Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information

A spray-drying continuous-flow method for simultaneous synthesis and shaping of microspherical high nuclearity MOF beads

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SECTION I: Optimisation of the synthesis of UiO-66 by spray-drying continuous flow method.

Spray-drying continuous flow-assisted synthesis of microspherical UiO-66 beads

A solution of $ZrCl_4$ 0.1 M and BDC 0.1 M in 15 mL of a mixture of DMF and H_2O (molar ratio Zr(IV):BDC:H_2O:DMF 1:1:x:135) was injected into a coil flow reactor (inner diameter: 3 mm) at a determined feed rate ($ml \cdot min^{-1}$) and a certain temperature (T_1). The resulting pre-heated solution was then spray dried at a T_2 of 180 ^oC and a flow rate of 336 $ml \cdot min^{-1}$ using a B-290 Mini Spray Dryer (BUCHI Labortechnik) at a flow rate of 336 $ml \cdot min^{-1}$ and inlet temperature of 180 ^oC, using a spray cap with a 0.5 mm diameter hole. Then, the resulting solid was dispersed in DMF at room temperature under stirring overnight and precipitated by centrifugation. This process was repeated twice with ethanol instead of DMF. The final product was dried for 12 h at 80 ^oC.

Supplementary Tables 1-3 show the different spray-drying continuous flow-assisted syntheses of UiO-66 performed by systematically varying the feed rate, residence time, equivalents of water (x) and the bath temperature T_1.

Table S1: Summary of the S_{BET} values, yield and purity obtained for different samples in the optimisation of the feed rate in the synthesis of UiO-66.

Equivalents of water (x)	*Feed rate ($ml\ min^{-1}$)*	*Residence time (s)*	*T_1 (^oC)*	*Yield (%)*	*Purity (%)*	*S_{BET} (m^2g^{-1})*	*Pore Volume (cm^3/g)[a]*
30	4.5	35	115	32	25	555	0.255
30	3.6	41	115	28	22	875	0.406
30	3.0	48	115	55	38	893	0.405
30	2.4	63	115	52	36	1044	0.485
30	1.8	94	115	77	48	667	0.273
30	1.2	130	115	90	57	687	0.278

[a] The micropore volume was determined by application of the Dubinin−Radushkevich equation to the N2 adsorption isotherm in an adequate range of linearity.

Table S2: Summary of the S_{BET} values, yield and purity obtained for different samples in the optimisation of the equivalents of water (x) in the synthesis of UiO-66.

Equivalents of water (x)	*Feed rate (ml min^{-1})*	*Residence time (s)*	*T_1 (^{o}C)*	*Yield (%)*	*Purity (%)*	*S_{BET} (m^2g^{-1})*	*Pore Volume (cm^3/g)[a]*
20	2.4	63	115	9	6	X	X
30	2.4	63	115	52	36	1044	0.485
40	2.4	63	115	70	54	1106	0.495
45	2.4	63	115	84	59	963	0.399

[a] The micropore volume was determined by application of the Dubinin−Radushkevich equation to the N2 adsorption isotherm in an adequate range of linearity

Table S3: Summary of the S_{BET} values, yield and purity obtained for different samples in the optimisation of the bath temperature (T_1) in the synthesis of UiO-66.

Equivalents of Water (x)	*Feed rate (ml min^{-1})*	*Residence Time (s)*	*T_1 (^{o}C)*	*Yield (%)*	*Purity (%)*	*S_{BET} (m^2g^{-1})*	*Pore Volume (cm^3/g)[a]*
45	2.4	63	92	68	50	465	0.192
45	2.4	63	101	71	52	648	0.263
45	2.4	63	105	65	46	935	0.391
45	2.4	63	110	84	59	931	0.408
45	2.4	63	115	84	59	963	0.399

[a] The micropore volume was determined by application of the Dubinin−Radushkevich equation to the N2 adsorption isotherm in an adequate range of linearity

- The yield was calculated based on zirconium and according to equation :

$$Yield\ (\%) = \frac{Mol\ Zr\ from\ Activated\ UiO-66}{Mol\ Zr\ from\ ZrCl4}\ x\ 100$$

- The purity was calculated according to equation :

$$Purity\ (\%) = \frac{Weight\ of\ purified\ product}{Weight\ of\ crude\ solid\ collected}\ x\ 100$$

- The STY was calculated according to equation :

$$STY = \frac{Production\ rate\ (\frac{Kg}{day})}{Feed\ rate\ \left(\frac{m^3}{h}\right) x\ 24h}$$

SECTION II: Supplementary Figures

FIGURE S1: FESEM images of UiO-66. a-b) Images showing a general view of the microspherical beads, c) Broken bead showing that these spheres are compact, and d) Single UiO-66 bead showing the assembly of nanocrystals. e,f) Elemental mapping with EDX performed on a single spherical bead of UiO-66, showing the homogeneous distribution of Zr (blue). Scale bars: a) 10 µm, b,e) 5 µm, c) 3 µm, and d) 1 µm.

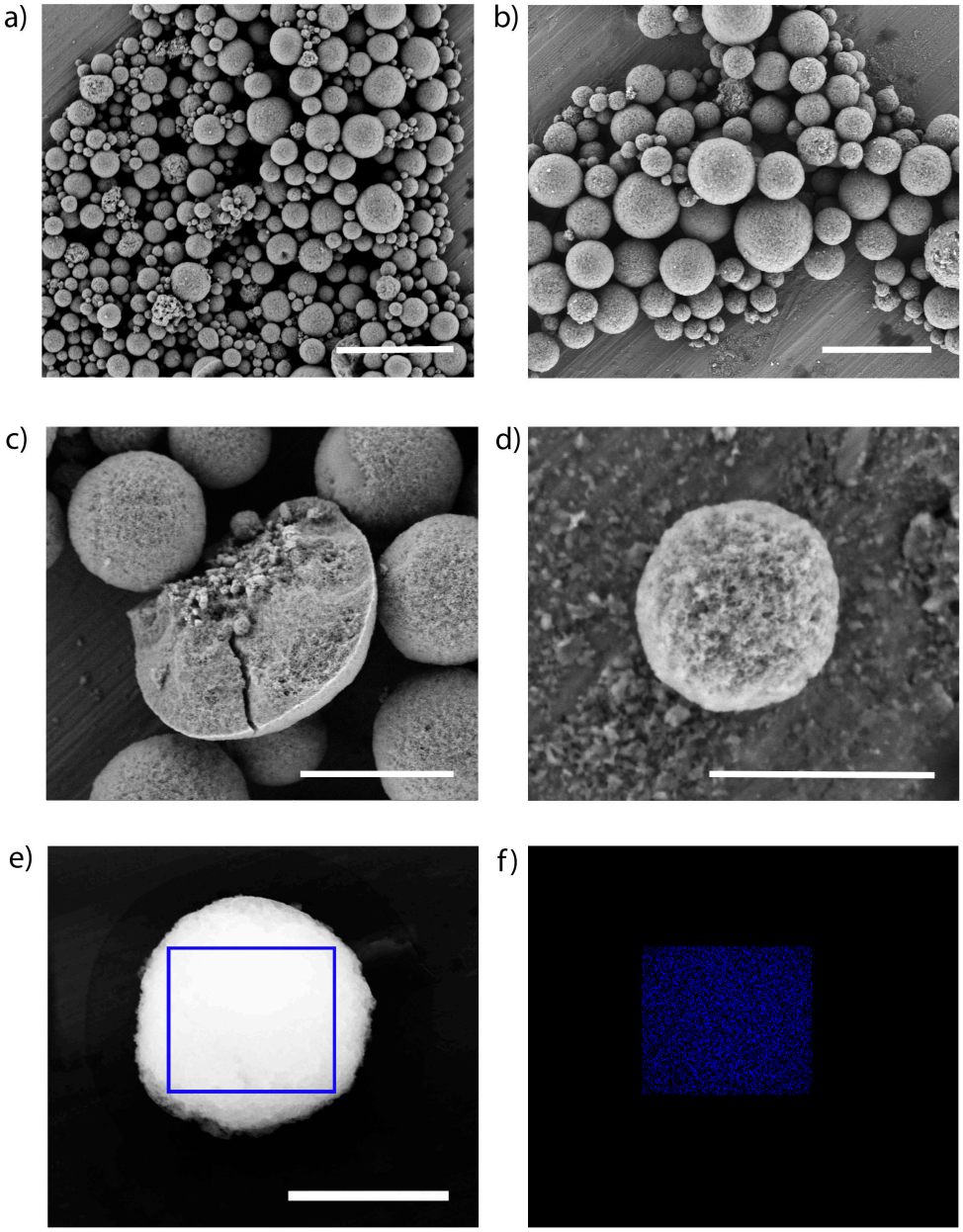
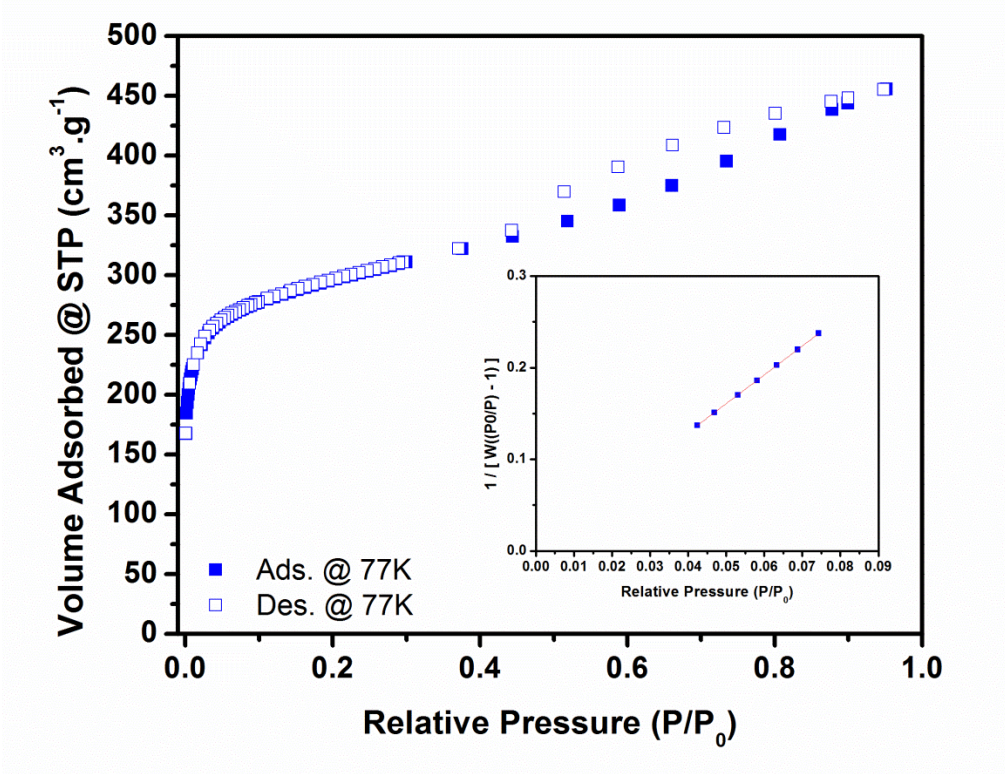


FIGURE S2: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66.



