ELECTRONIC SUPPLEMENTARY INFORMATION

Solvent-dependent textural properties of defective UiO-66 after acidic and basic treatment

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Chemicals and reagents

All chemicals and solvents were purchased from commercial suppliers (VWR, Sigma-Aldrich, Fluka, ABCR, Alfa Aesar, Merck) and used as received without further purification. After opening, the solvents were flushed with argon to ensure minimum variation in the water content.

Nitrogen physisorption analysis

Samples were activated in a Micromeritics VacPrep 061 sample preparation system for 16-20 hours at 120 °C under vacuum, then cooled before being flushed with nitrogen and weighed. All nitrogen sorption isotherms were measured on a Micromeritics 3Flex Physisorption instrument at 77 K. The specific surface area was determined according to the Brunauer-Emmett-Teller (BET) method by fitting the isotherms in the 0.002 to 0.05 p/p_0 range to meet the consistency criteria described by Gómez-Gualdrón *et al.*[1]

Powder X-Ray Diffraction (PXRD) analysis

All PXRD measurements were conducted on a Bruker D8 Advance diffractometer working in Bragg-Brentano geometry, with Cu $K\alpha_1$ radiation wavelength of 1.541 Å. Diffraction was measured in the 2θ range between 4° and 40°. Approximately 50 mg of powder were placed on a sample holder and pressed to minimize preferential orientation of the crystals. All the samples were measured after nitrogen physisorption.

Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analyses were performed in a Netzsch STA 449 C Jupiter instrument. The samples were heated from 30 °C to 750 °C with a heating rate of 5 °C/min under a flow of nitrogen (32 cm^3/min) and oxygen (8 cm^3/min).

Synthesis and characterization of highly defective UiO-66 (HD-UiO-66)

Terephthalic acid (H_2BDC) (2.09 g, 12.6 mmol) and zirconium tetrachloride (2.92 g, 12.6 mmol) were dissolved in dimethylformammide (DMF) (100 mL). Acetic acid (21.5 mL, 376 mmol) and water (1.35 mL) were added to the mixture and stirred at room temperature for 30 minutes to give a cloudy white suspension. This was split into eight separate 20 mL crimp cap vials, which were heated in an oven to 120 °C with a 2 °C/min ramp. After 24 hours, the vials were transferred to a water bath and cooled rapidly from 70 °C to 20 °C and were then vented by piercing the septum with a needle. After centrifuging and decanting, the solid was washed twice with DMF (35 mL) and once with methanol (35 mL) and was left to soak in methanol (25 mL) overnight. It was centrifuged, decanted and transferred to a glass vial and then dried in vacuum at 75 °C overnight. The PXRD pattern of the product is comparable to that of a defect-free UiO-66 structure (Figure S1). Nitrogen physisorption deviates significantly from a type-I towards a type-II isotherm, indicating the presence of mesopores (Figure S2).[2] The surface area calculated with the BET method was of 2020 m^2/g.

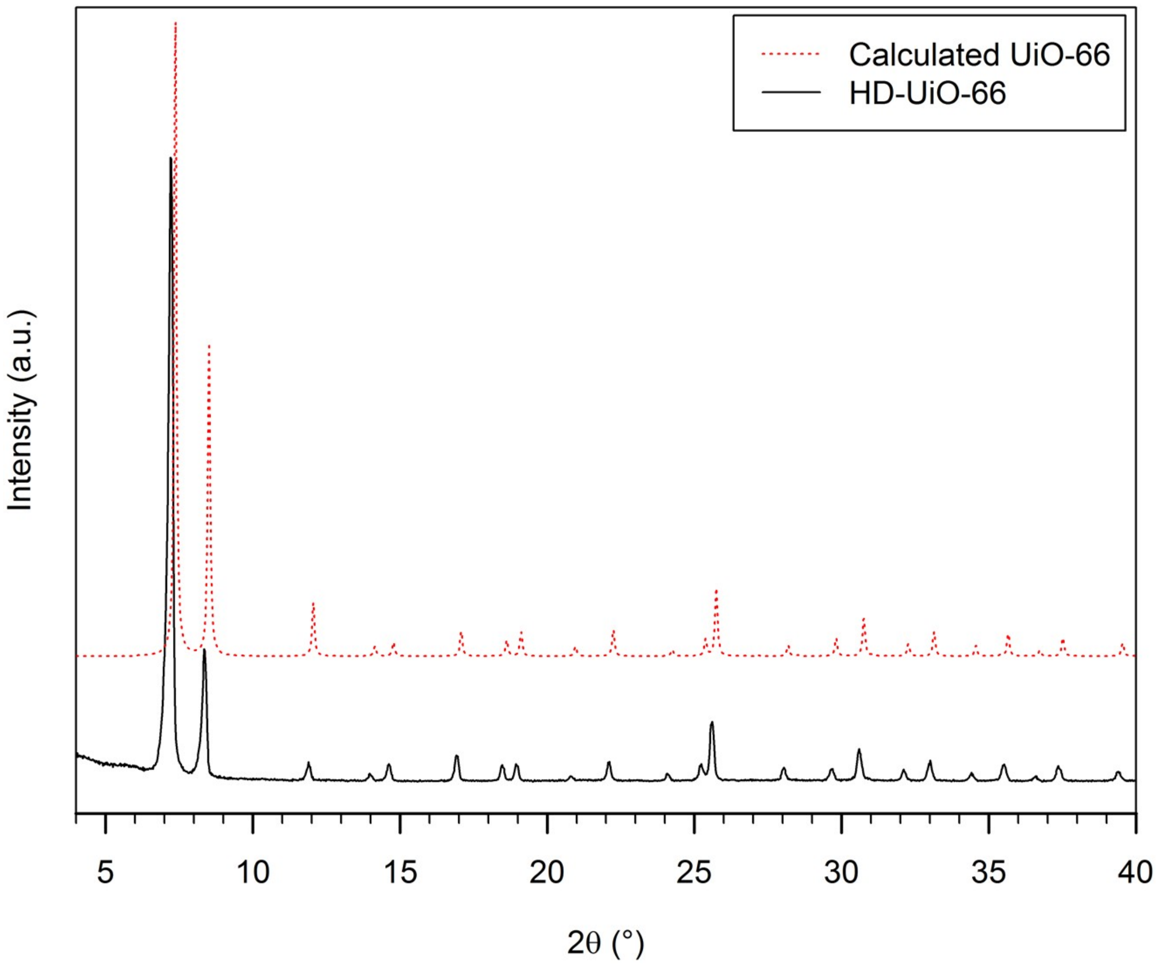

Figure S1: PXRD pattern of HD-UiO-66 (black line). The calculated PXRD pattern for a defect-free UiO-66 is added as a reference (red dotted line).

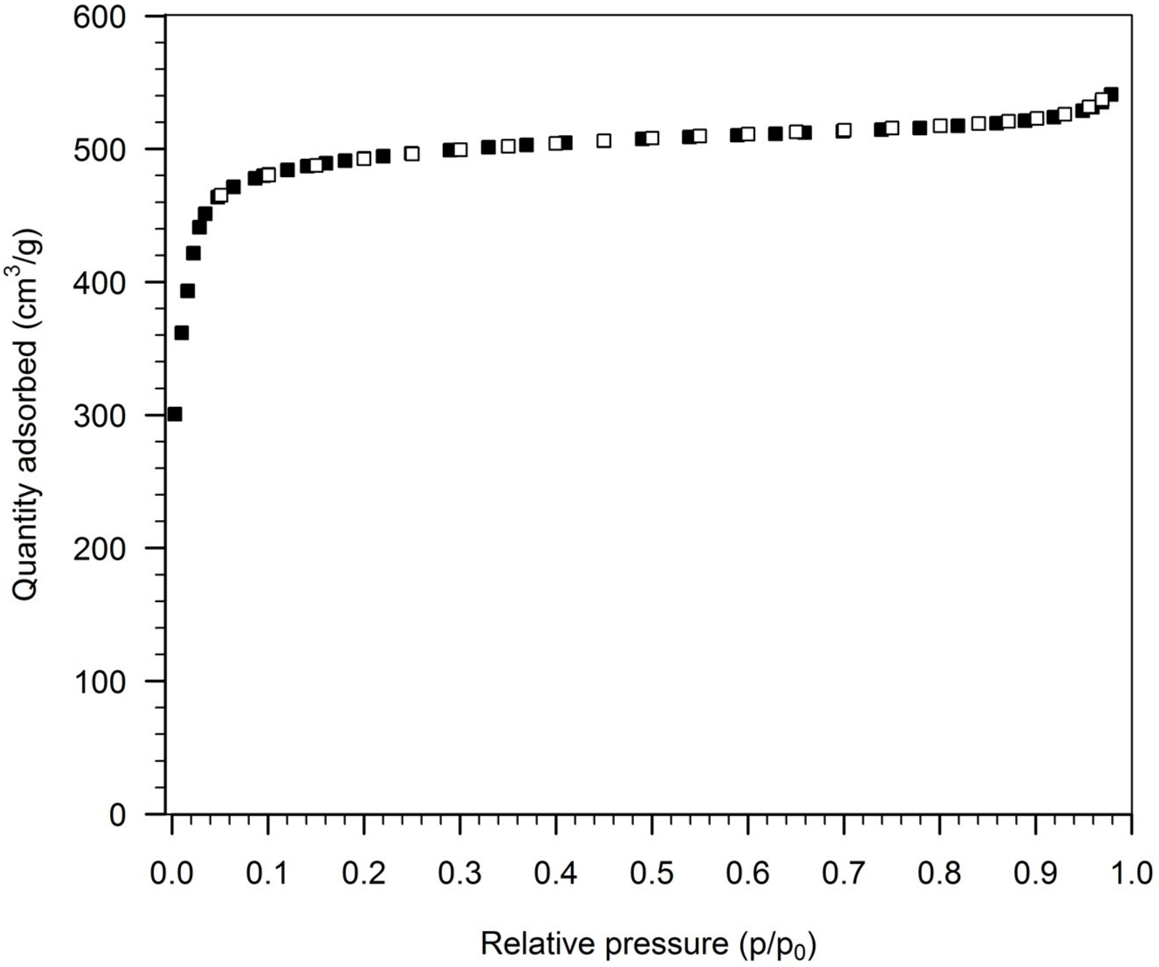

Figure S2: Nitrogen physisorption isotherm of HD-UiO-66, adsorption represented by filled squares, desorption by open squares.

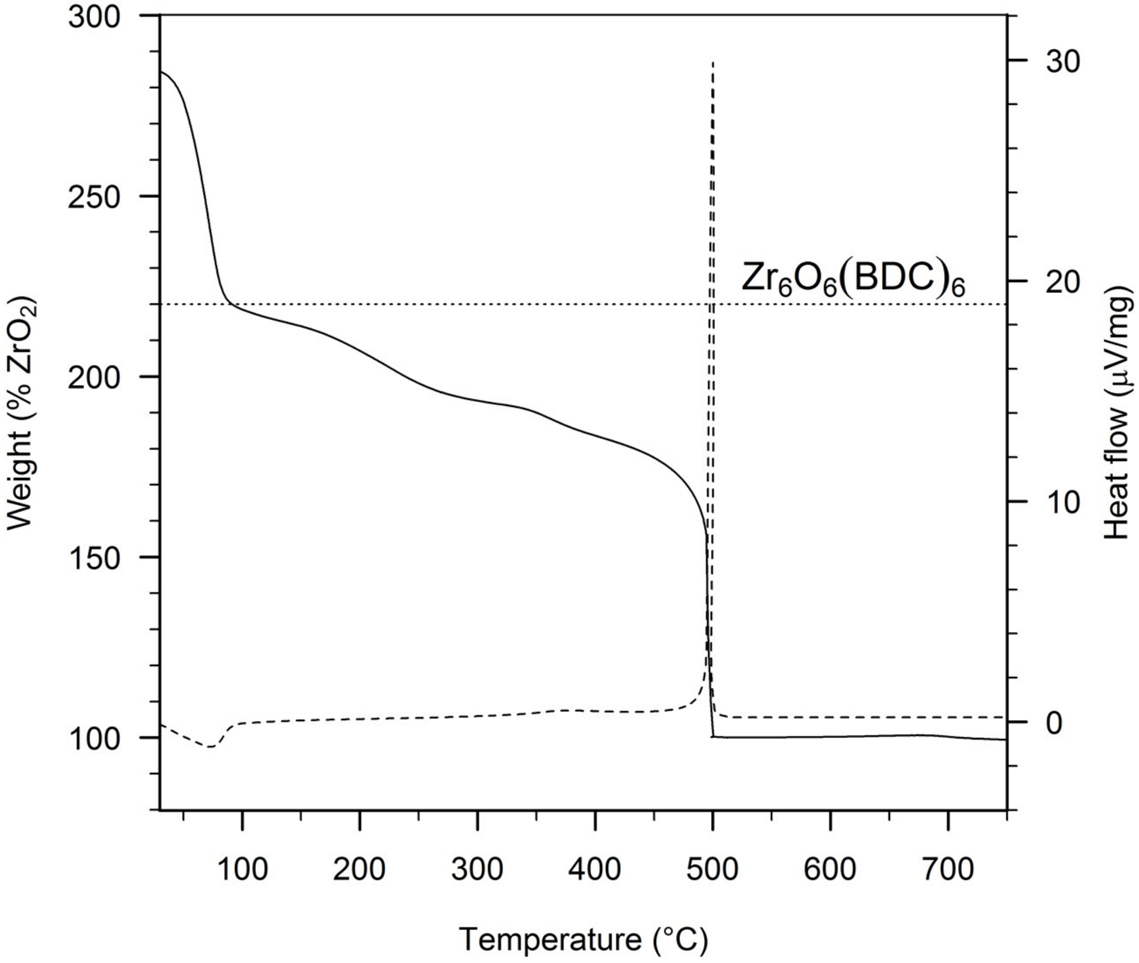

Figure S3: TGA-DSC curve of HD-UiO-66.

