$\text{No. BDC molecules} = \frac{\text{BDC integral}}{\text{No. H Rep. (= 4)}}$$

$$\text{Relative No. ABDC molecules} = \frac{\text{Mean ABDC integral}}{\text{No. H Rep (= 1)}}$$

$$\text{mol\%. ABDC} = \frac{\text{Rel. No. ABDC molecule}}{\text{No. BDC molecule} + \text{Rel. No. ABDC molecule}}$$

G) Synthesis, PXRD and ^1H NMR spectra of mixed linker–MOFs series prepared with M:L=1:2, and 2 molar equivalent of HCl at 220 °C.

Table S3. Synthesis of Mixed linker-MOFs prepared at 220 °C					
MOFs	Reagent amount				
	ZrCl ₄ (g)	BDC (g)	ABDC (g)	HCL (ml)	DMF (ml)
UiO-66	3.52	5.02	0	2.68	91.25
ML-MOF-1	3.52	3.77	1.37	2.68	91.25
ML-MOF-2	3.52	2.51	2.73	2.68	91.25
ML-MOF-3	3.52	1.25	4.10	2.68	91.25
UiO-66-NH ₂	3.52	0	5.64	2.68	91.25

In this series of samples, the total amount of DMF was split in two/three equal parts for the synthesis of phase pure/mixed linker–MOFs respectively. ZrCl₄, BDC and ABDC were dissolved separately in different portions of DMF. All 35% HCl was added to the flask designated to ZrCl₄ prior to the addition of metal salt. Following the successful dissolution of all synthesis components, the two/three solutions were mixed together, transferred to 200 ml Teflon-lined autoclaves, and heated to 220 °C for 20 hours under static conditions. The powder precipitates were filtered, washed in boiling water and finally dried at 60 °C in air.

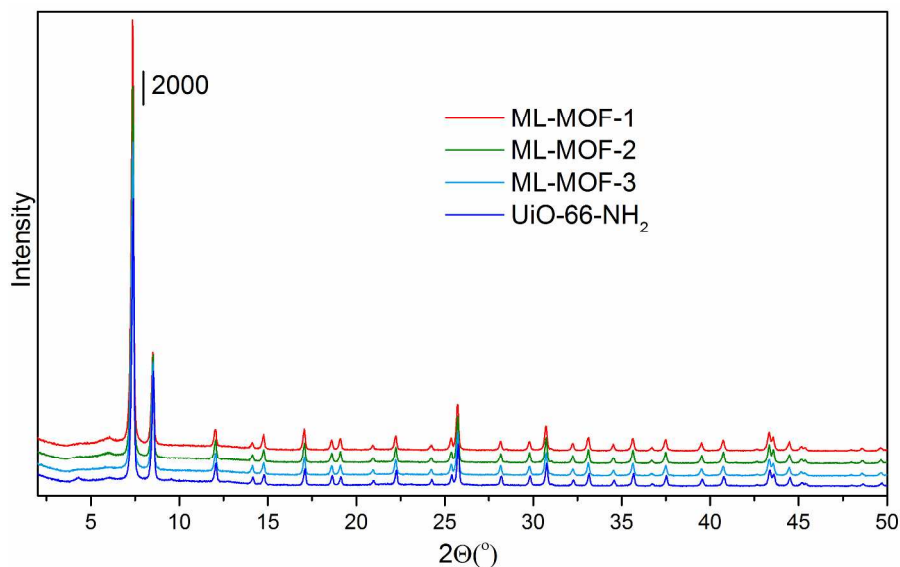


Figure S5. Comparison of the PXRD patterns of the mixed linker-MOFs.