BET surface area: 1105.884 m²/g

Slope: 3.146 g/cm^3 STP

Intercept: 3.547e-03 g/cm^3 STP

Correlation coefficient: 0.999992

C constant: 887.886

Molecular cross-sectional area: 0.1620 nm²

FIGURE S3: Synthesis of UiO-66 using only the spray drying technique. a) FESEM images showing the amorphous material, and b) XRPD diffractogram of the non-porous amorphous solid compared with the simulated powder pattern for UiO-66 (black). Scale bar: 10 µm.

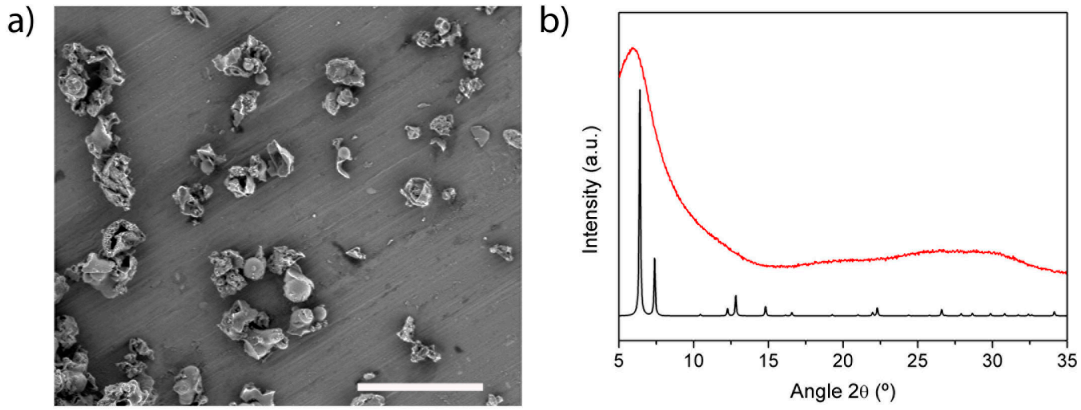


FIGURE S4: Synthesis of UiO-66 using only the continuous flow synthesis. a) FESEM images of the collected sample showing the formation of nanoparticles, b) XRPD diffractogram of this powder compared to the simulated powder pattern for UiO-66 (black), and c) N_2 Adsorption isotherm of the collected powder. Scale bar: 1 µm.

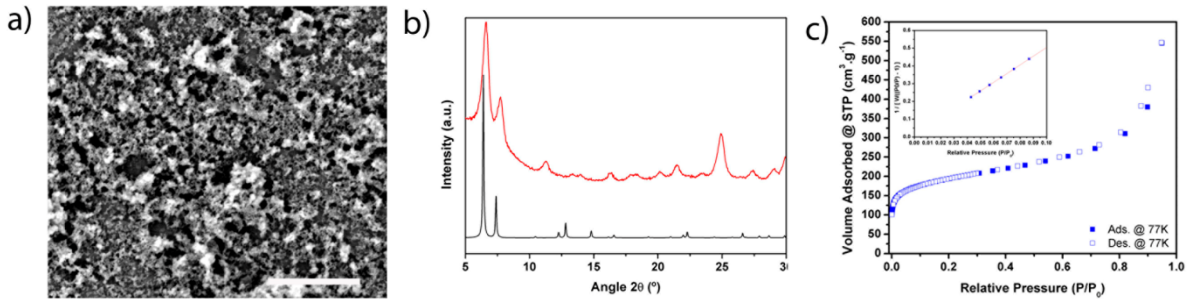


FIGURE S5: XRPD diffractograms of the UiO-66 powders collected after their synthesis at different reaction times (Red: t = 35 s; feed rate = 4.5 ml·min^{-1}, Blue: t = 41 s; feed rate = 3.6 ml·min^{-1}, Pink: t = 48 s; feed rate = 3.0 ml·min^{-1}, Green: t = 63 s; feed rate = 2.4 ml·min^{-1}, Orange: t = 94 s; feed rate = 1.8 ml·min^{-1}, Purple: t = 130 s; feed rate = 1.2 ml·min^{-1}), as compared to the simulated powder pattern for UiO-66 (black).

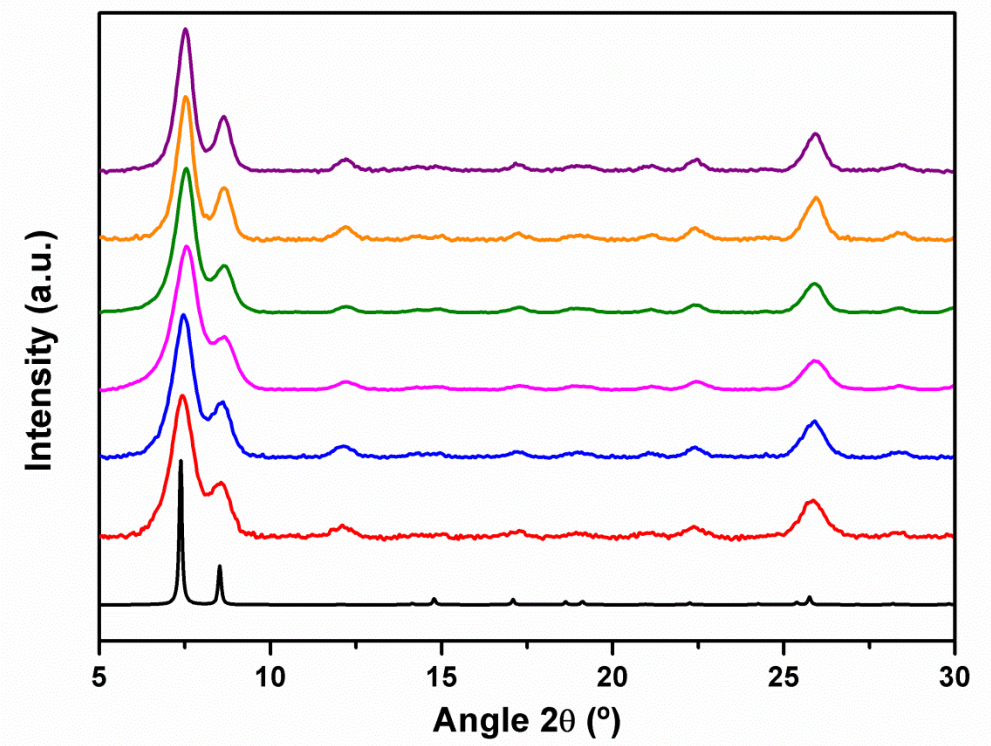


FIGURE S6: Synthesis of UiO-66 using only the continuous flow synthesis. a) FESEM images of the collected sample showing the formation of nanoparticles, b) XRPD diffractogram of this powder compared to the simulated powder pattern for UiO-66 (black), and c) N_2 Adsorption isotherm of the collected powder. Scale bar: 5 µm.

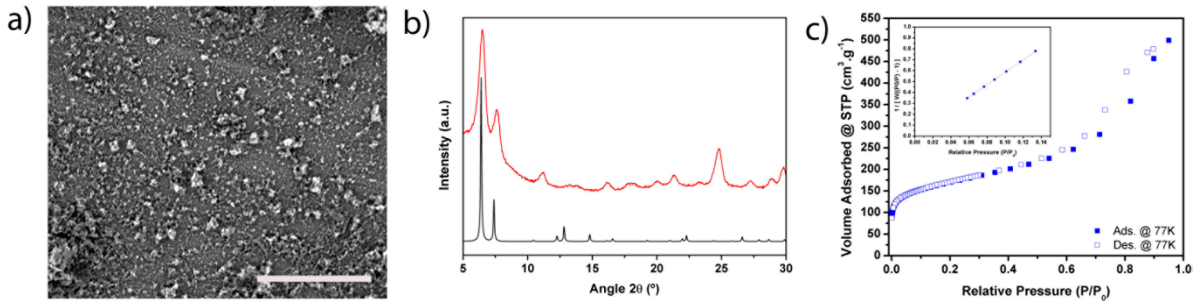


FIGURE S7: XRPD diffractograms of the UiO-66 powders collected after their synthesis at different equivalents of water (Red: x = 20; Blue: x = 30; Pink: x = 40; Green: x = 45), as compared to the simulated powder pattern for UiO-66 (black).

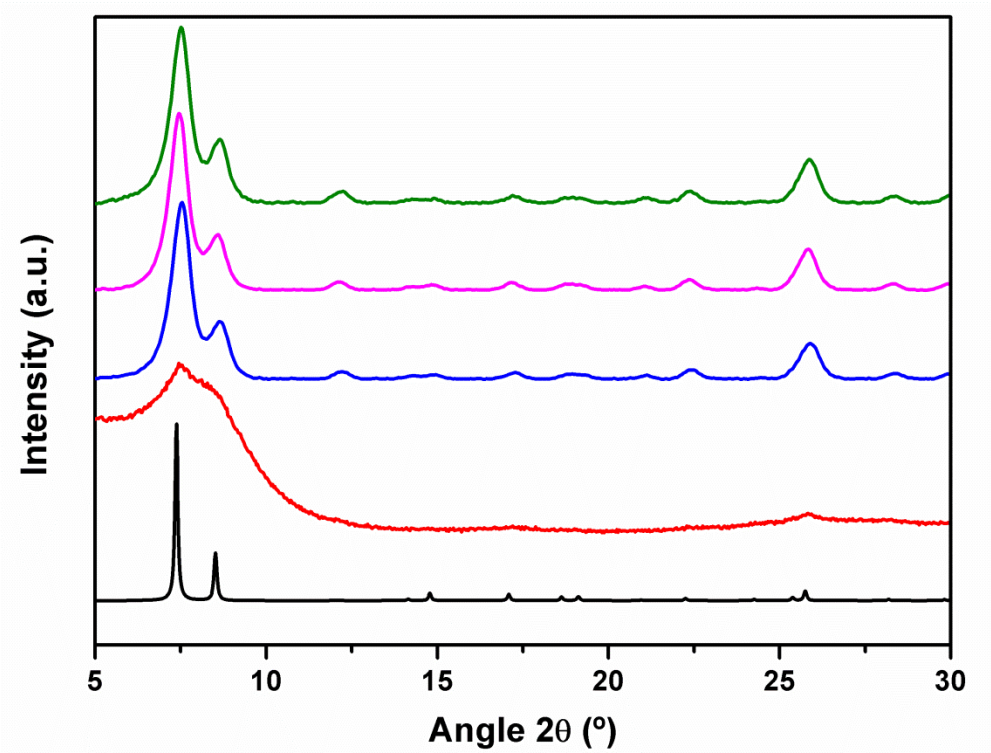


FIGURE S8: XRPD diffractograms of the UiO-66 powders collected after their synthesis at different bath temperatures (T_1) (Red: 115 °C, Blue: 110 °C, Pink: 105 °C, Green: 100 °C, Orange: 90 °C), as compared to the simulated powder pattern for UiO-66 (black).