Synthesis and characterization of defective UiO-66 (D-UiO-66)

H_2BDC (2.09 g, 12.6 mmol) and zirconium tetrachloride (2.92 g, 12.6 mmol) were dissolved in DMF (100 mL). Acetic acid (21.5 mL, 376 mmol) and water (1.35 mL) were added to the mixture and stirred at room temperature for 30 minutes to give a cloudy white suspension. This was split into eight separate 20 mL crimp cap vials, which were heated in an oven to 120 °C with a 2 °C/min ramp. After 24 hours, the vials were allowed to slowly cool to room temperature, and were then vented by piercing the septum with a needle. After centrifuging and decanting, the solid was washed twice with DMF (35 mL) and soaked overnight in DMF (20 ml), then washed once with methanol (35 mL) and soaked in methanol (25 mL) over the weekend. It was centrifuged, decanted and transferred to a glass vial, and then dried in vacuum at 75 °C overnight. The PXRD pattern of the product is comparable to that of a defect-free UiO-66 structure (Figure S4). The nitrogen physisorption isotherm shows a similar shape to that of HD-UiO-66 but with a lower uptake (Figure S5). TGA (Figure S6) shows a linker-to-node ratio of around 3.1.

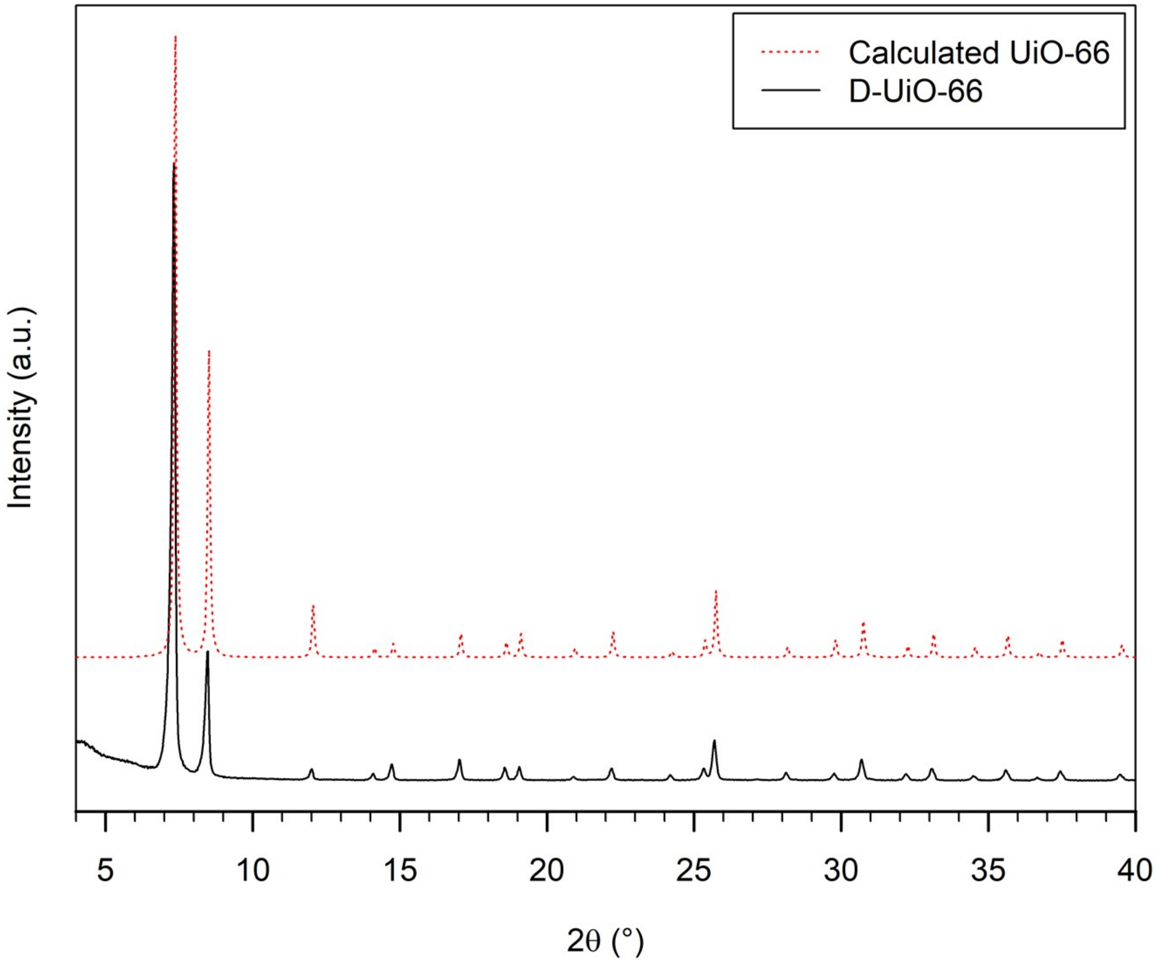

Figure S4: PXRD pattern of D-UiO-66 (black line). The calculated PXRD pattern for a defect-free UiO-66 is added as a reference (red dotted line).

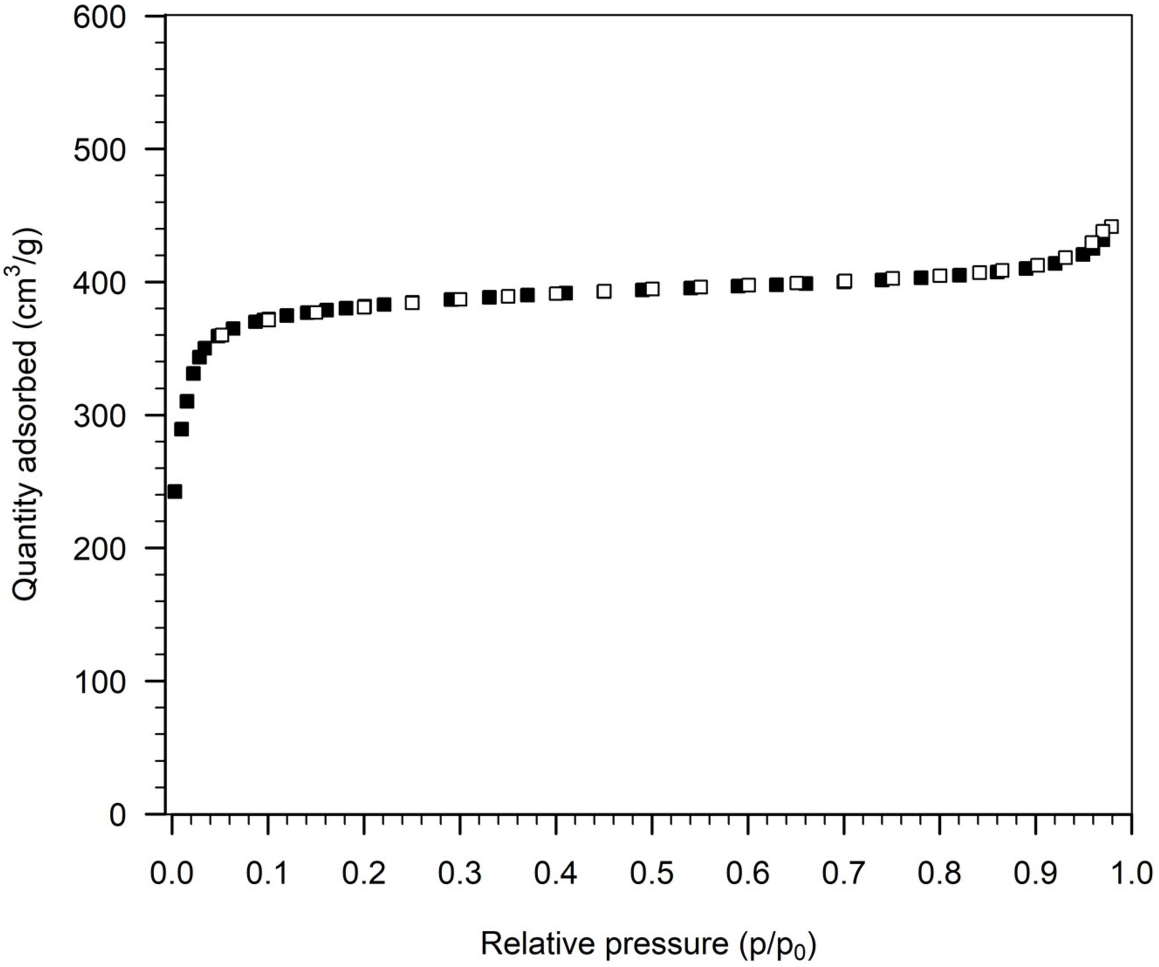

Figure S5: Nitrogen physisorption isotherm of D-UiO-66, adsorption represented by filled squares, desorption by open squares.

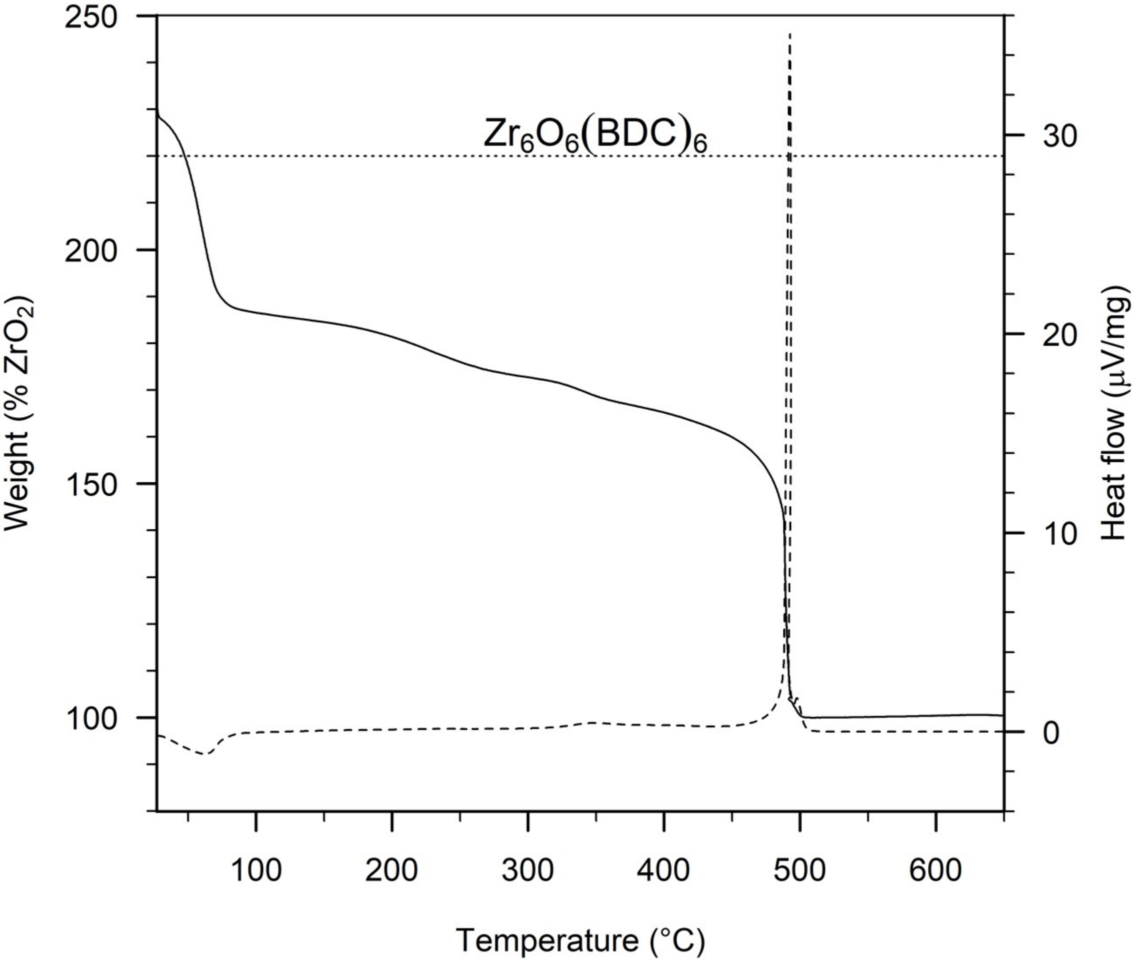

Figure S6: TGA-DSC curve of D-UiO-66.

Treatment with acids and bases in different solvents

The acid (sulphuric acid (H_2SO_4), trifluoroacetic acid (TFA) or acetic acid (AcOH)) or the base (potassium carbonate (K_2CO_3), 1,1,3,3-tetramethylguanidine (TMG) and triethylamine (Et_3N)) was used in 10-fold excess, the solvent volume was such that the concentration of acid or base would be 0.1 mol/L.

HD-UiO-66 or D-UiO-66 (100 mg) was weighed in a centrifuge tube. Solvent exchange was performed by adding 10 mL of the reaction solvent (H_2O, THF, or DCM) and mixing it on a Vortex mixer for five minutes, followed by centrifugation for 10 minutes at 8000 RPM and decantation. The solvent (5 ml) and acid/base (0.5 mmol) were added and the tubes were shaken on an incubator stand at 600 RPM at room temperature for 24 hours. Shaking was chosen over stirring to avoid mechanical stress. After the test, the samples were centrifuged and washed twice with 10 mL of clean solvent. The samples were subsequently dried in vacuum for 16 hours at room temperature and analysed within two days to limit potential decomposition. The mass variation in the sample was assessed by weighing it before nitrogen physisorption after activation. Table S1 shows the values for the BET surface area and the recovered mass of all the samples obtained by chemical treatment of HD-UiO-66. The PXRD patterns in the manuscript highlight the signals at higher angles; Figures S7-S27 give the raw diffraction patterns. Table S2 provides a comparison of the retained surface area for the samples obtained by chemical treatment of HD-UiO-66 and of D-UiO-66.