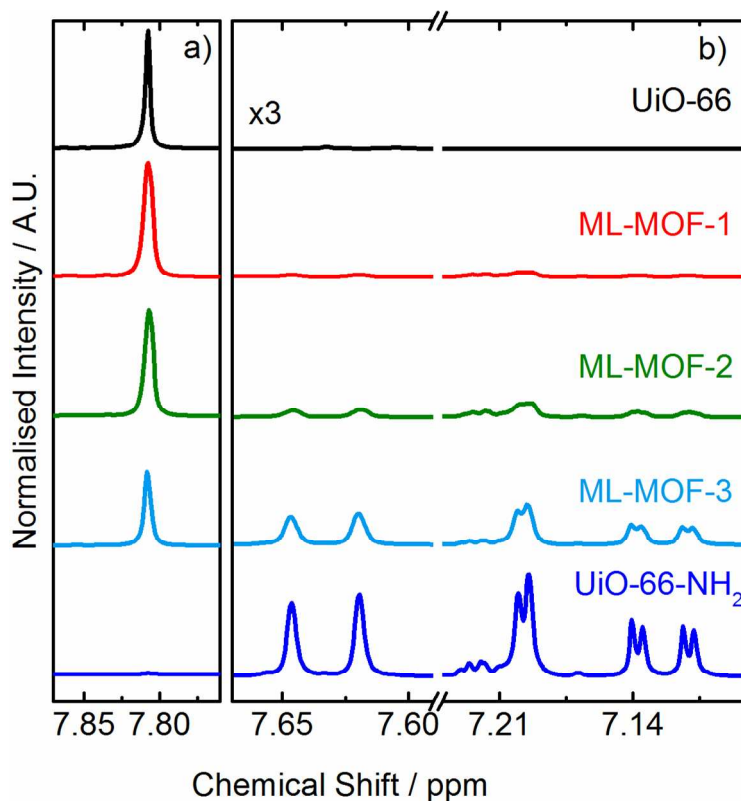


Figure S6. Normalized ^1H NMR spectra of digested samples of a mixed linker-MOF series prepared at 220°C and with a metal to linker ratio of 1:2. Samples were digested for 24h in a 1M solution of NaOH in D_2O . Signals of ABDC proton in part b are multiplied by factor of 3, for easy visual comparison of the signal intensities.

Table S4. mol% of ABDC determined by ^1H NMR spectroscopy.

Sample	mol % of ABDC
ML-MOF-1	4
ML-MOF-2	15
ML-MOF-3	53
UiO-66-NH ₂	100

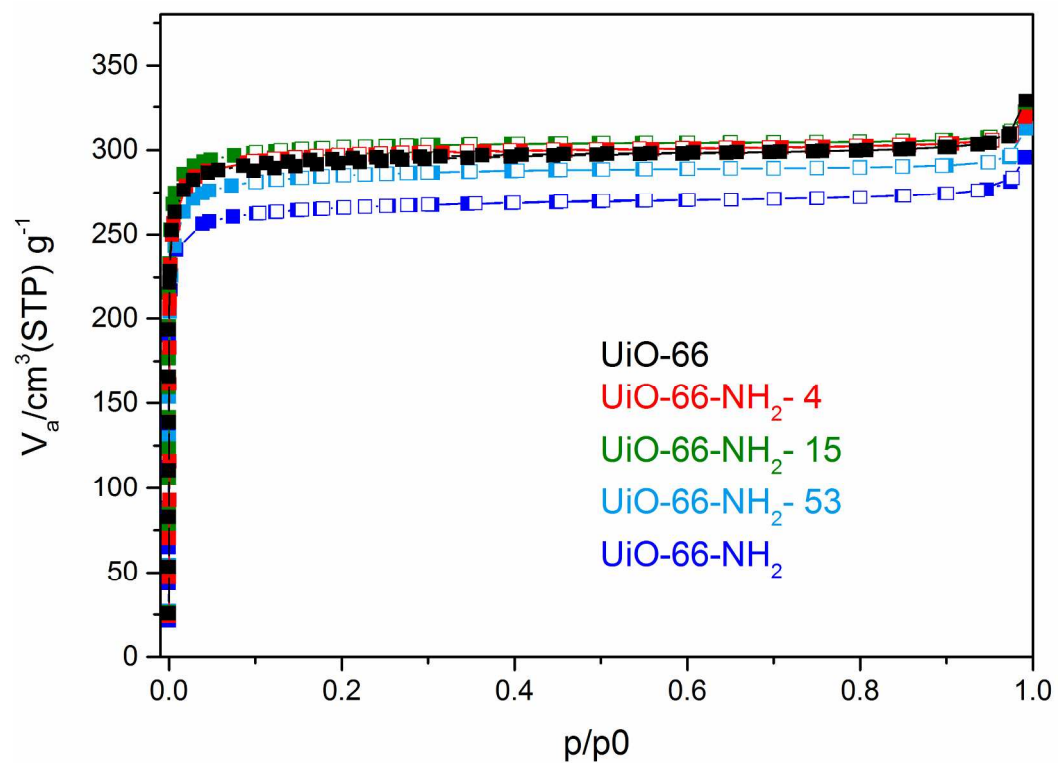


Figure S7. N₂ adsorption at 77K on the set of mixed linker-MOF prepared at 220 °C with 1:2 metal to linker ration, and with addition of HCl.

H) Comparison of TG-DTA results of UiO-66-NH₂-50 with 1:1 physical mixture of UiO-66 + UiO-66-NH₂.