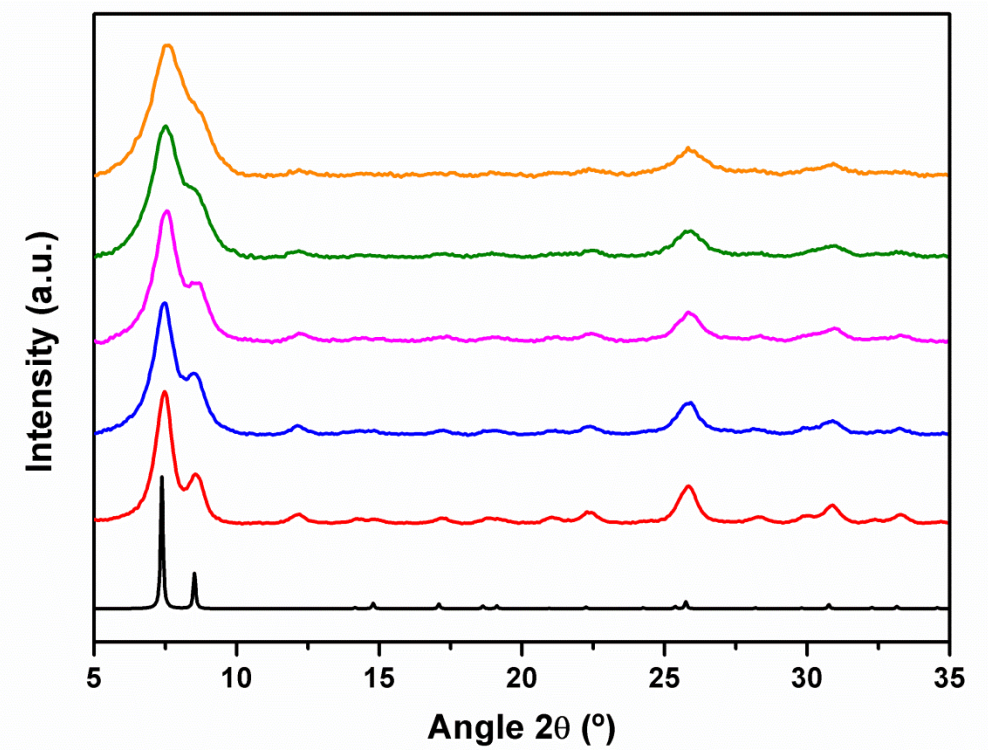


FIGURE S9: FESEM images of a) UiO-66-Acetamido and b) UiO-66-1,4-NDC. Scale bars: 10 μm.

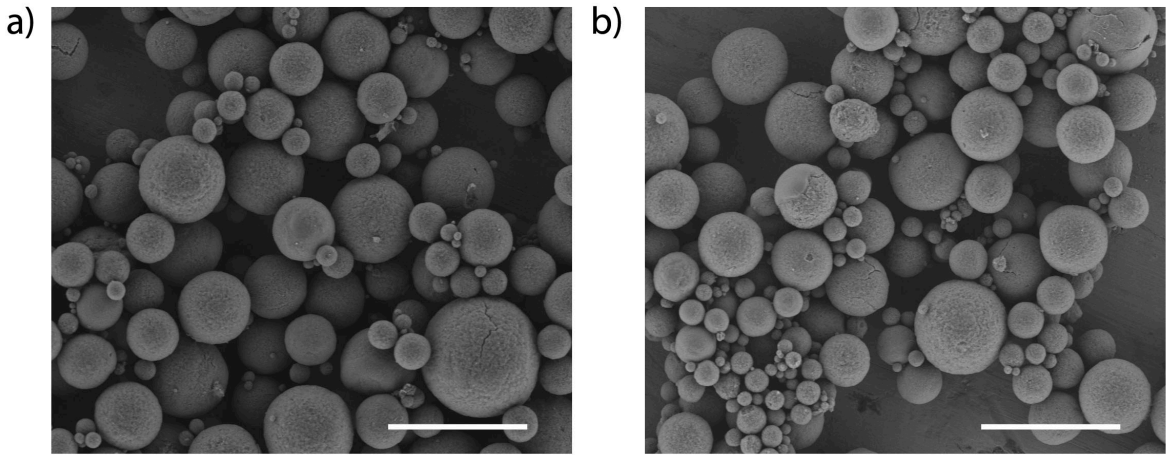
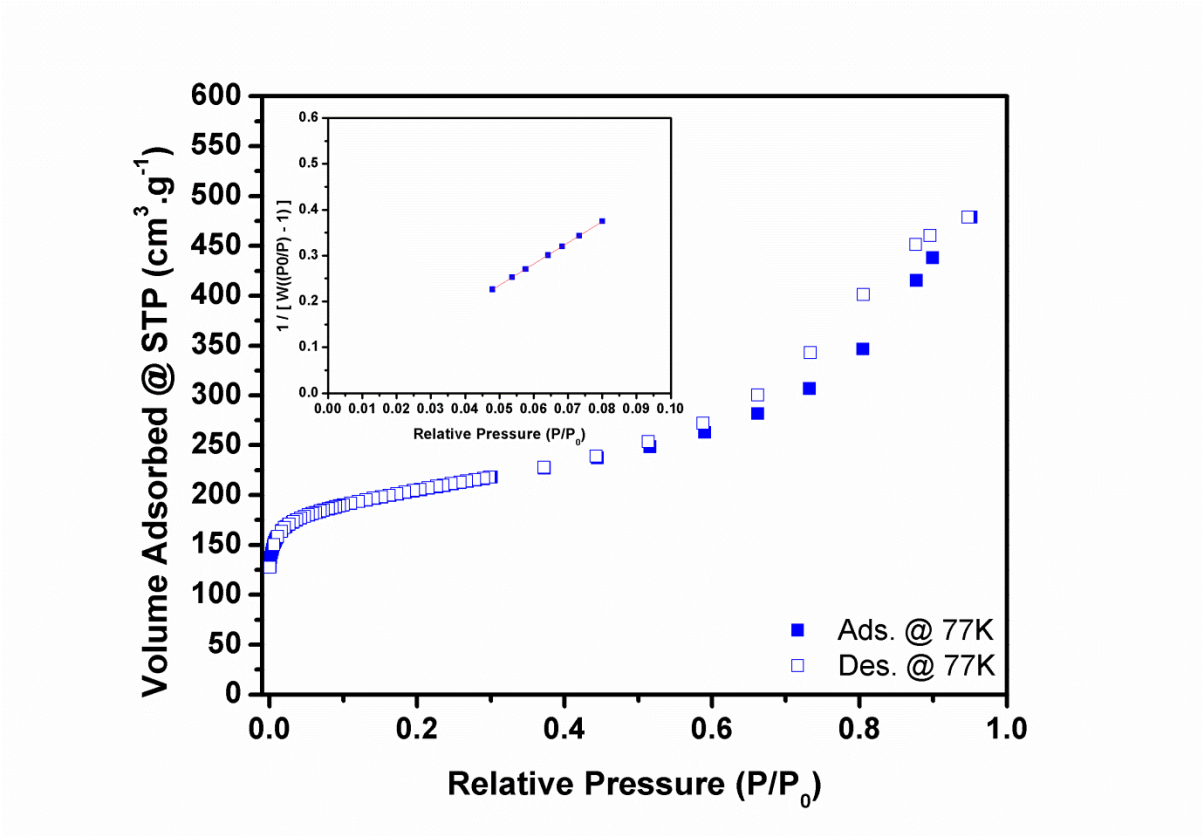


Table S4: Summary of the average particle sizes of the different MOFs prepared by the spray-drying continuous-flow method, measured by laser diffraction measurements (LD).

MOF	***Average diameter (µm)***
UiO-66	4.3 ± 2.6
UiO-66-NH_2	4.8 ± 2.2
UiO-66- NO_2	4.9 ± 2.0
UiO-66-Acetamido	3.6 ± 1.7
UiO-66-Br	3.1 ± 1.8
UiO-66-$(OH)_2$	5.4 ± 2.2
UiO-66-1,4-NDC	7.3 ± 1.9
UiO-66-2,6-NDC	4.7 ± 2.6
Fe-BTC/MIL-100	4.1 ± 1.9
$[Ni_8(OH)_4(H_2O)_2(L)_6]_n$	4.7 ± 1.1

FIGURE S10: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66-NH_2.