Table S1: BET surface area, percentage of retained surface area and percentage of retained mass for all samples obtained by chemical treatment of HD-UiO-66.

Entry	Solvent	Acid/Base	BET surface area (m^2/g)	Surface area ratio sample/pristine (%)	Mass ratio sample/pristine (%)
1	-	Pristine	2020	-	-
2	H_2O	-	1590	79	59
3	H_2O	H_2SO_4	1630	81	88
4	H_2O	TFA	1700	84	99
5	H_2O	AcOH	1820	90	91
6	H_2O	K_2CO_3	540	27	49
7	H_2O	TMG	980	49	54
8	H_2O	Et_3N	1020	50	62
9	THF	-	1620	80	73
10	THF	H_2SO_4	50	2	103
11	THF	TFA	1510	75	106
12	THF	AcOH	1700	84	100
13	THF	K_2CO_3	1060	52	156
14	THF	TMG	470	23	111
15	THF	Et_3N	1760	87	73
16	DCM	-	1850	92	72
17	DCM	H_2SO_4	70	3	120
18	DCM	TFA	680	34	64
19	DCM	AcOH	1950	97	79
20	DCM	K_2CO_3	680	34	121
21	DCM	TMG	640	32	84
22	DCM	Et_3N	1710	85	57

Table S2: Retained BET surface area upon chemical treatment of HD-UiO-66 and D-UiO-66 with solvents and acids or bases.

Entry	Solvent	Acid/Base	Retained BET SA HD-UiO-66[a] (%)	Retained BET SA D-UiO-66 (%)
1	H_2O	-	79	92[b]
2	H_2O	H_2SO_4	81	8[b]
3	H_2O	TFA	84	93[b]
4	H_2O	AcOH	90	102[b]
5	H_2O	K_2CO_3	27	15[b]
6	H_2O	TMG	49	45[b]
7	H_2O	Et_3N	50	50[b]
8	THF	-	80	101[b]
9	THF	H_2SO_4	2	2[b]
10	THF	TFA	75	84[c]
11	THF	AcOH	84	97[c]
12	THF	K_2CO_3	52	48[c]
13	THF	TMG	23	35[c]
14	THF	Et_3N	87	96[c]
15	DCM	-	92	102[b]
16	DCM	H_2SO_4	3	11[b]
17	DCM	TFA	34	38[c]
18	DCM	AcOH	97	92[c]
19	DCM	K_2CO_3	34	8[c]
20	DCM	TMG	32	35[c]
21	DCM	Et_3N	85	89[c]

[a] HD-UiO-66: BET surface area of the starting material = 2020 m^2/g

[b] D-UiO-66: BET surface area of the starting material = 1730 m^2/g

[c] D-UiO-66: BET surface area of the starting material = 1550 m^2/g.

PXRD patterns of the materials obtained from chemical treatment of HD-UiO-66

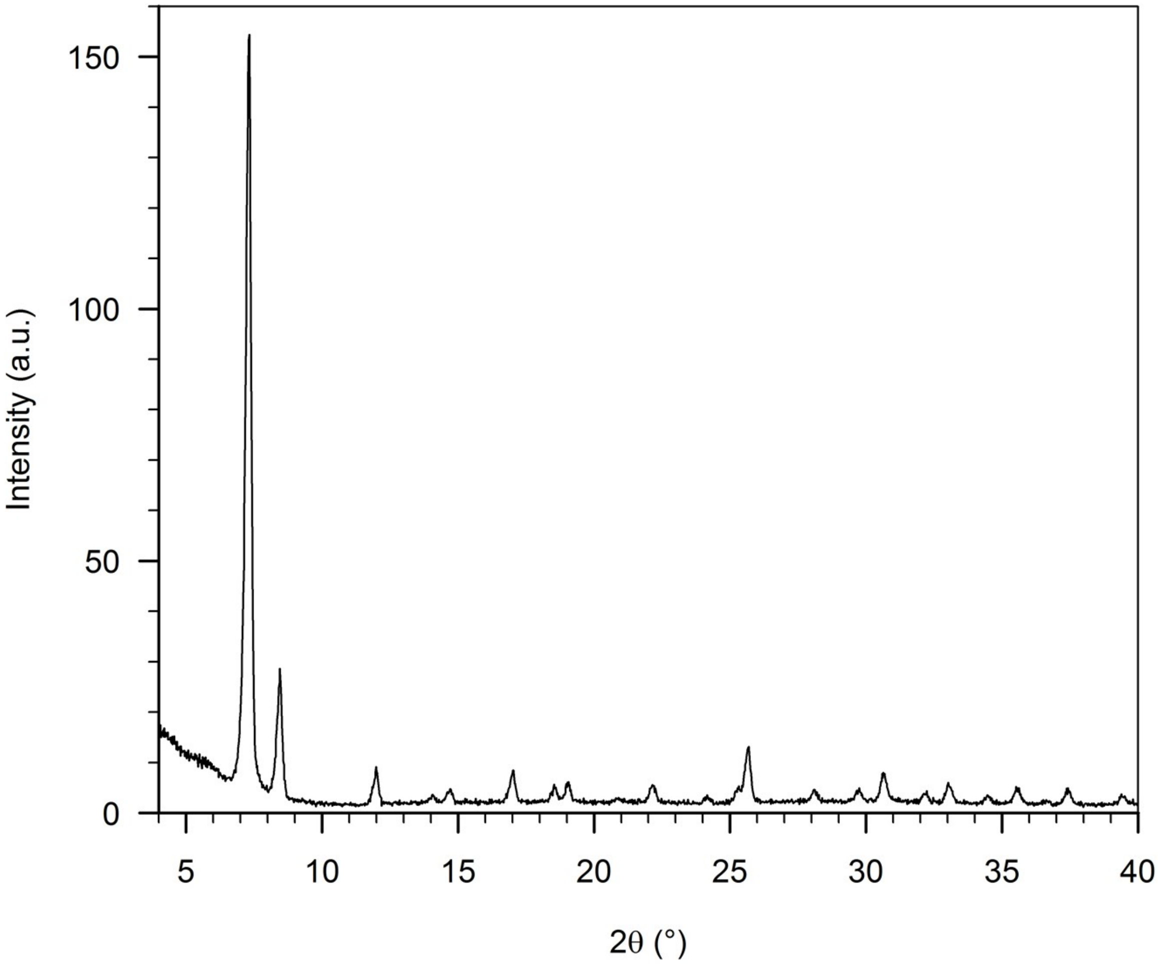

Figure S7: PXRD pattern of HD-UiO-66 treated with water.

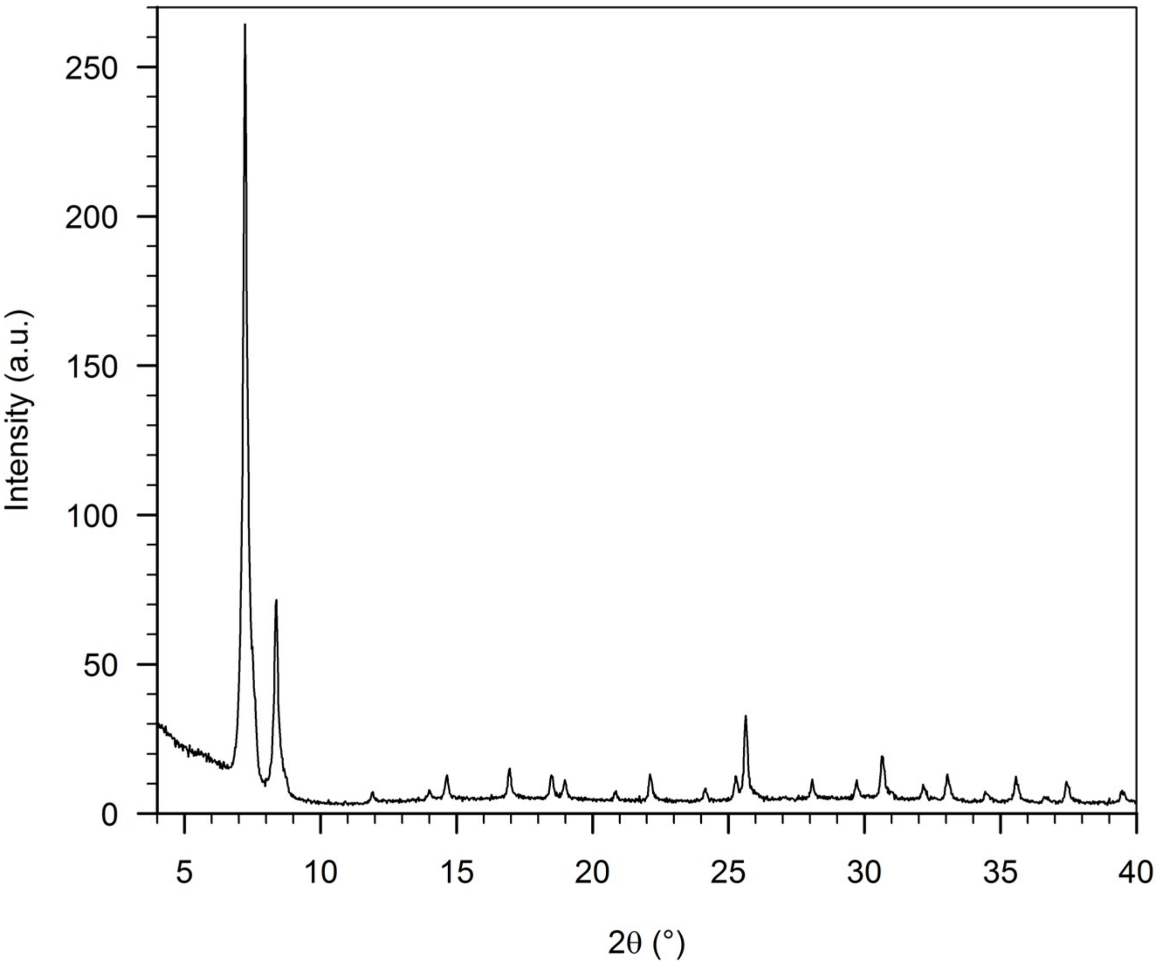

Figure S8: PXRD pattern of HD-UiO-66 treated with H_2SO_4 in water.

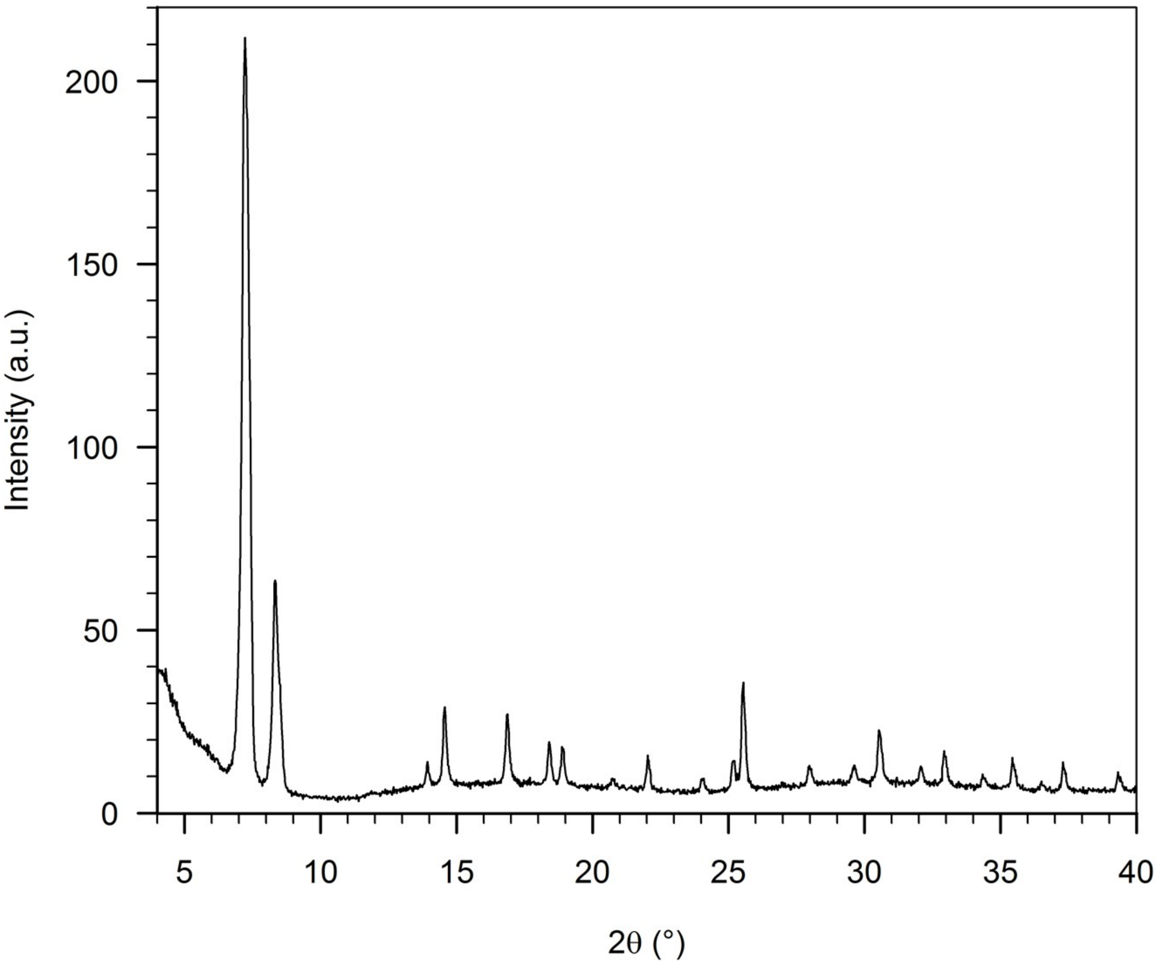

Figure S9: PXRD pattern of HD-UiO-66 treated with TFA in water.