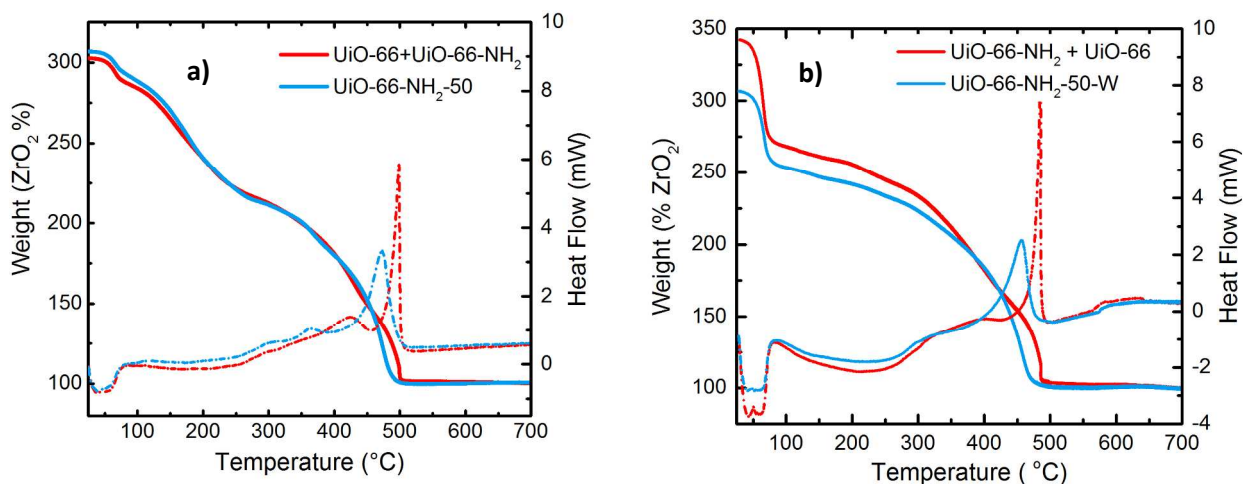


Figure S8. TGA-DSC analyses of physically prepared mixture with 1:1 molar ratio of UiO-66 and UiO-66-NH₂, with UiO-66-NH₂-50. Part A and B show the data obtained on as prepared and water washed samples respectively. Samples were heated from 25 to 700 °C, at rate of 1 °C min⁻¹ under dry air flux (N₂, at 20ml/min and O₂ at, 5ml/min).

As previously seen, very little difference in the weight loss behavior and the distinct, broad heat signal for UiO-66-NH₂-50 is observed for water washed samples. This not only confirms the reproducibility of the data but also prove our proposed hypothesis that the sample prepared here indeed contain randomly distributed linker and not the mixture of separate phase.