BET surface area: 751.512 m²/g

Slope: 4.630 g/cm^3 STP

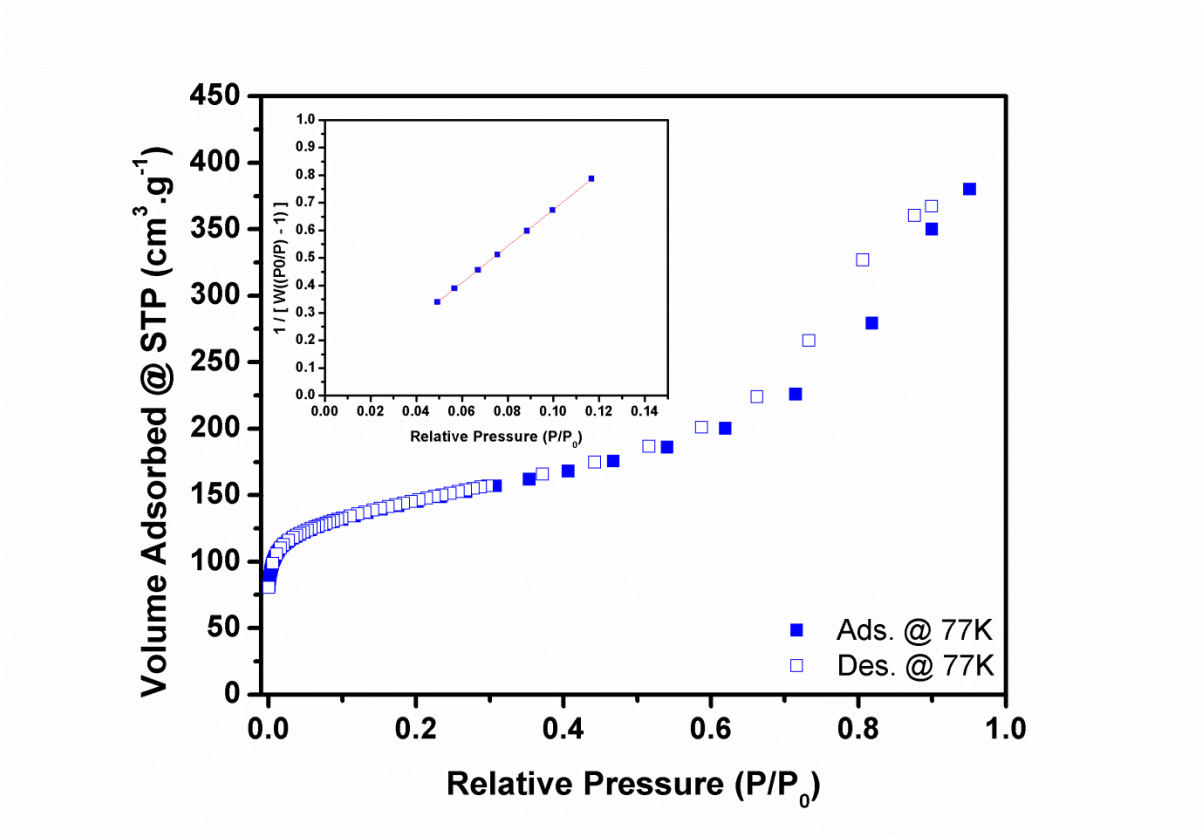
Intercept: 3.790e-03 g/cm^3 STP

Correlation coefficient: 0.999996

C constant: 1222.770

Molecular cross-sectional area: 0.1620 nm²

FIGURE S11: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66-NO_2.



BET surface area: 678.550 m²/g

Slope: 5.126 g/cm^3 STP

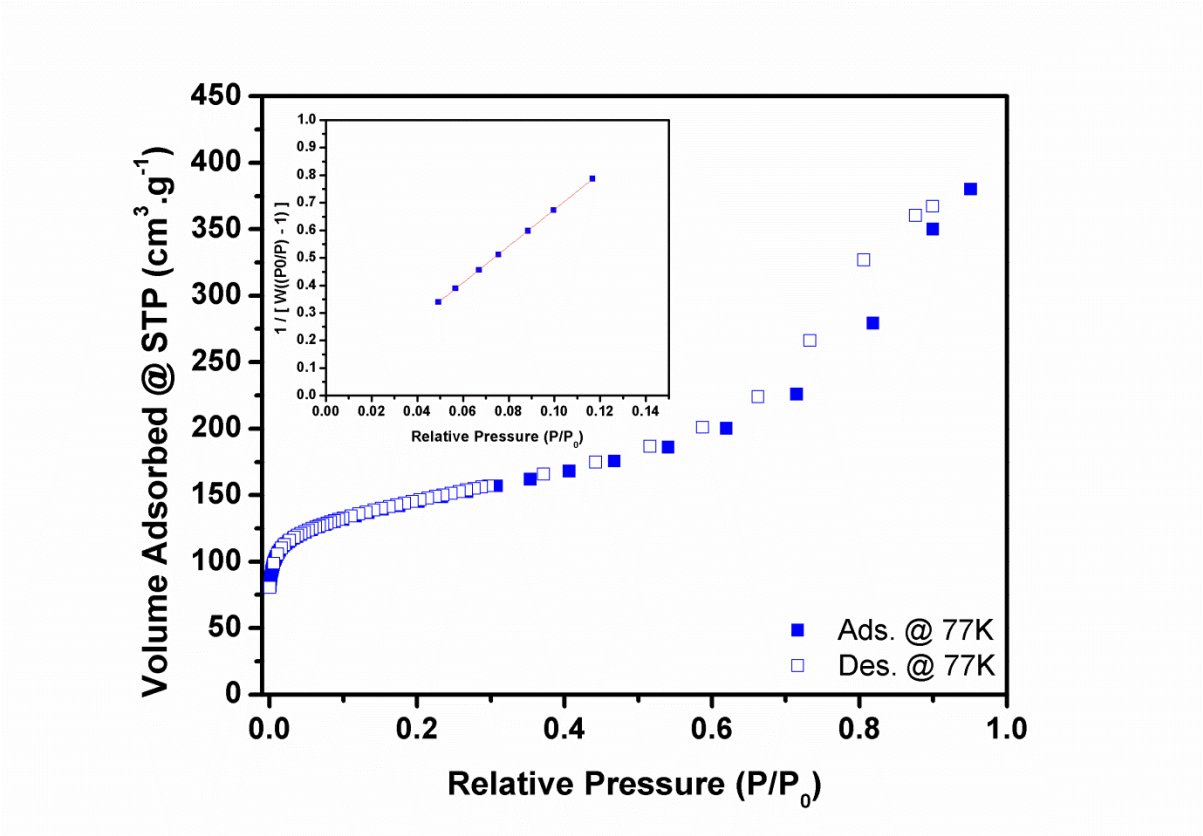
Intercept: 5.994e-03 g/cm^3 STP

Correlation coefficient: 0.999993

C constant: 856.222

Molecular cross-sectional area: 0.1620 nm²

FIGURE S12: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66-Br.



BET surface area: 527.842 m²/g

Slope: 6.636 g/cm^3 STP

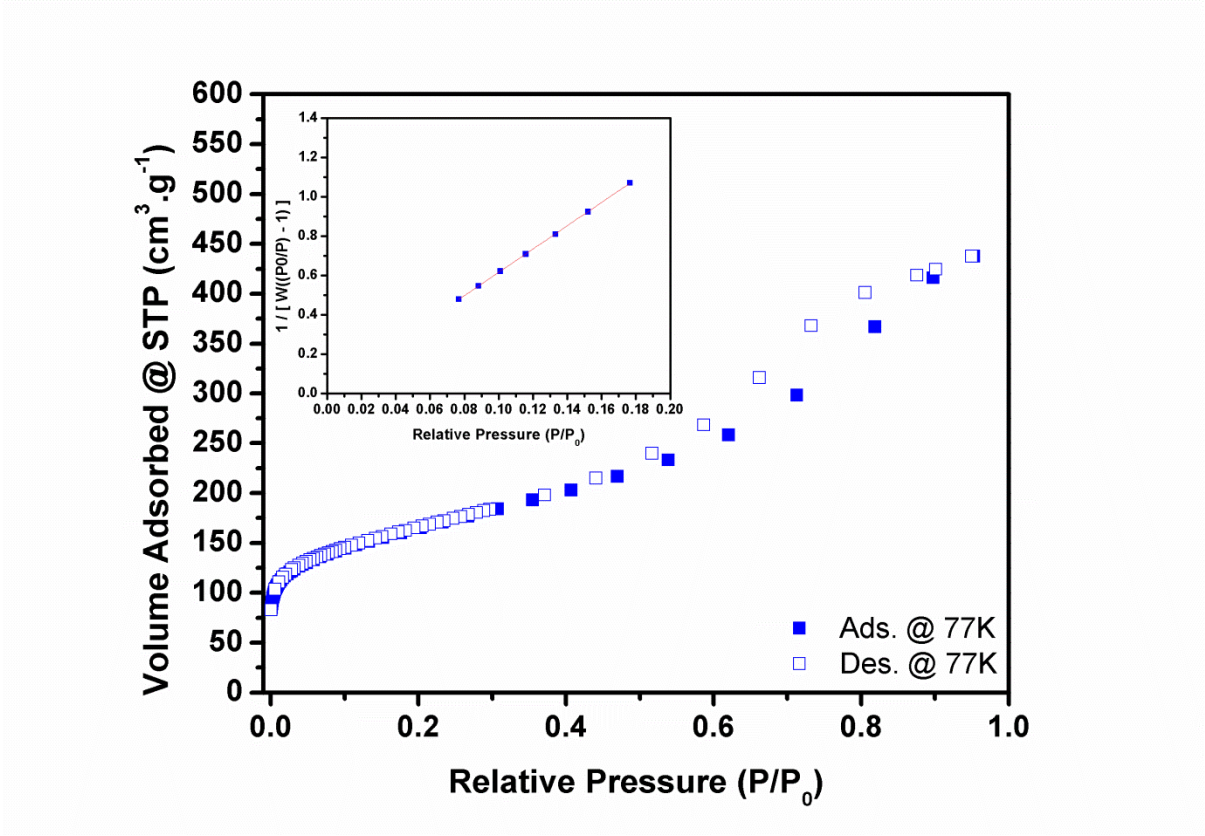
Intercept: 1.191e-02 g/cm^3 STP

Correlation coefficient: 0.999985

C constant: 558.039

Molecular cross-sectional area: 0.1620 nm²

FIGURE S13: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66-Acetamido.