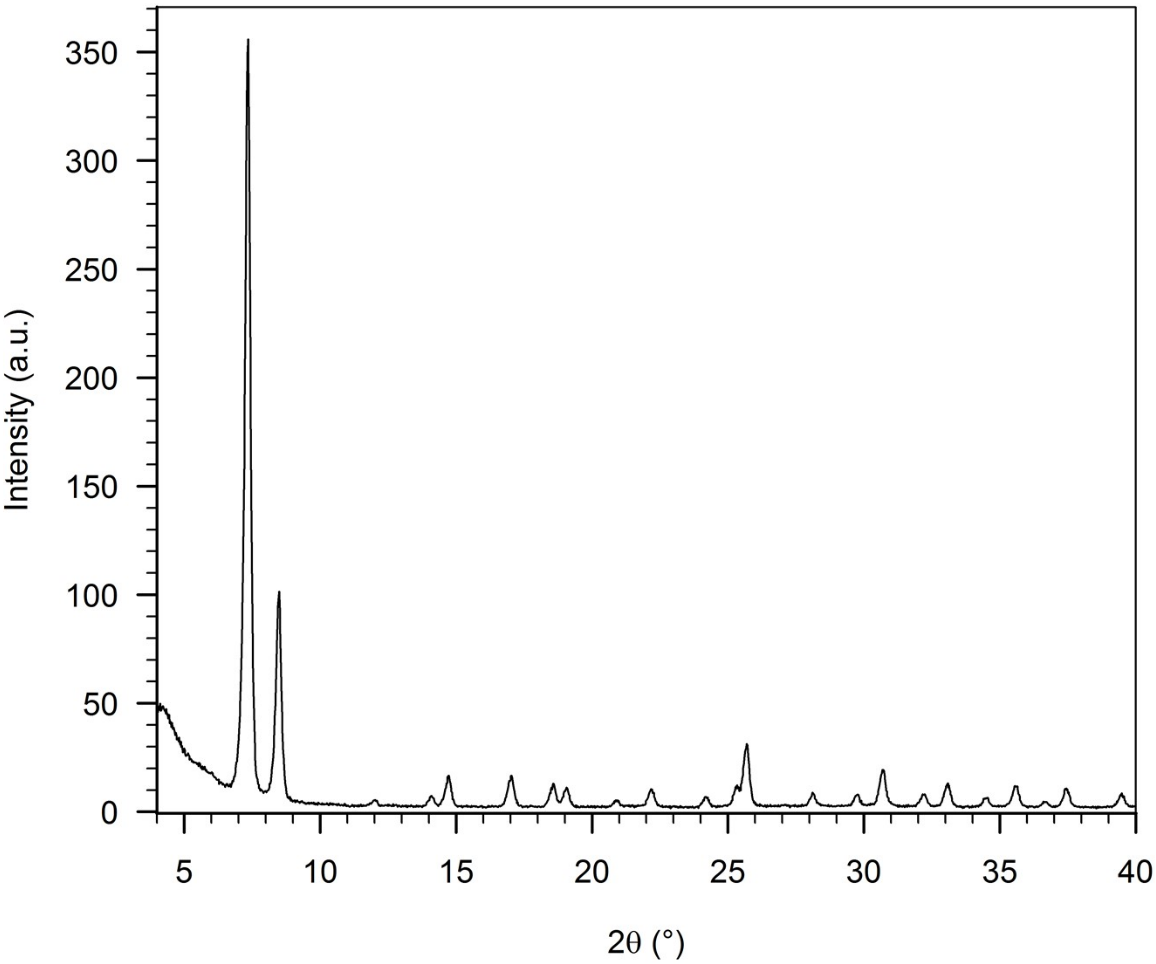

Figure S10: PXRD pattern of HD-UiO-66 treated with AcOH in water.

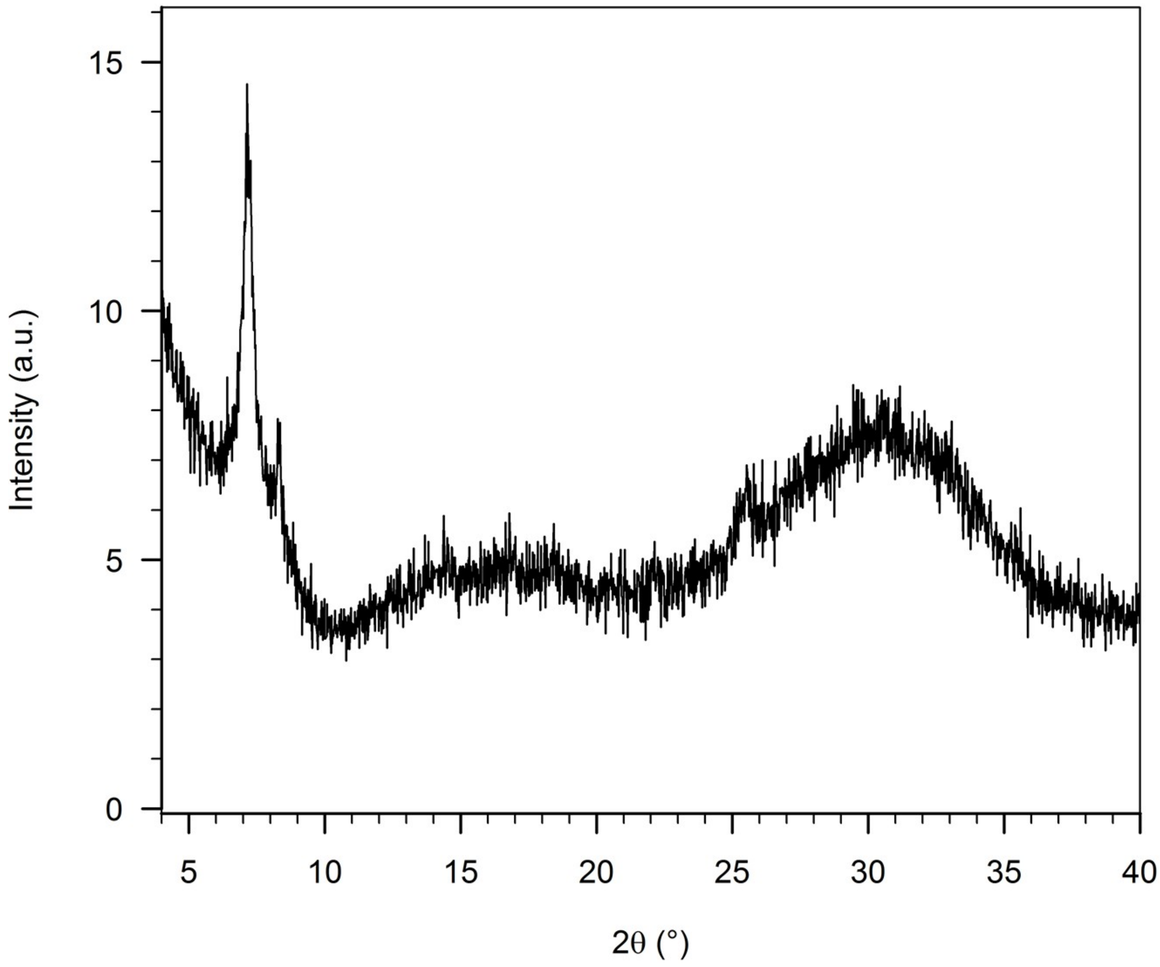

Figure S11: PXRD pattern of HD-UiO-66 treated with K_2CO_3 in water.

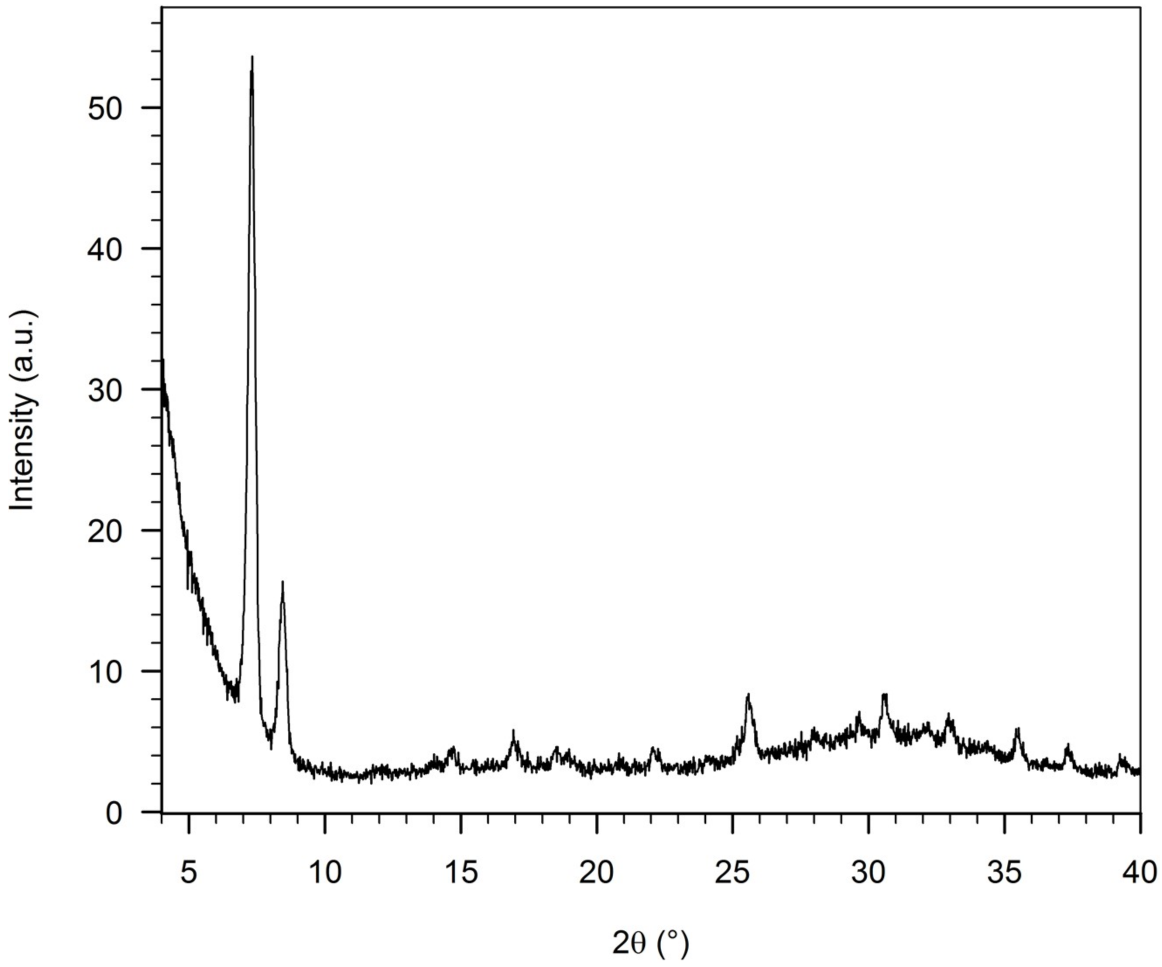

Figure S12: PXRD pattern of HD-UiO-66 treated with TMG in water.