I) Thermal stability of mixed linker –MOFs :PXRD

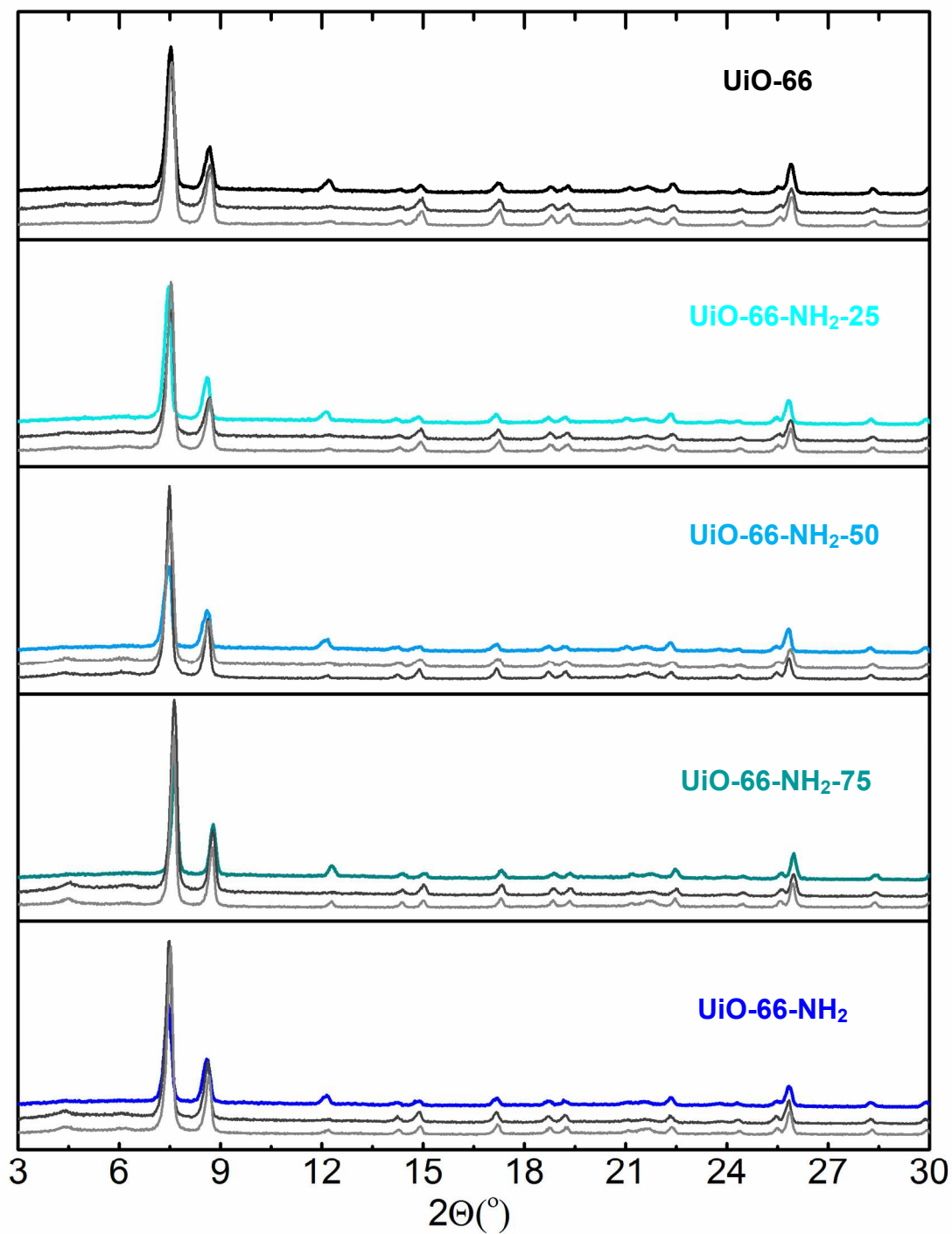


Figure S9: Powder XRD patterns of a) UiO-66, b) UiO-66-NH₂-25, c) UiO-66-NH₂-50, d) UiO-66-NH₂-75 and e) UiO-66-NH₂. Within each plot are three curves which from top to bottom represent the sample as synthesized (with the same color code used in previous figures), water washed (dark grey) and after heating at 200 °C for 12h in air (grey).

J) PXRD after N₂ sorption experiments

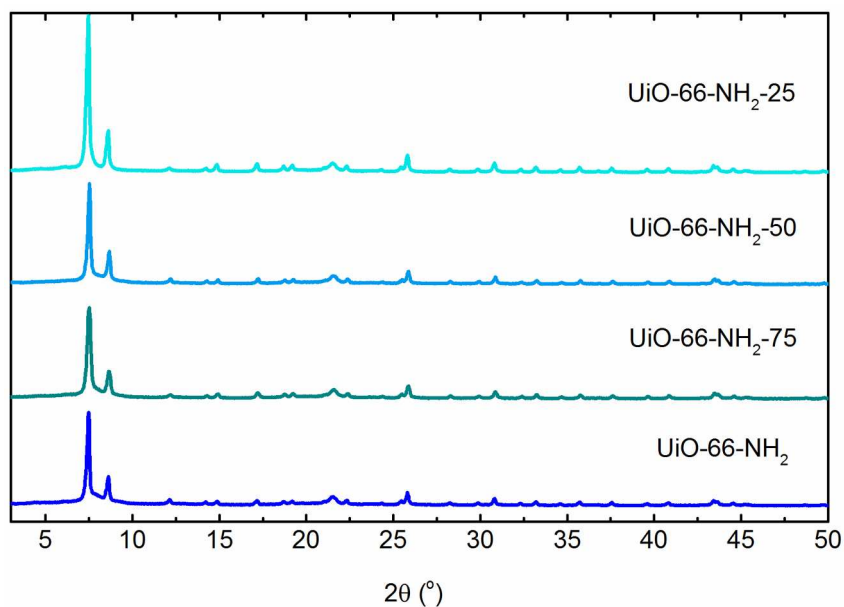


Figure S10: PXRD patterns of the mixed linker -MOFs after N₂ sorption experiments, elucidating the framework stability to the removal of solvents.

K) Chemical stability of UiO-66-NH₂-25 and UiO-66-NH₂-75.