BET surface area: 585.778 m²/g

Slope: 5.921 g/cm^3 STP

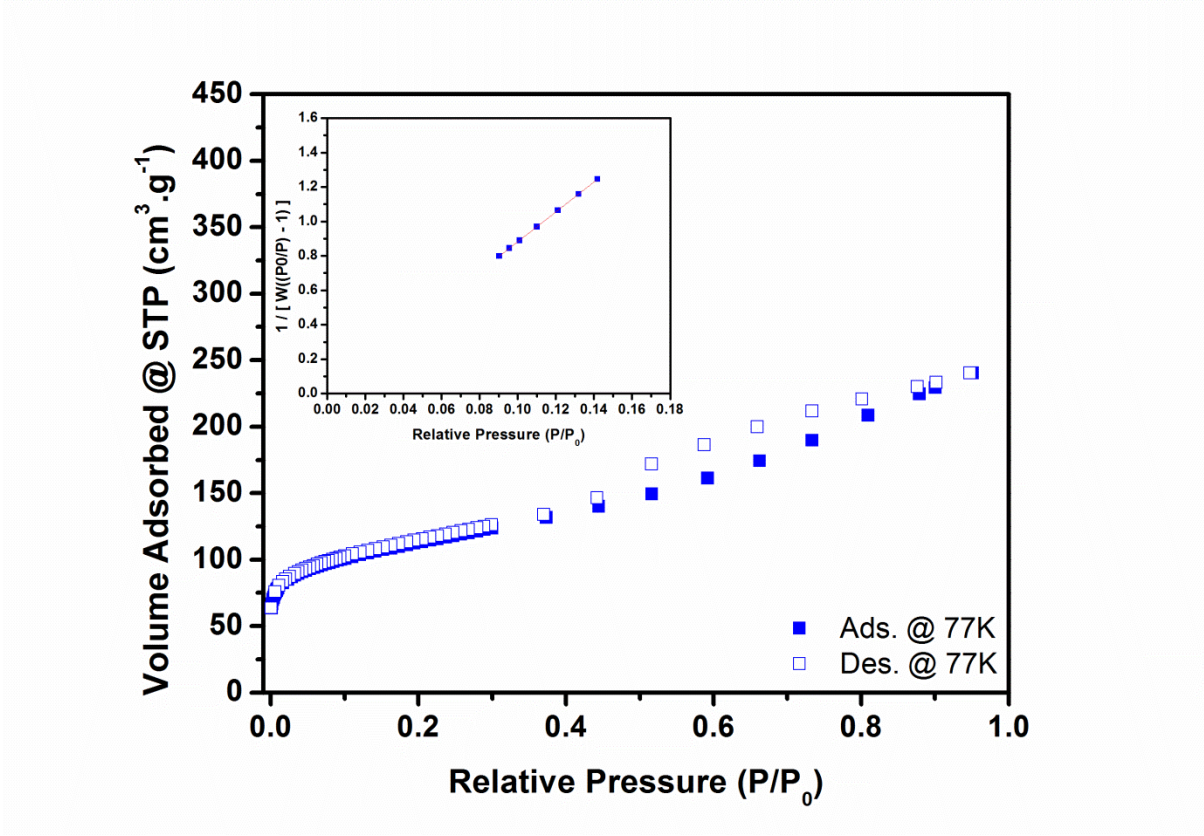
Intercept: 2.444e-02 g/cm^3 STP

Correlation coefficient: 0.999988

C constant: 243.264

Molecular cross-sectional area: 0.1620 nm²

FIGURE S14: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66-$(OH)_2$.



BET surface area: 401.089 m²/g

Slope: 8.667 g/cm^3 STP

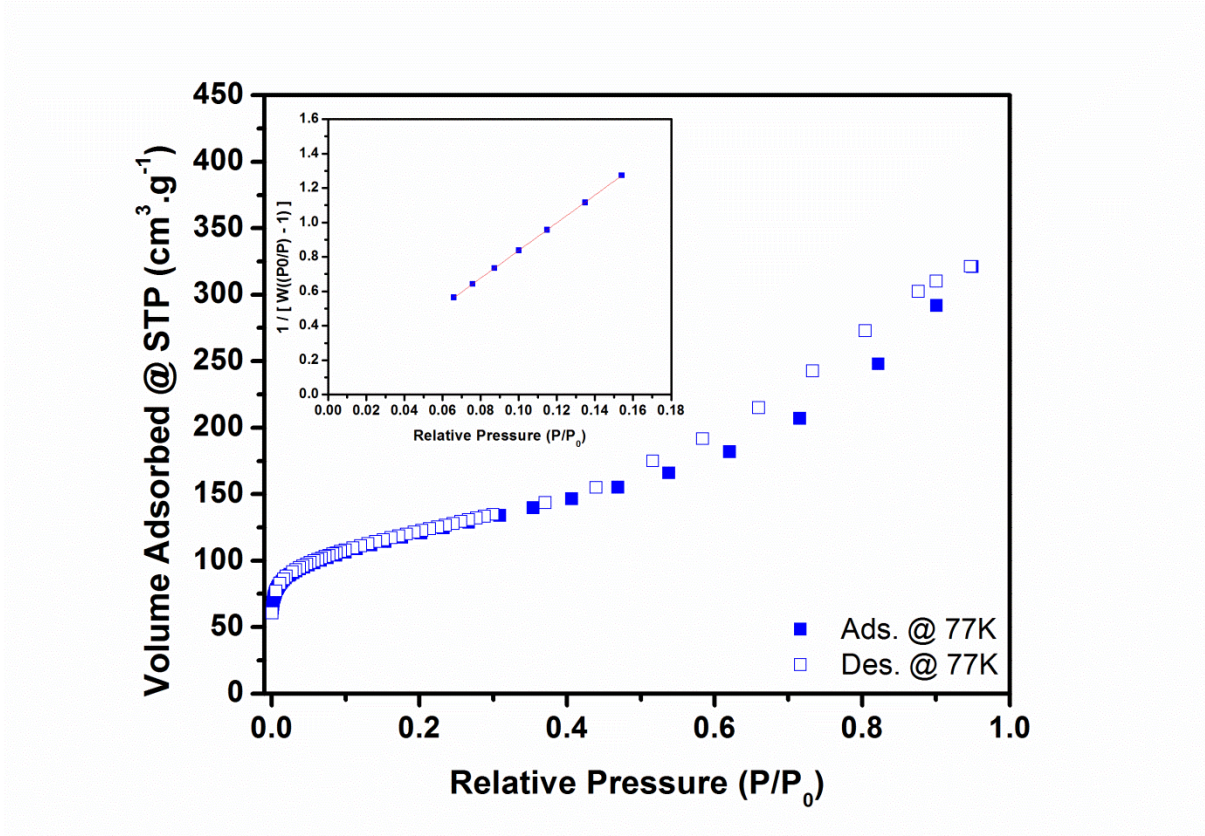
Intercept: 1.609e-02 g/cm^3 STP

Correlation coefficient: 0.999992

C constant: 539.505

Molecular cross-sectional area: 0.1620 nm²

FIGURE S15: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66-1,4-NDC.



BET surface area: 431.150 m²/g

Slope: 8.044 g/cm^3 STP

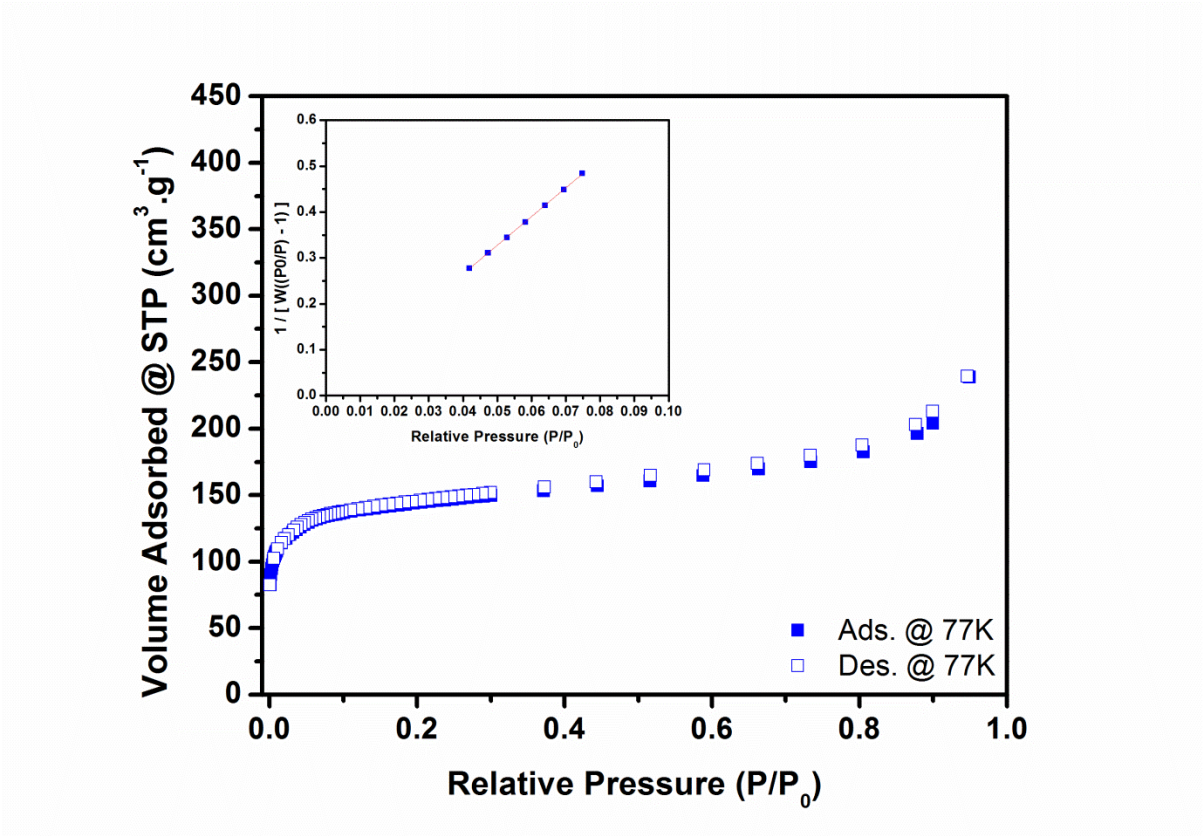
Intercept: 3.293e-02 g/cm^3 STP

Correlation coefficient: 0.999993

C constant: 245.260

Molecular cross-sectional area: 0.1620 nm²

FIGURE S16: N_2 adsorption isotherm and BET linear fit for the synthesised UiO-66-2,6-NDC.