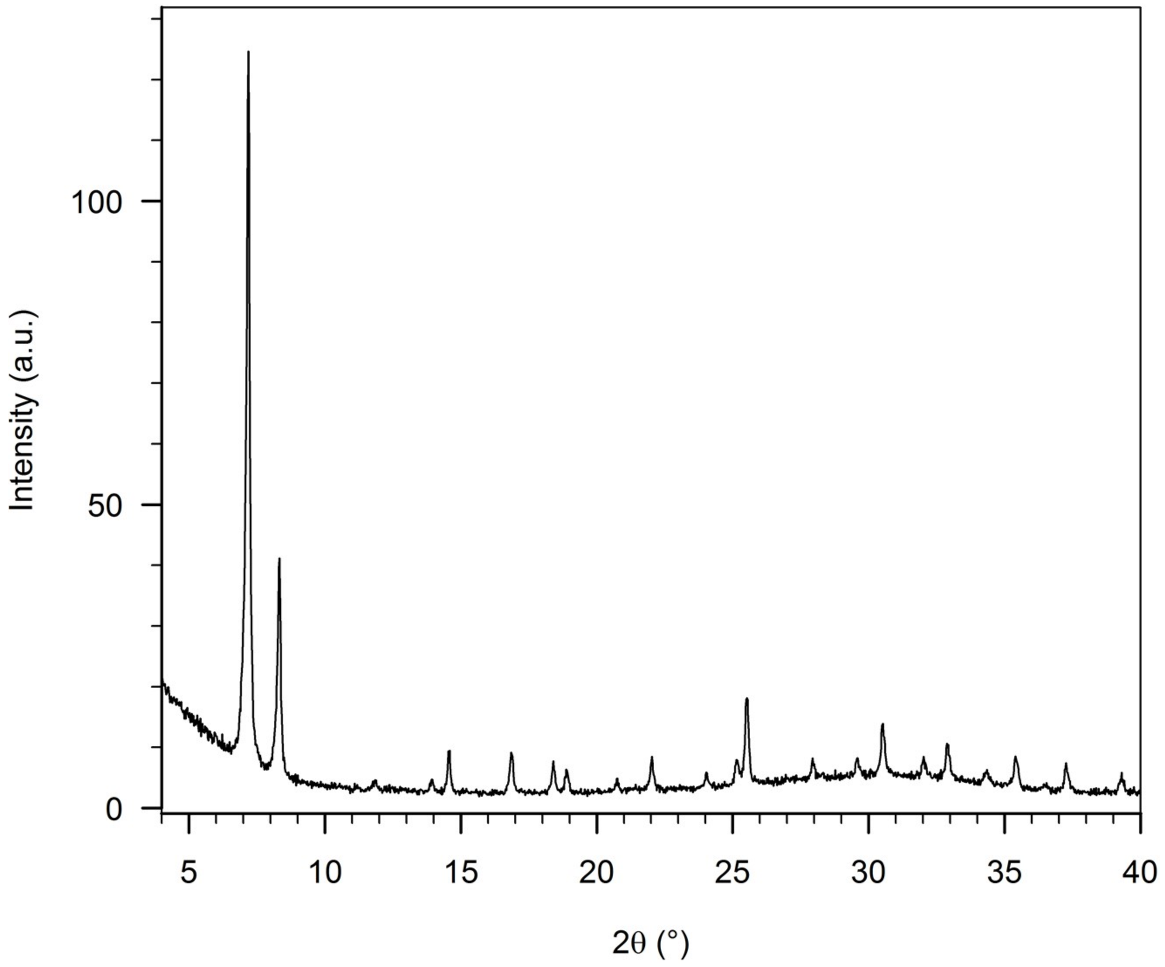

Figure S13: PXRD pattern of HD-UiO-66 treated with Et_3N in water.

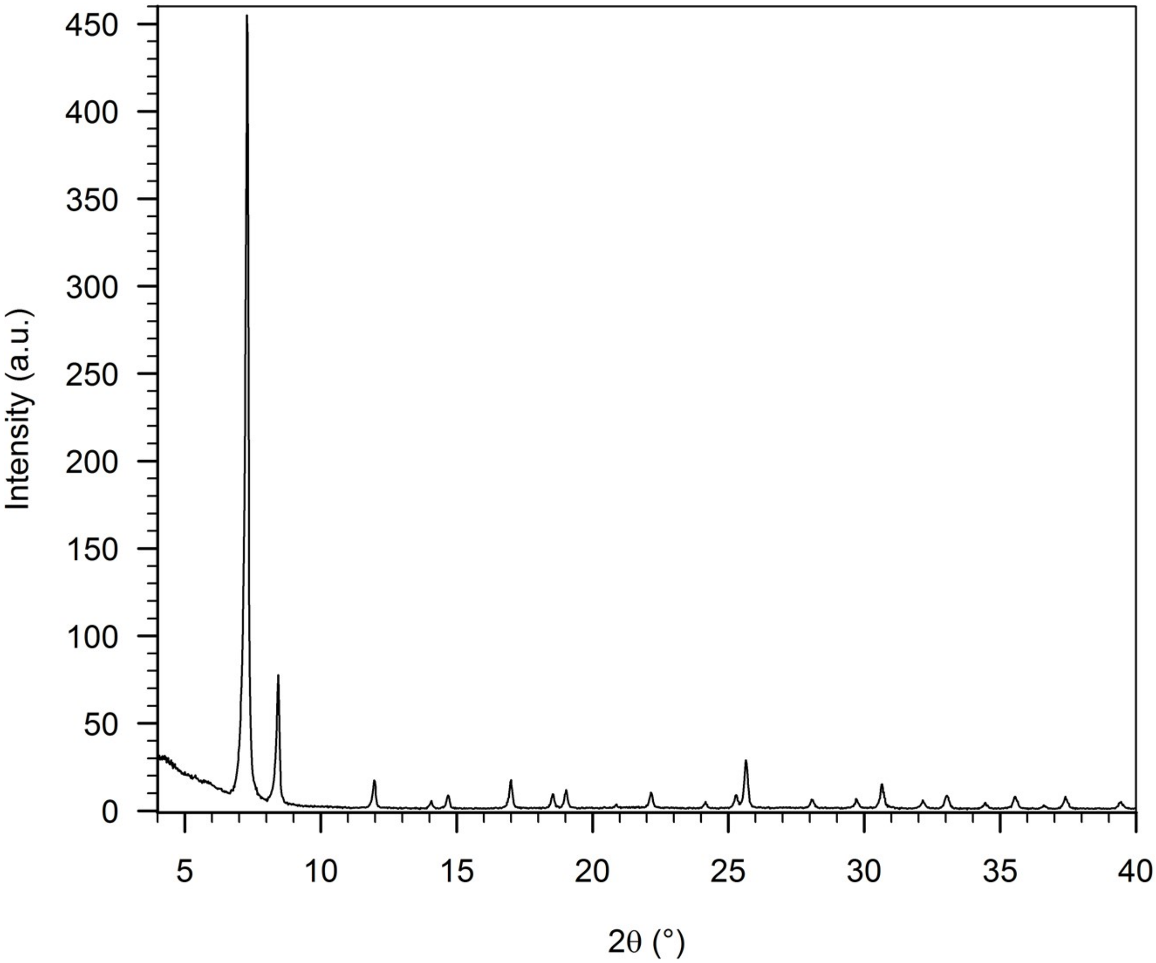

Figure S14: PXRD pattern of HD-UiO-66 treated with THF.

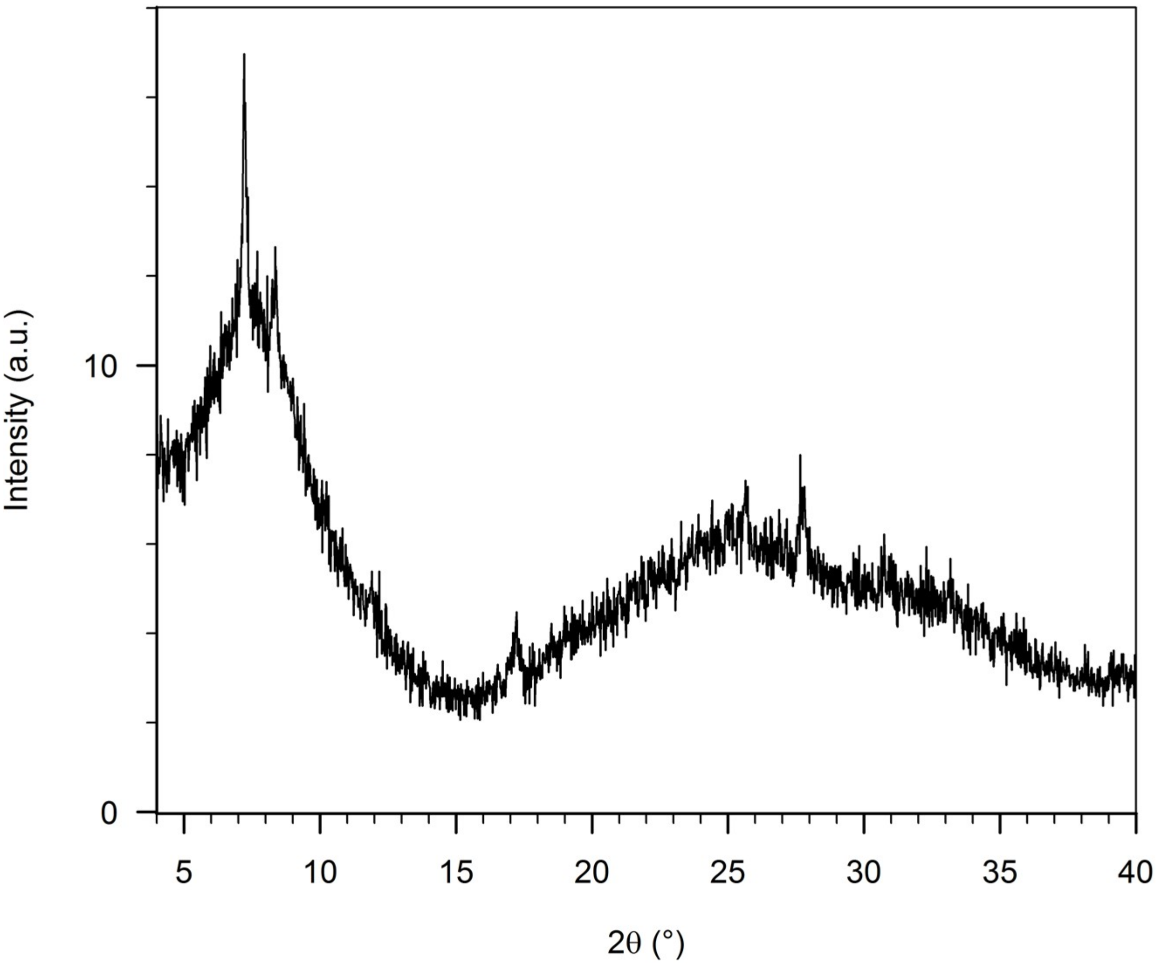

Figure S15: PXRD pattern of HD-UiO-66 treated with H_2SO_4 in THF.

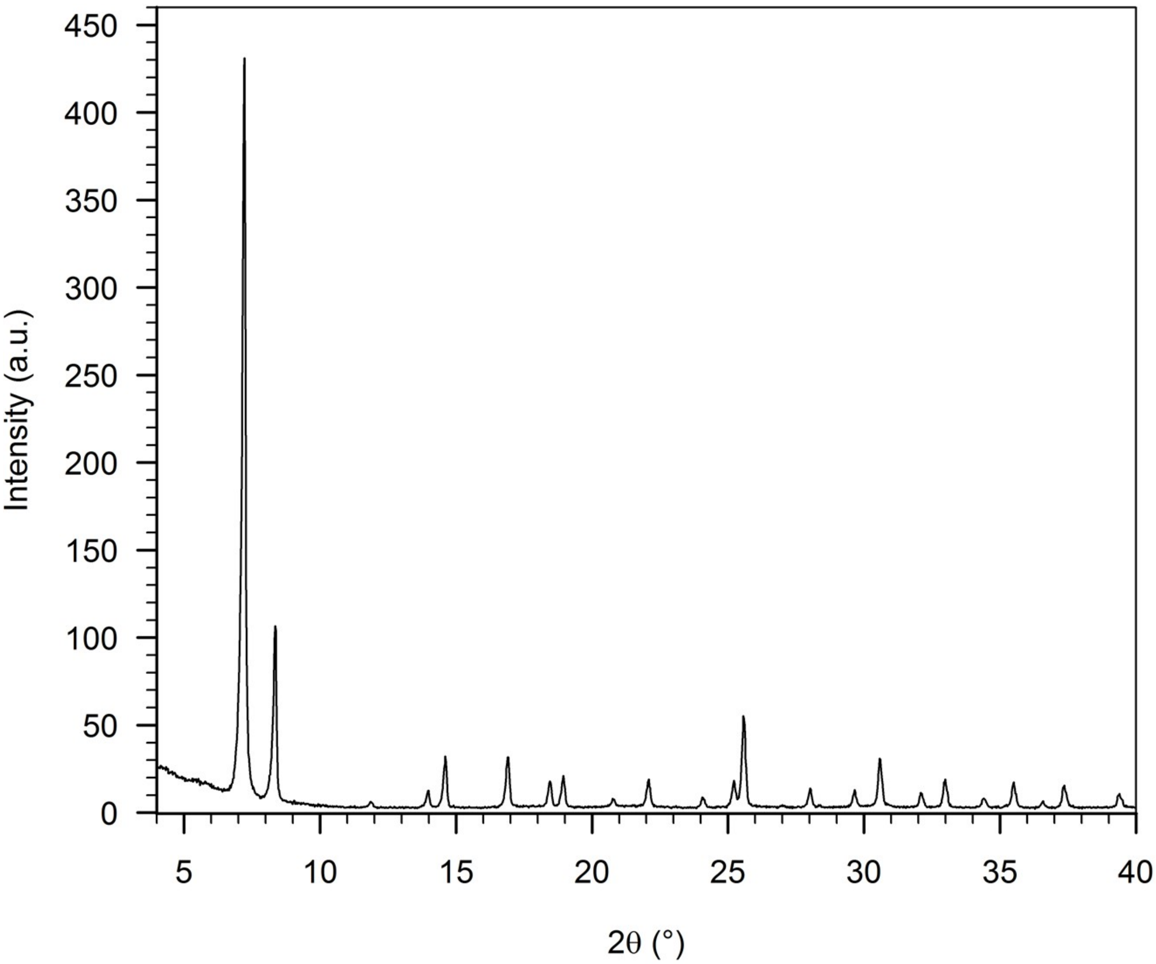

Figure S16: PXRD pattern of HD-UiO-66 treated with TFA in THF.