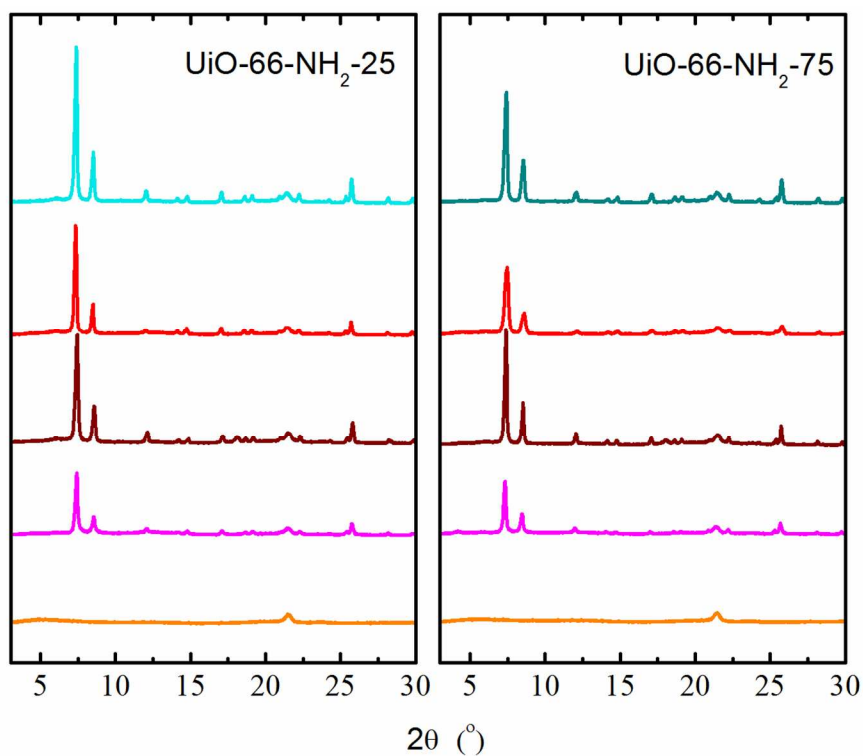


Figure S11: PXRD patterns of MOFs as prepared (with same color code used in previous figures), and after the treatment of 1 month in water (red), 24h reflux in water (brown), 24h in 1M HCl (magenta) and 24h 1M NaOH (orange).

L) N₂ adsorption on MOFs refluxed in water for 24h.

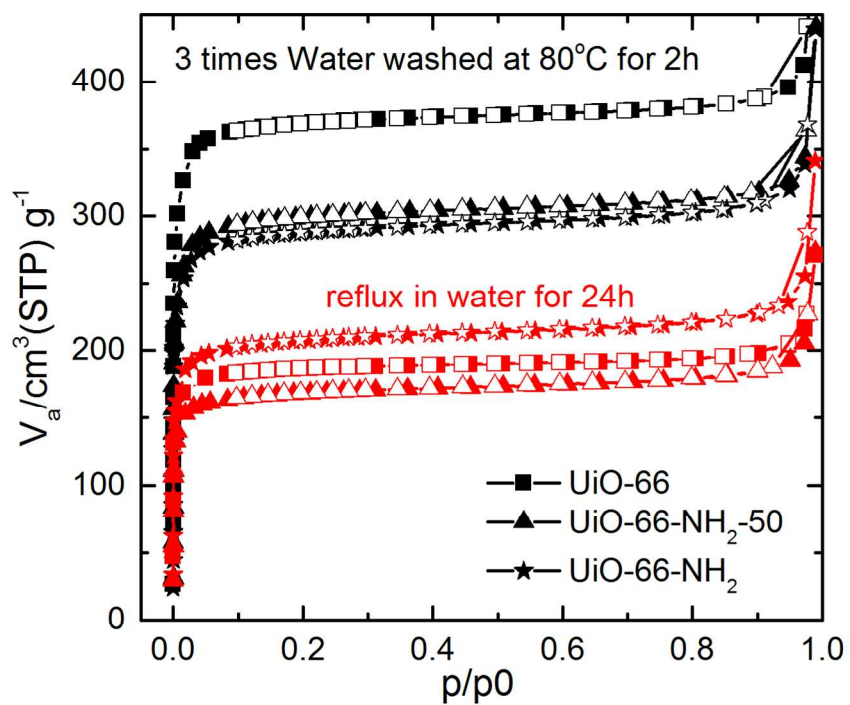


Figure S12. N₂ sorption of MOFs; UiO-66 (square), UiO-66-NH₂-50 (triangle) and UiO-66-NH₂ (star) water washed at 80 °C (black) and after reflux in water for 24h (red).