BET surface area: 557.479 m²/g

Slope: 6.254 g/cm^3 STP

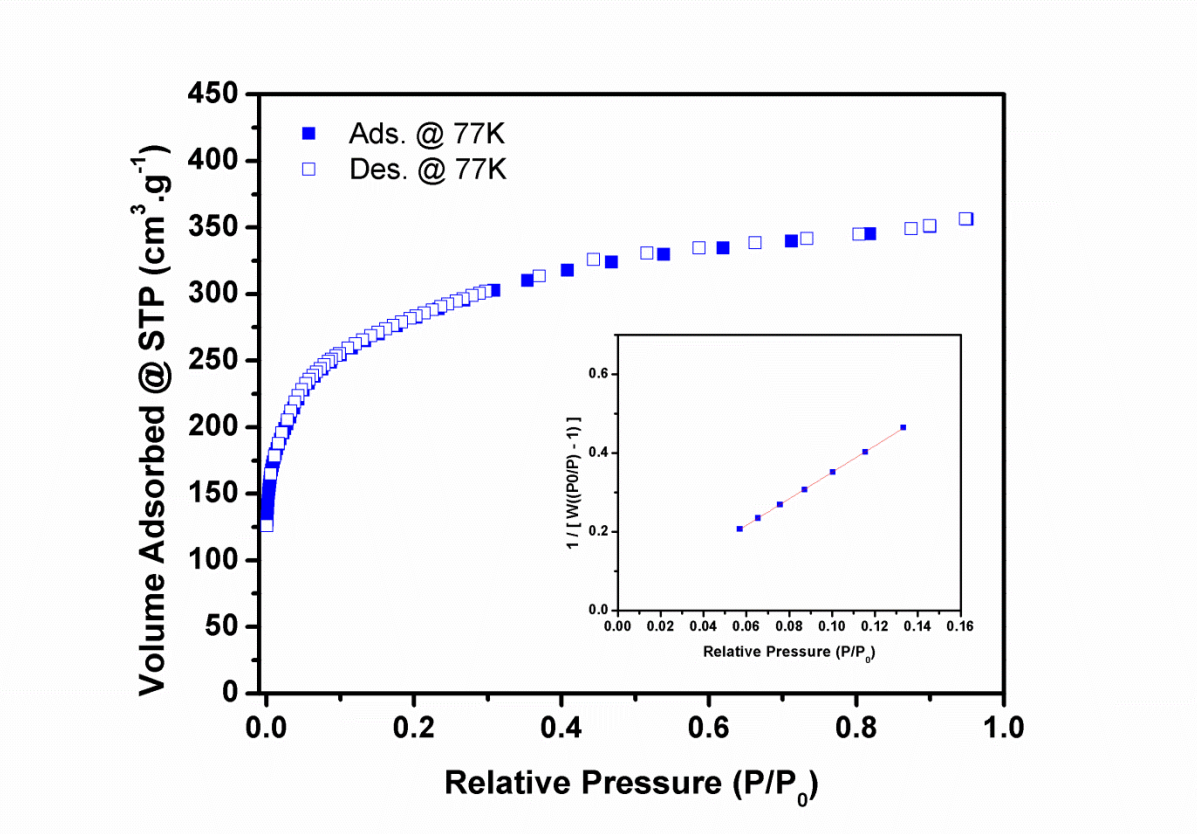
Intercept: 1.494e-02 g/cm^3 STP

Correlation coefficient: 0.999942

C constant: 419.586

Molecular cross-sectional area: 0.1620 nm²

FIGURE S17: N_2 adsorption isotherm and BET linear fit for the synthesised MIL-100.



BET surface area: 1039.859 m²/g

Slope: 3.367 g/cm^3 STP

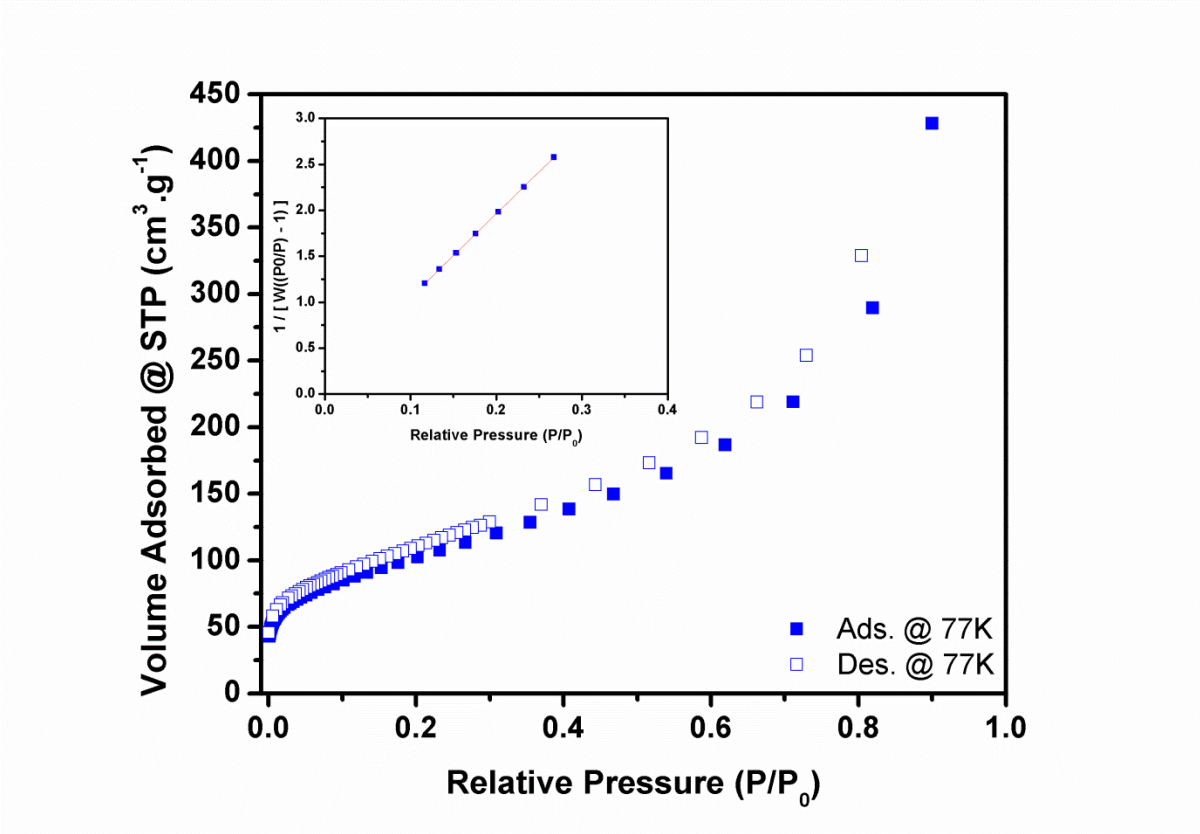
Intercept: 1.4665e-02 g/cm^3 STP

Correlation coefficient: 0.999943

C constant: 230.636

Molecular cross-sectional area: 0.1620 nm²

FIGURE S18: N_2 adsorption isotherm and BET linear fit for the synthesised $Ni_8(OH)_4(H_2O)_2(L)_6$.



BET surface area: 376.635 m²/g

Slope: 9.105 g/cm^3 STP

Intercept: 1.418e-01 g/cm^3 STP

Correlation coefficient: 0.999991

C constant: 65.206

Molecular cross-sectional area: 0.1620 nm²

FIGURE S19: SEM images of MTV-UiO-66 series. a) MTV-UiO-66 showing BDC:BDC-Br molar ratio of 1:0.6, b) MTV-UiO-66 showing BDC:BDC-Br molar ratio of 1:1.3, c) MTV-UiO-66 showing BDC:BDC-Br molar ratio of 1:2.3, and d) MTV-UiO-66 showing BDC:BDC-Br:BDC-NH_2 molar ratio of 1:1.1:0.6. Scale bars: a,c,d) 10 µm, b) 20 µm.

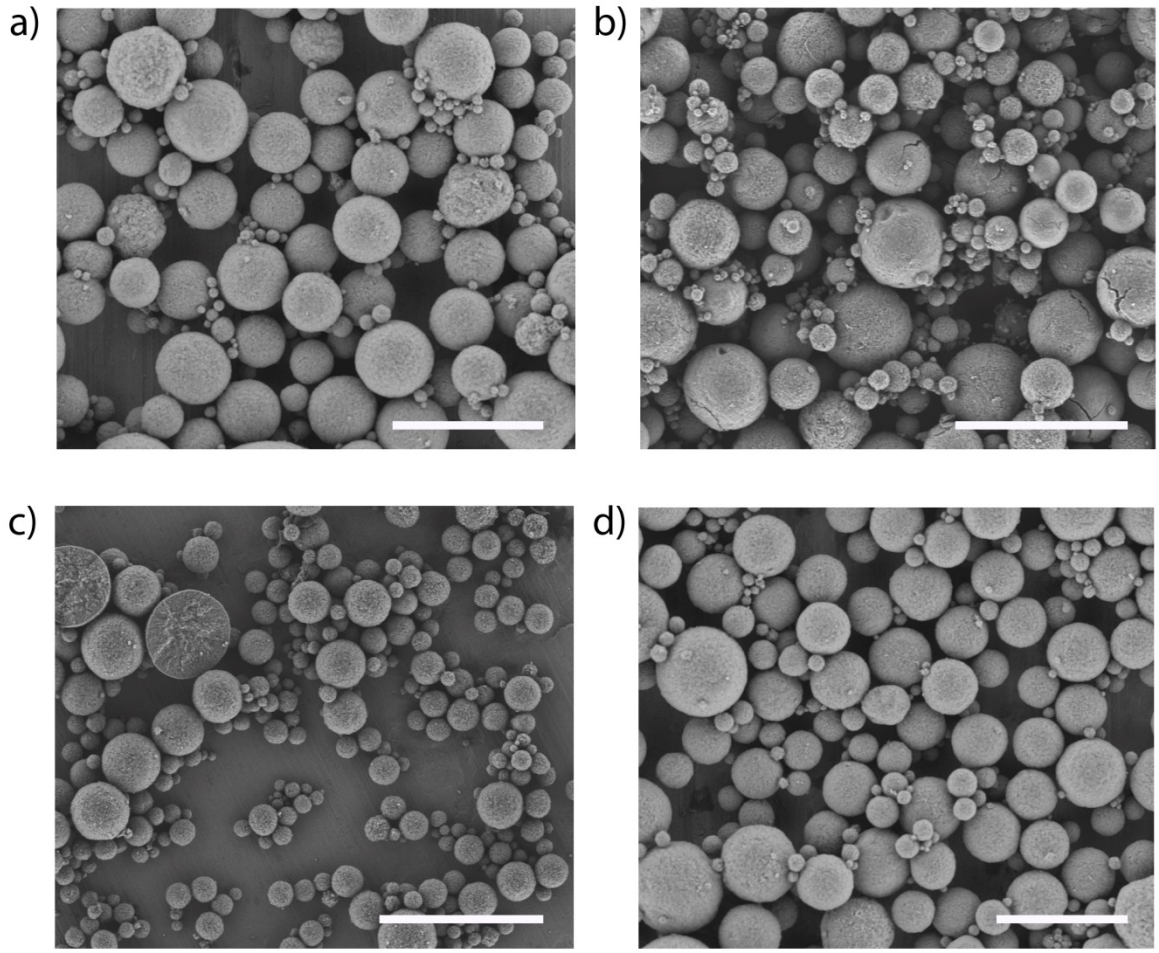


FIGURE S20: ^{1}H-NMR spectra of the digested samples of the MTV-UiO-66 synthesised at different BDC/BDC-Br molar ratios. a) BDC/BDC-Br = 1:2.3, b) BDC/BDC-Br = 1:1.3, and c) BDC/BDC-Br = 1:0.6.