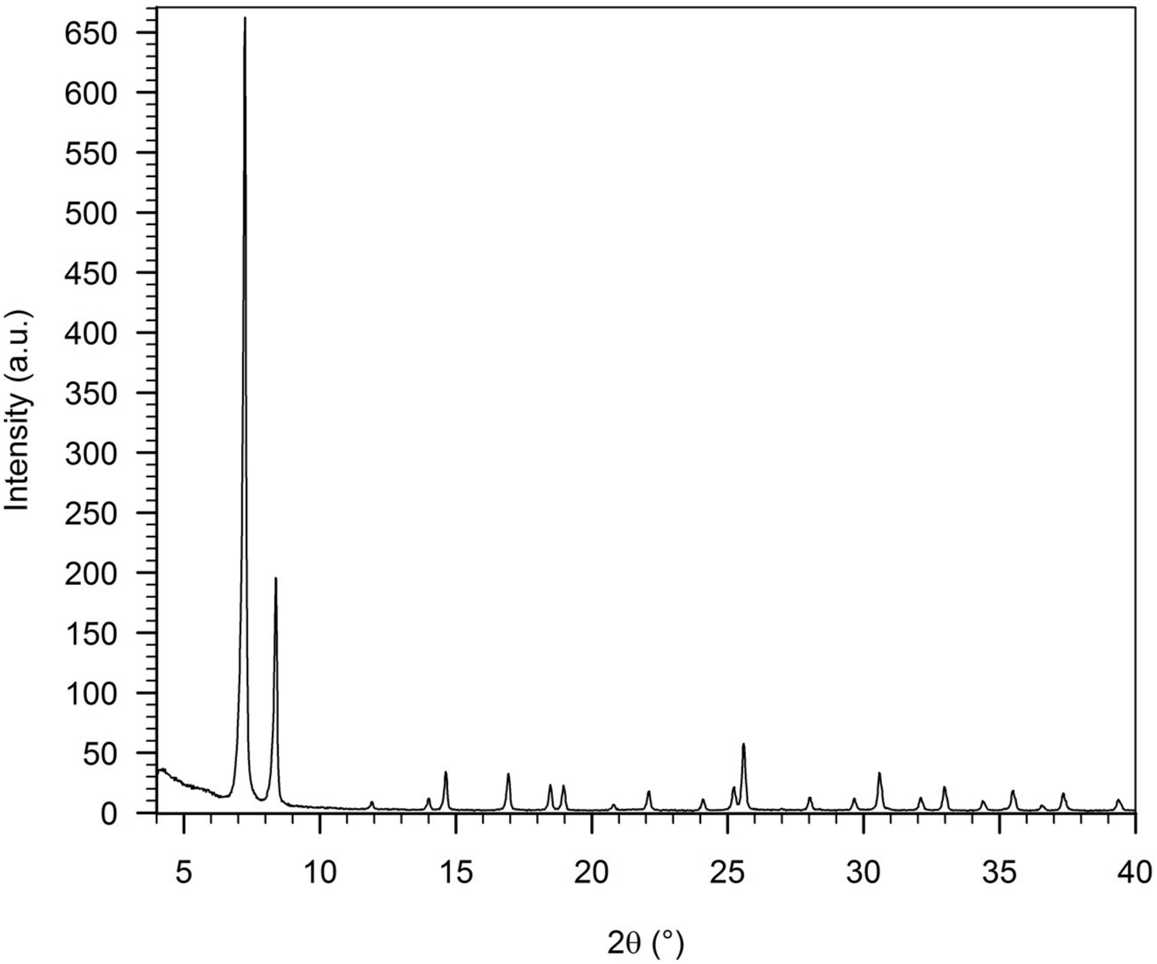

Figure S17: PXRD pattern of HD-UiO-66 treated with AcOH in THF.

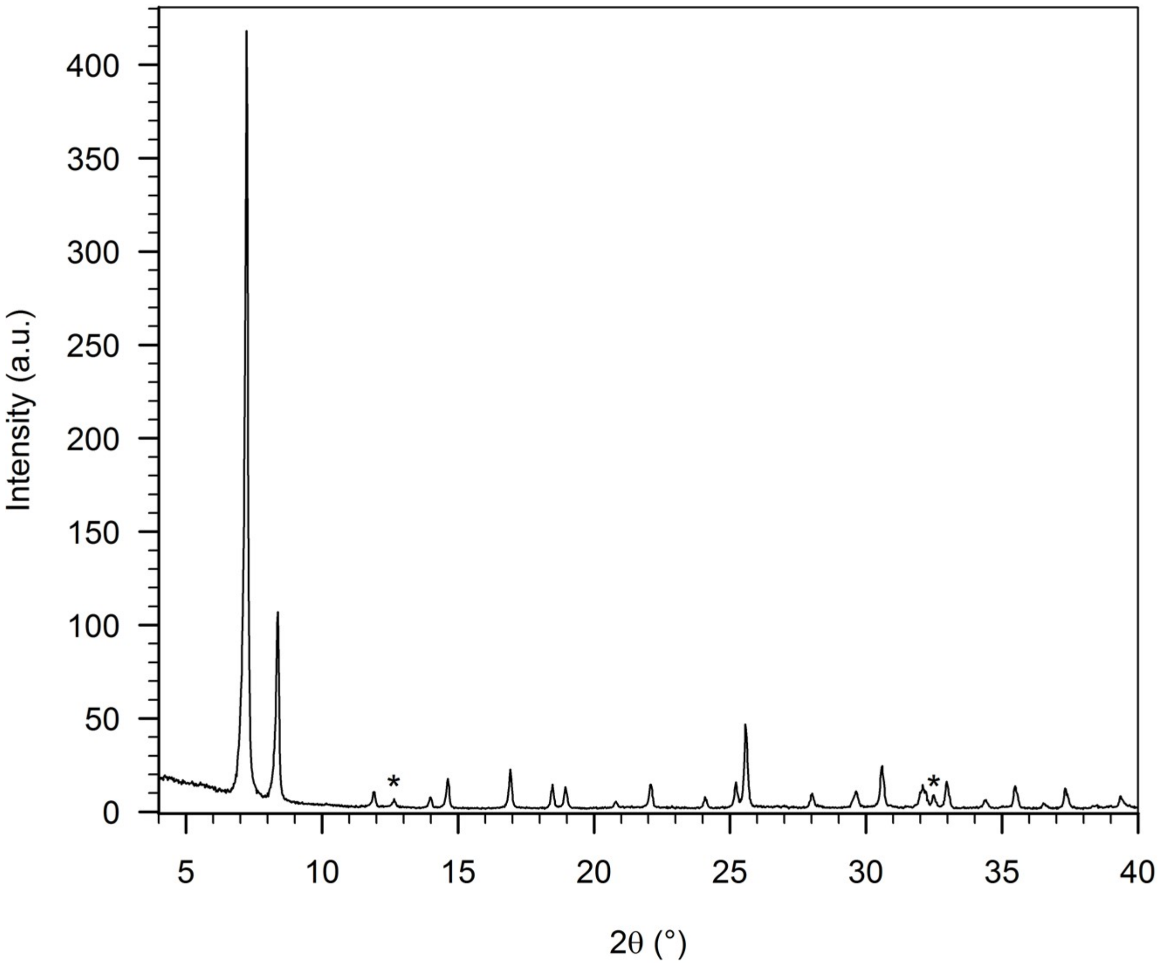

Figure S18: PXRD pattern of HD-UiO-66 treated with K_2CO_3 in THF. K_2CO_3 residues are indicated by a star.

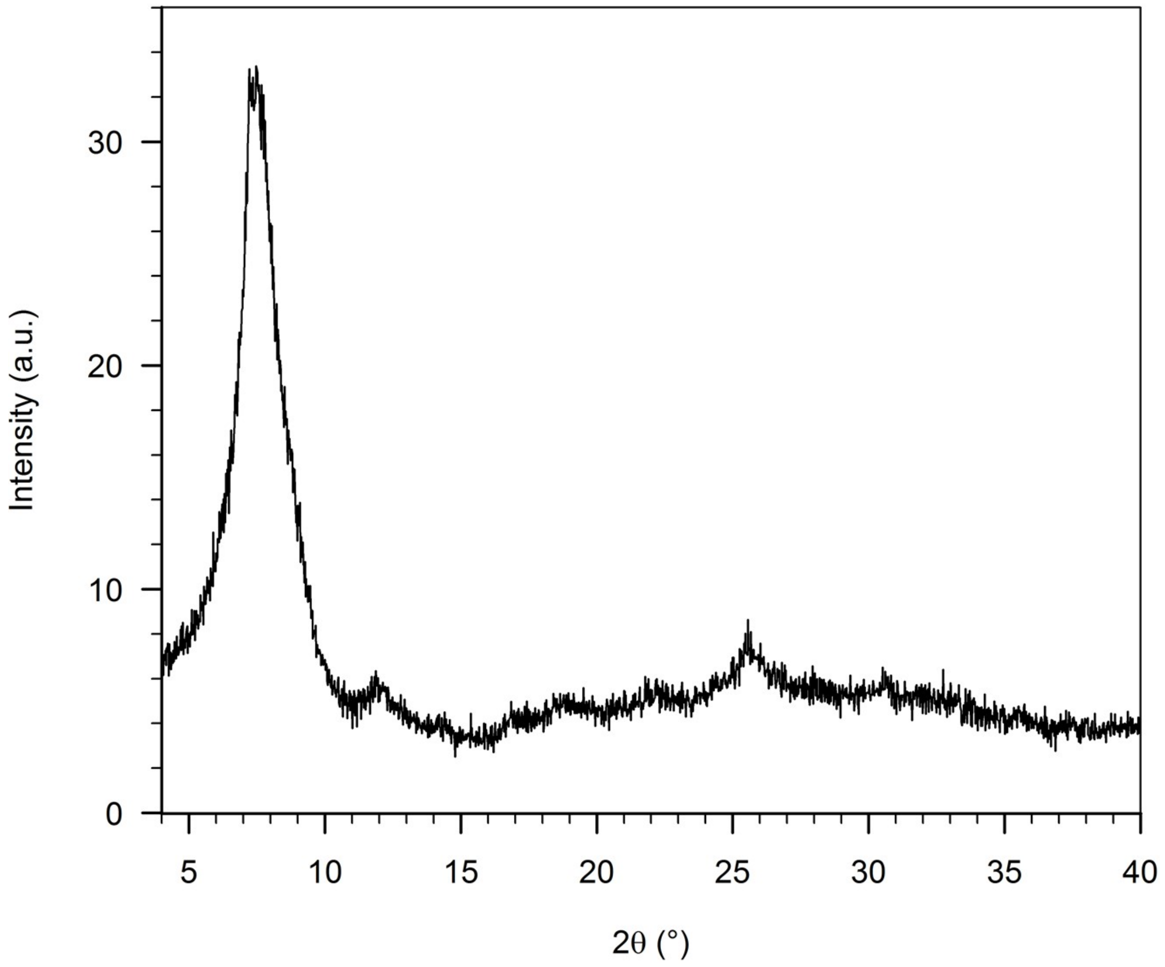

Figure S19: PXRD pattern of HD-UiO-66 treated with TMG in THF.

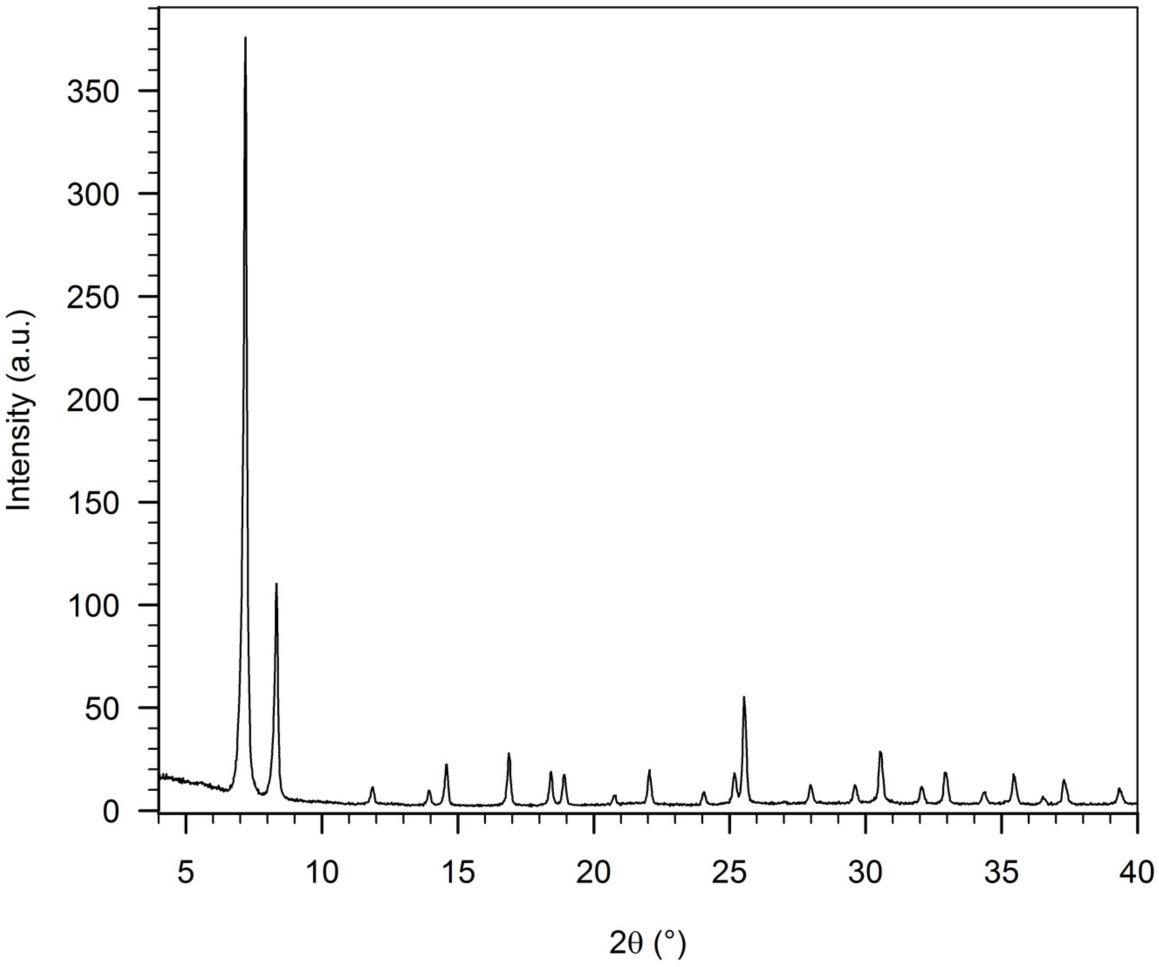

Figure S20: PXRD pattern of HD-UiO-66 treated with Et_3N in THF.

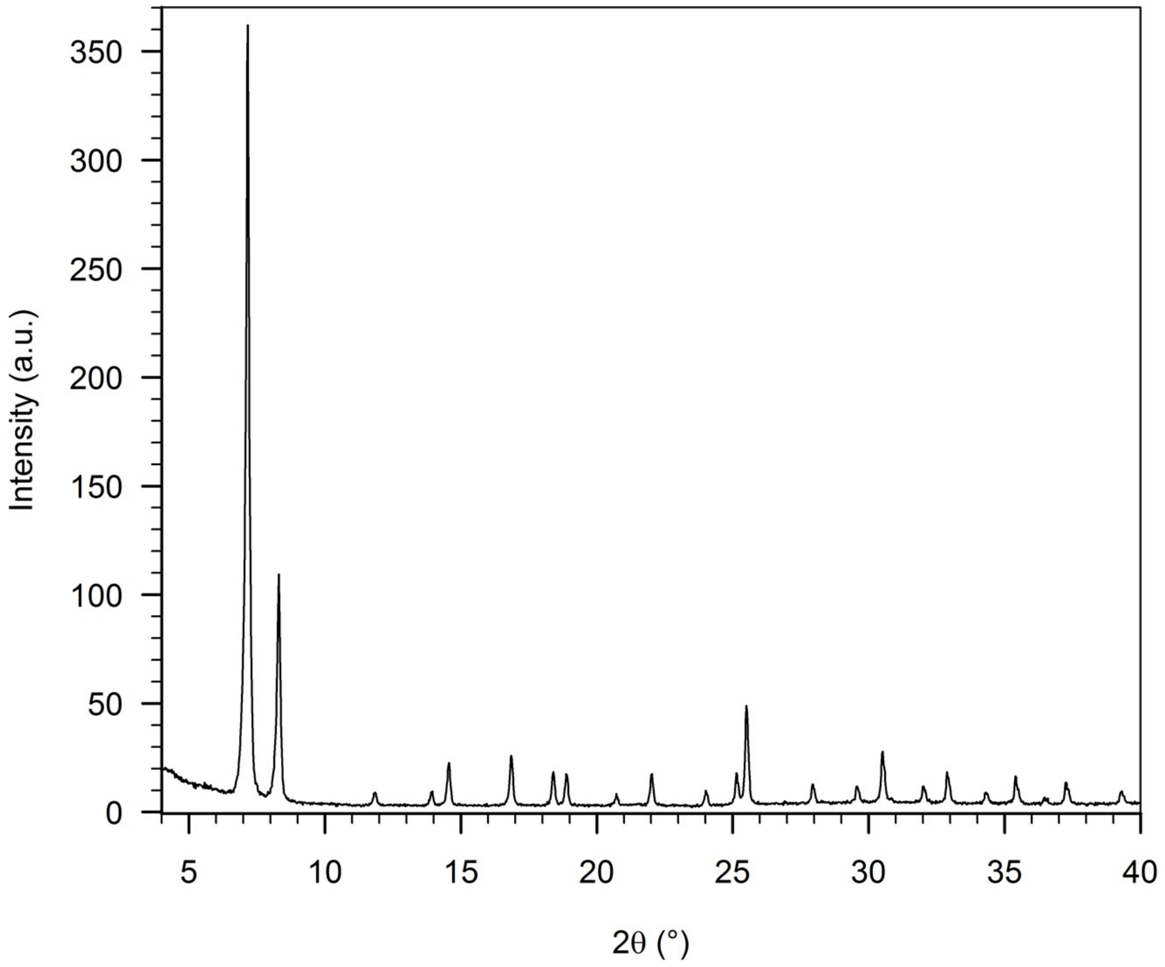

Figure S21: PXRD pattern of HD-UiO-66 treated with DCM.

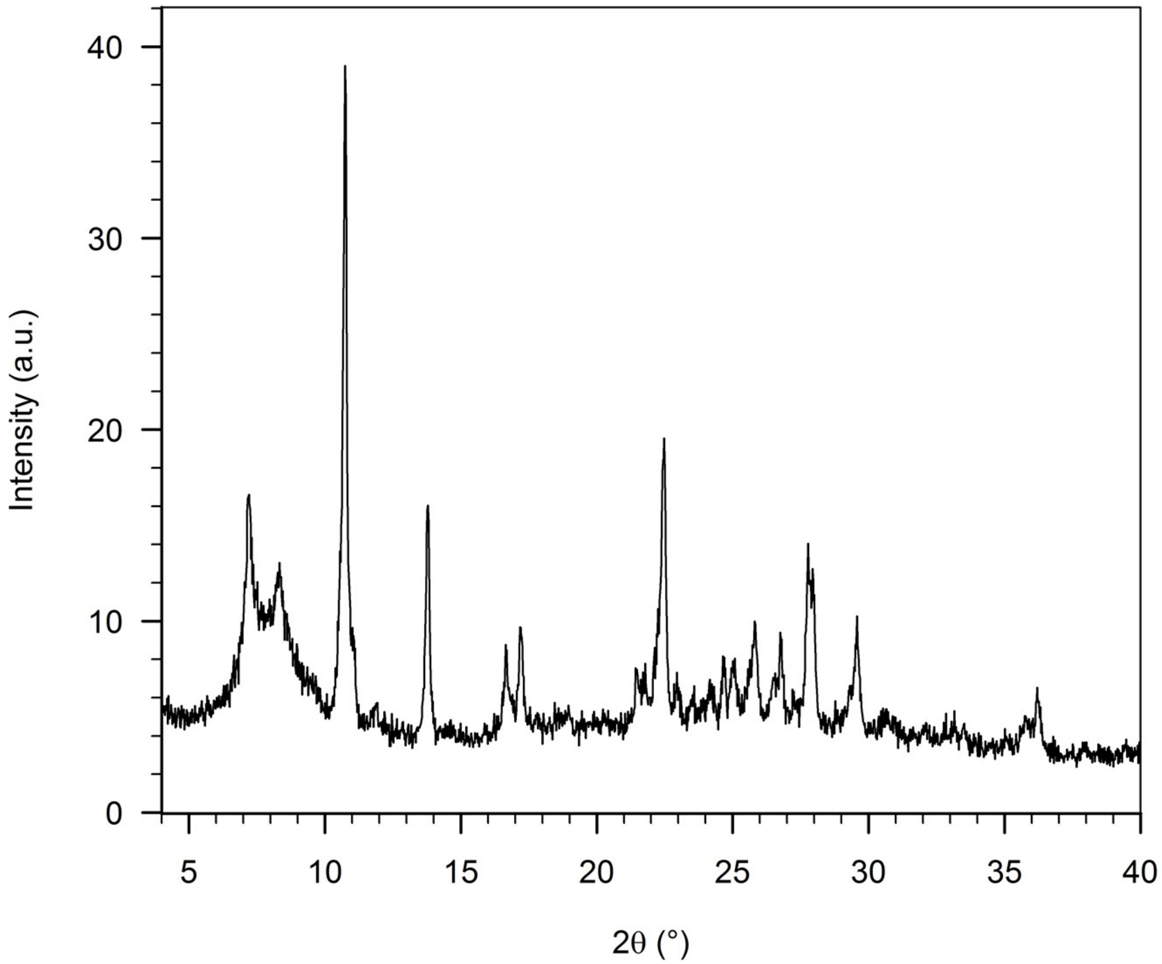

Figure S22: PXRD pattern of HD-UiO-66 treated with H_2SO_4 in DCM.

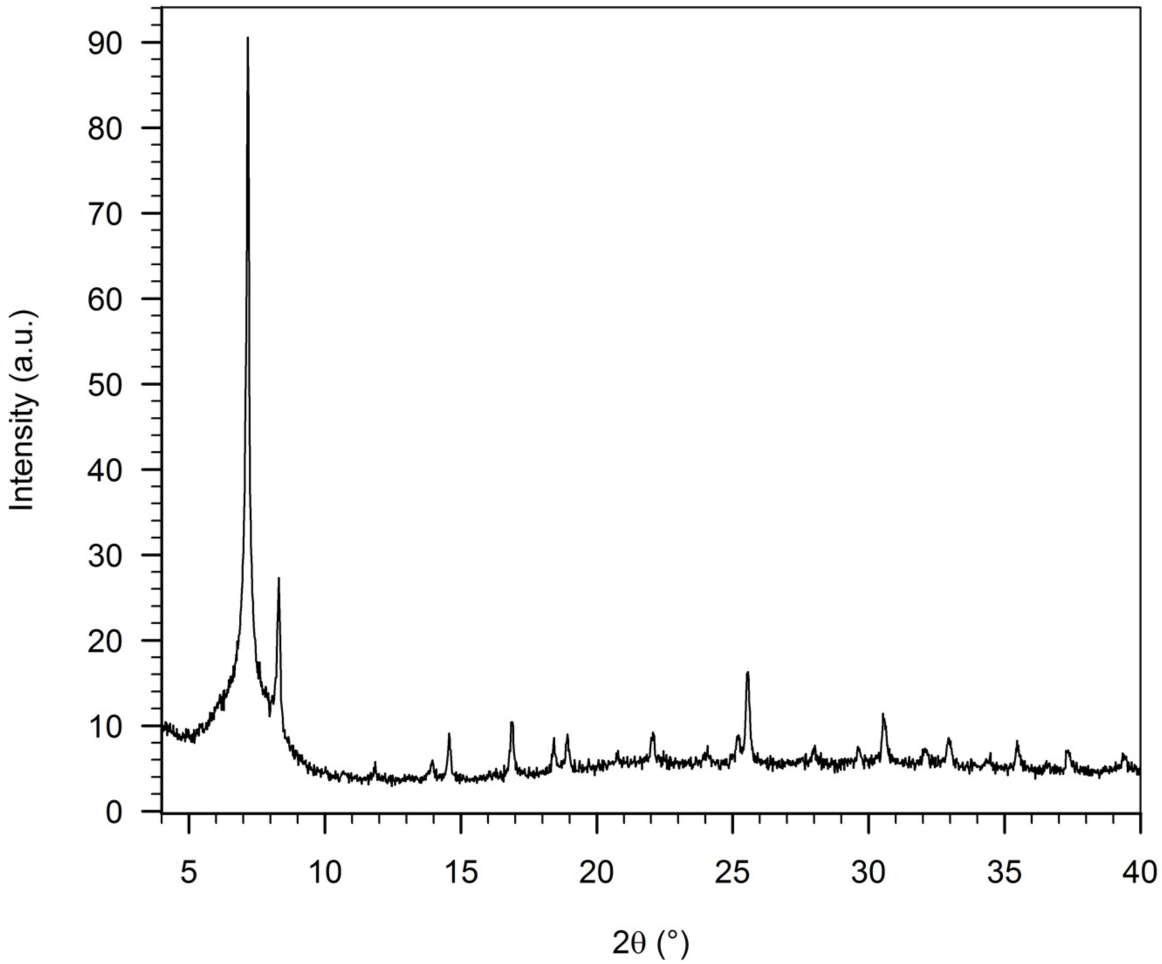

Figure S23: PXRD pattern of HD-UiO-66 treated with TFA in DCM.