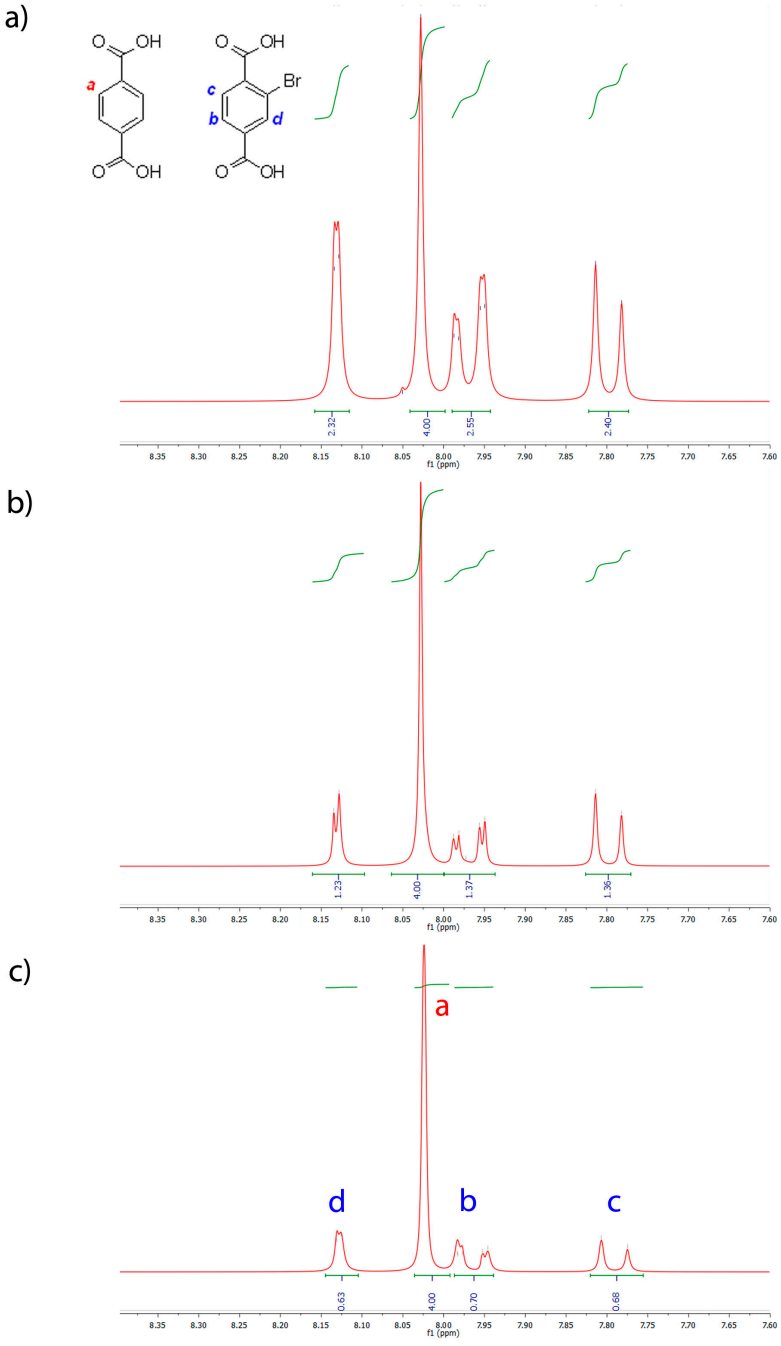
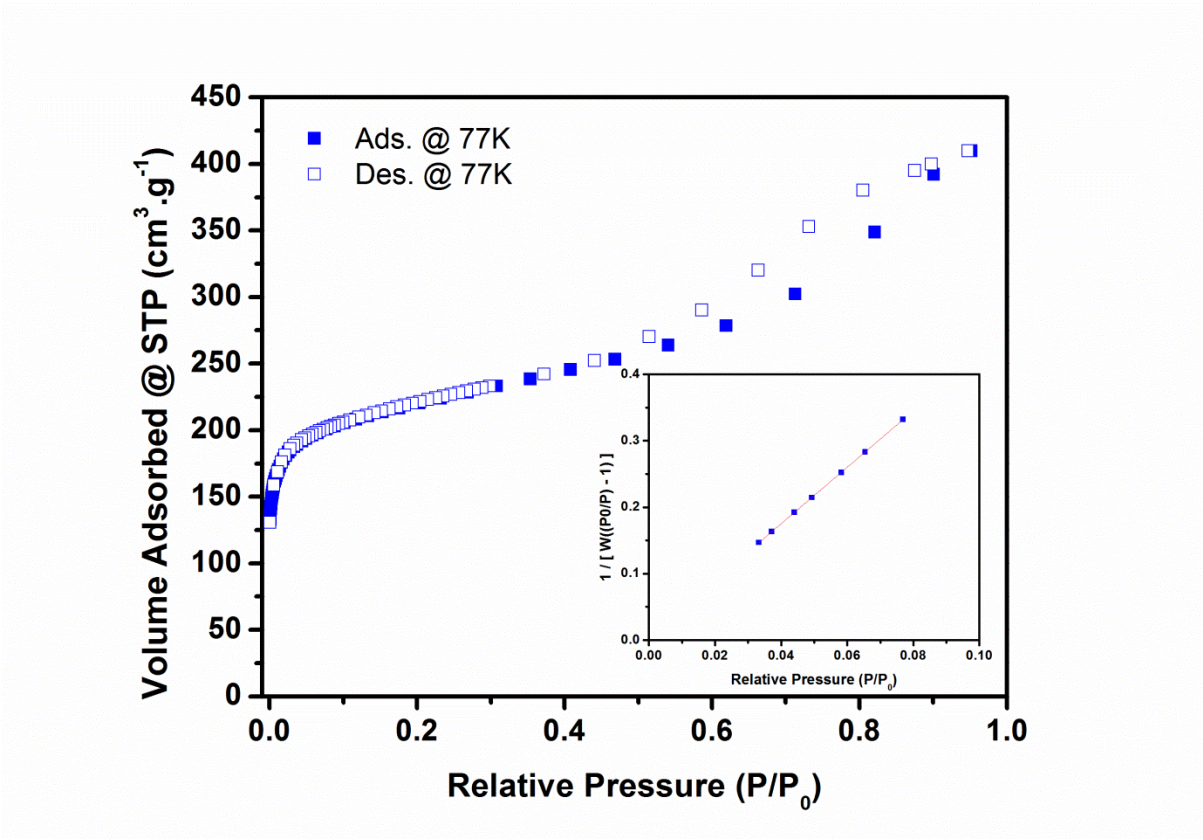


FIGURE S21: N_2 adsorption isotherm and BET linear fit for the synthesised MTV-UiO-66 with BDC:BDC-Br molar ratio of 1:0.6.



BET surface area: 818.142 m²/g

Slope: 4.252 g/cm^3 STP

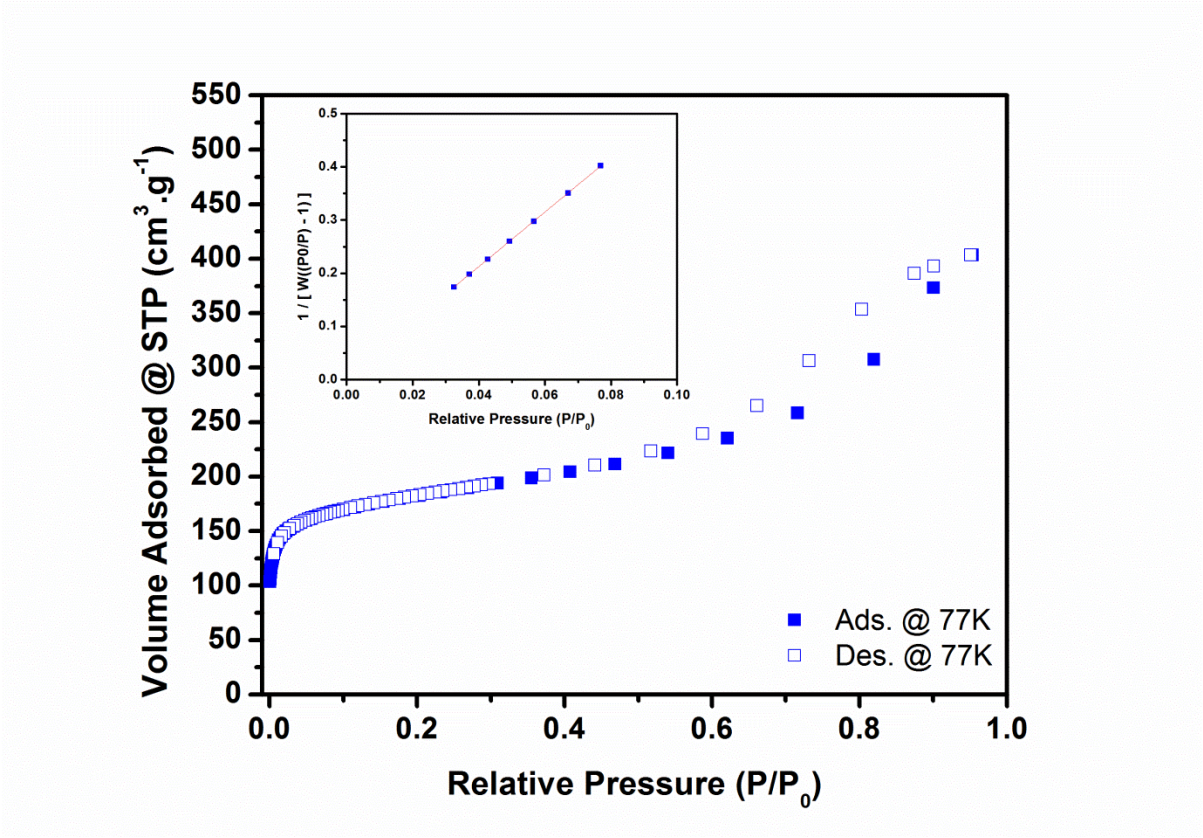
Intercept: 5.073e-03 g/cm^3 STP

Correlation coefficient: 0.999992

C constant: 839.082

Molecular cross-sectional area: 0.1620 nm²

FIGURE S22: N_2 adsorption isotherm and BET linear fit for the synthesised MTV-UiO-66 with BDC:BDC-Br molar ratio of 1:1.3.