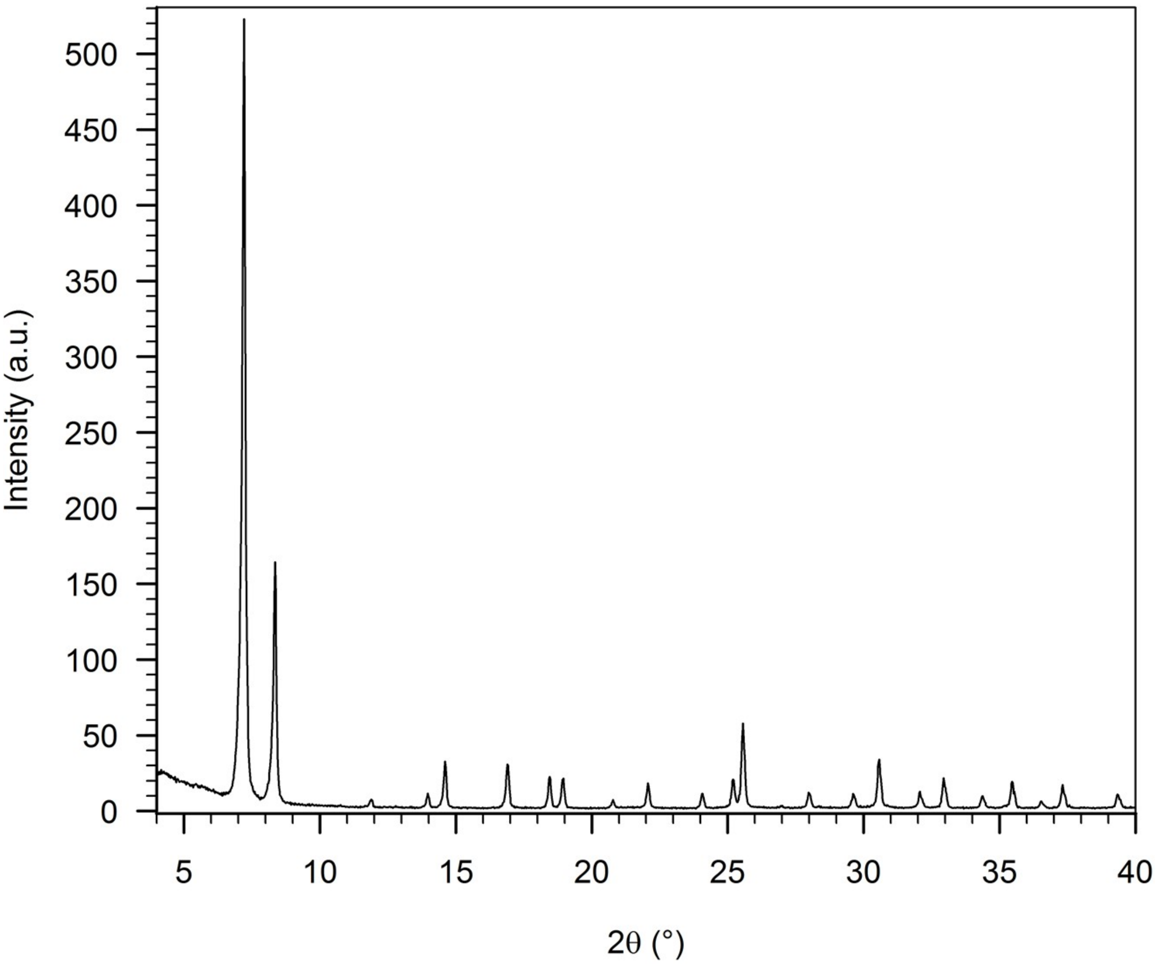

Figure S24: PXRD pattern of HD-UiO-66 treated with AcOH in DCM.

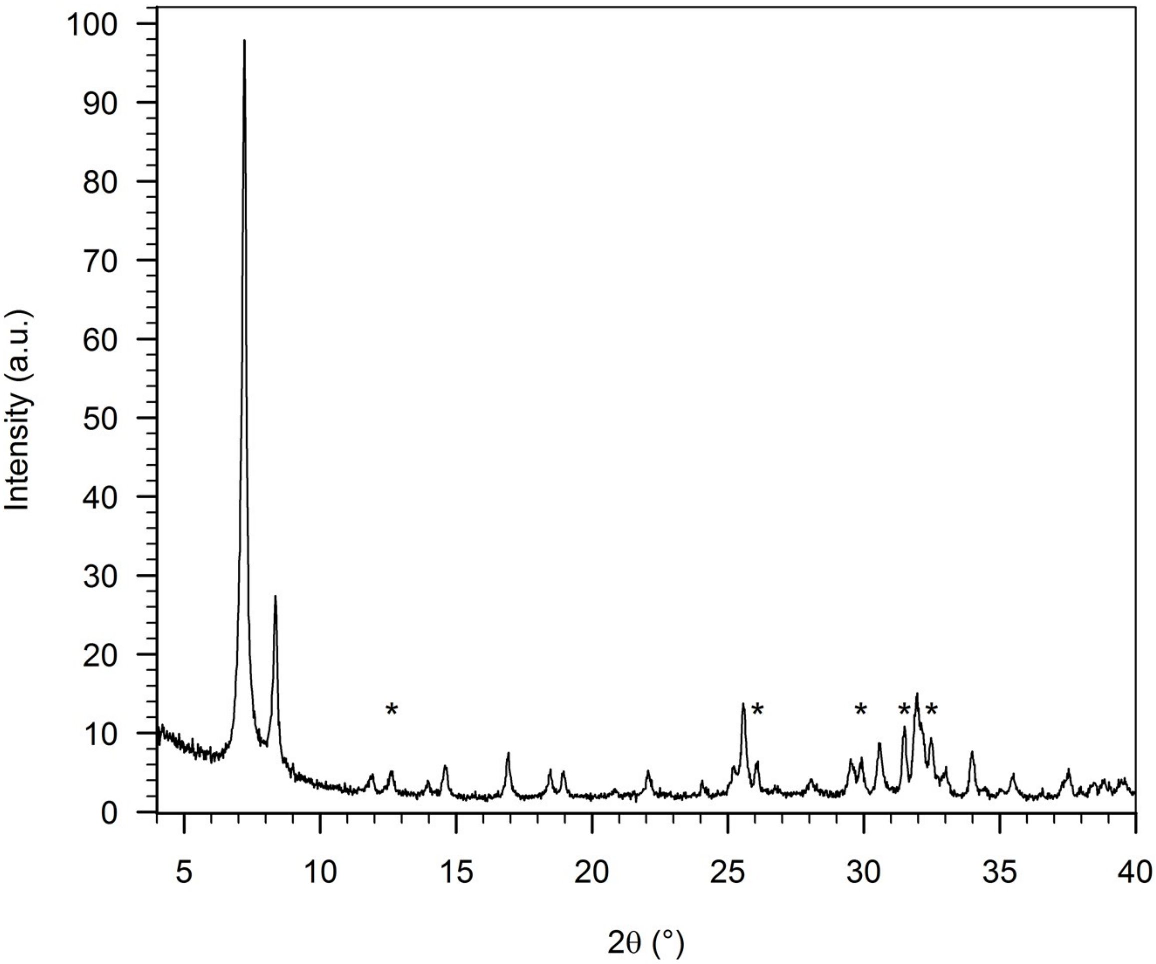

Figure S25: PXRD pattern of HD-UiO-66 treated with K_2CO_3 in DCM. K_2CO_3 residues are indicated by a star.

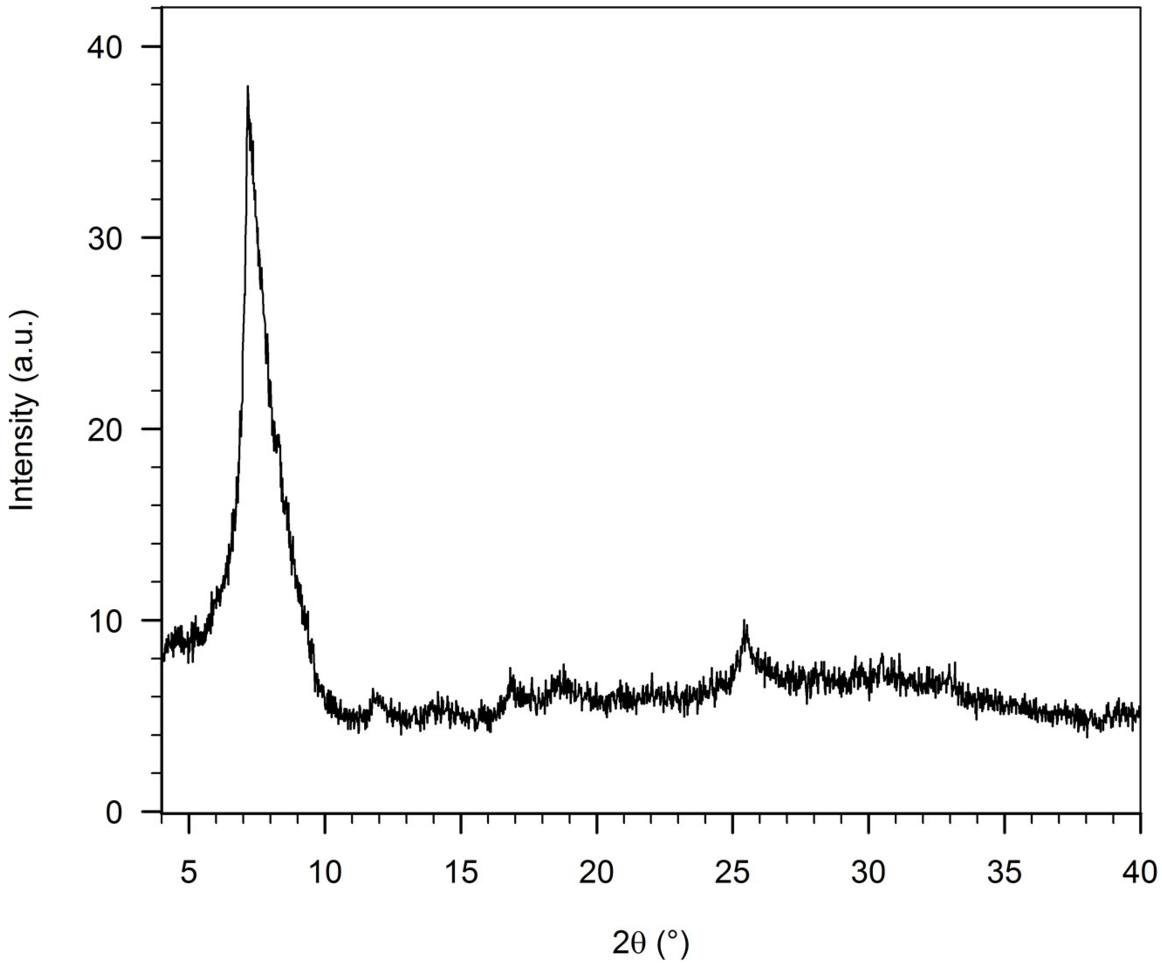

Figure S26: PXRD pattern of HD-UiO-66 treated with TMG in DCM.

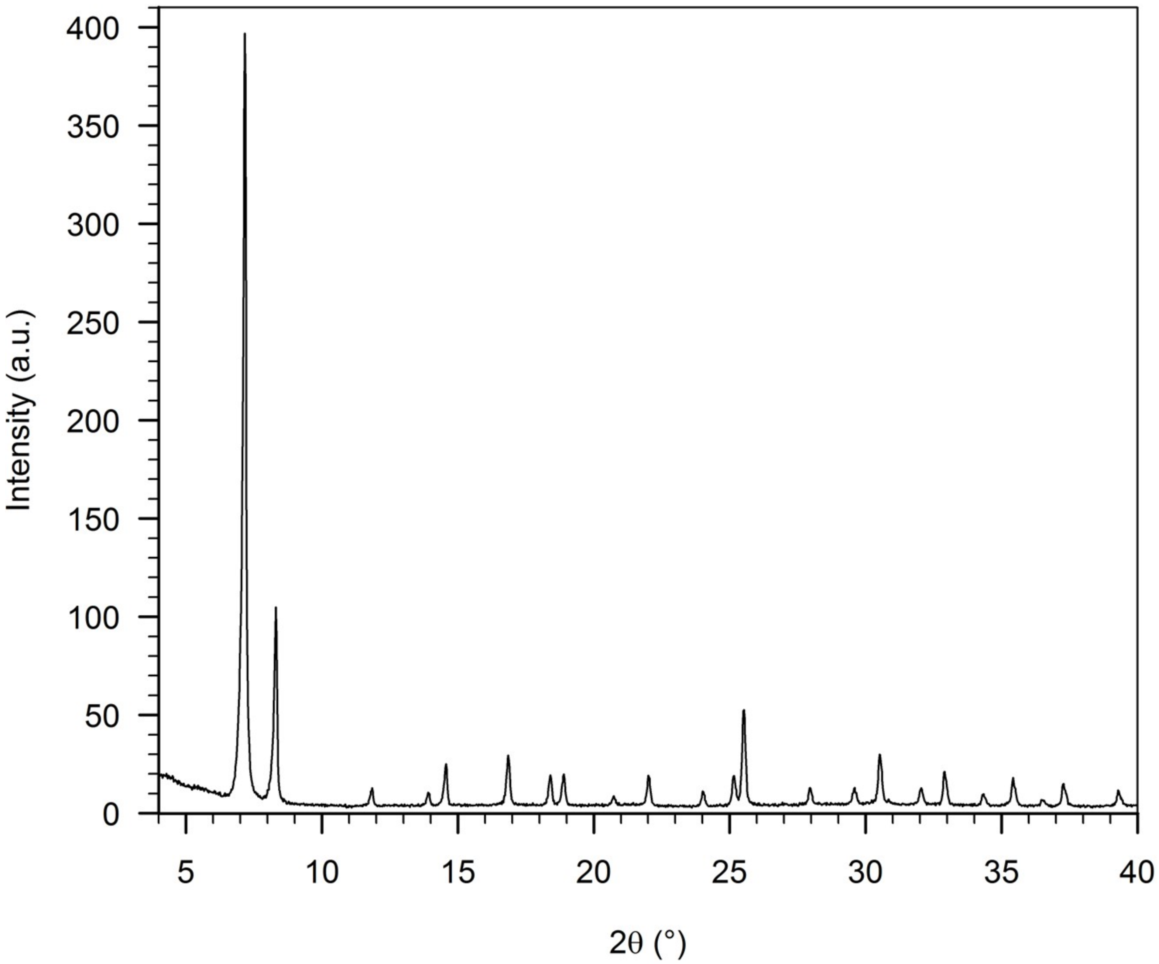

Figure S27: PXRD pattern of HD-UiO-66 treated with Et_3N in DCM.

References

1. D. A. Gómez-Gualdrón, P. Z. Moghadam, J. T. Hupp, O. K. Farha and R. Q. Snurr, Application of Consistency Criteria To Calculate BET Areas of Micro- And Mesoporous Metal–Organic Frameworks, *J. Am. Chem. Soc.*, 2016, **138**, 215-224.
2. H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, Unusual and Highly Tunable Missing-Linker Defects in Zirconium Metal–Organic Framework UiO-66 and Their Important Effects on Gas Adsorption, *J. Am. Chem. Soc.*, 2013, **135**, 10525-10532.