BET surface area: 677.500 m²/g

Slope: 5.133 g/cm^3 STP

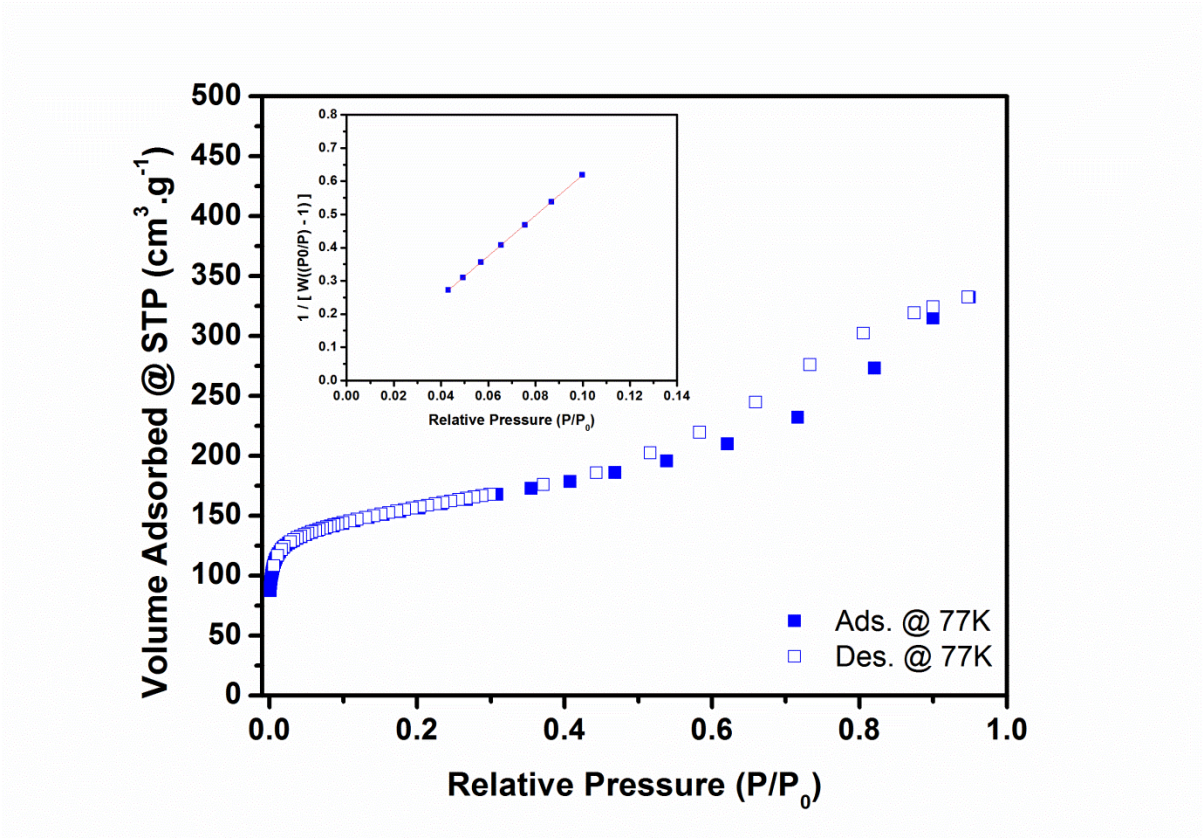
Intercept: 7.292e-03 g/cm^3 STP

Correlation coefficient: 0.999996

C constant: 704.900

Molecular cross-sectional area: 0.1620 nm²

FIGURE S23: N_2 adsorption isotherm and BET linear fit for the synthesised MTV-UiO-66 with BDC:BDC-Br molar ratio of 1:2.3.



BET surface area: 569.627 m²/g

Slope: 6.109 g/cm^3 STP

Intercept: 8.376e-03 g/cm^3 STP

Correlation coefficient: 0.999988

C constant: 730.303

Molecular cross-sectional area: 0.1620 nm²

FIGURE S24: XRPD diffractogram of the MTV-UiO-66 synthesised by mixing BDC, BDC-Br and BDC-NH_2 ligands (red), as compared to the simulated powder pattern for UiO-66 (black).

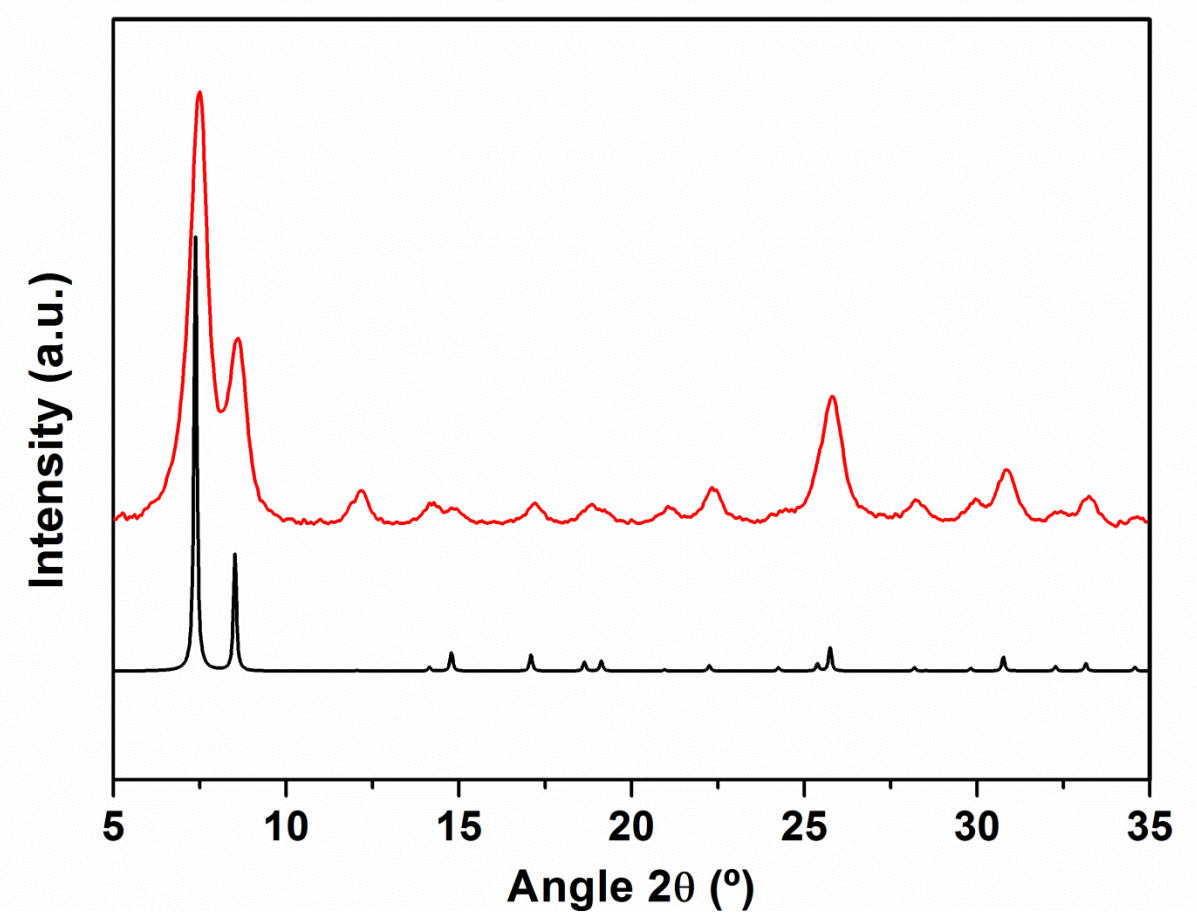
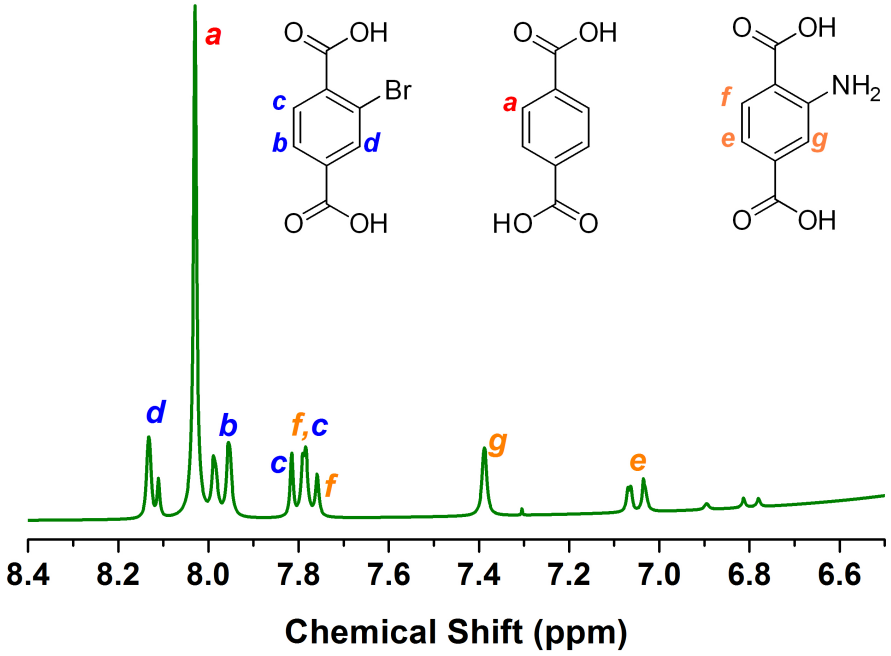
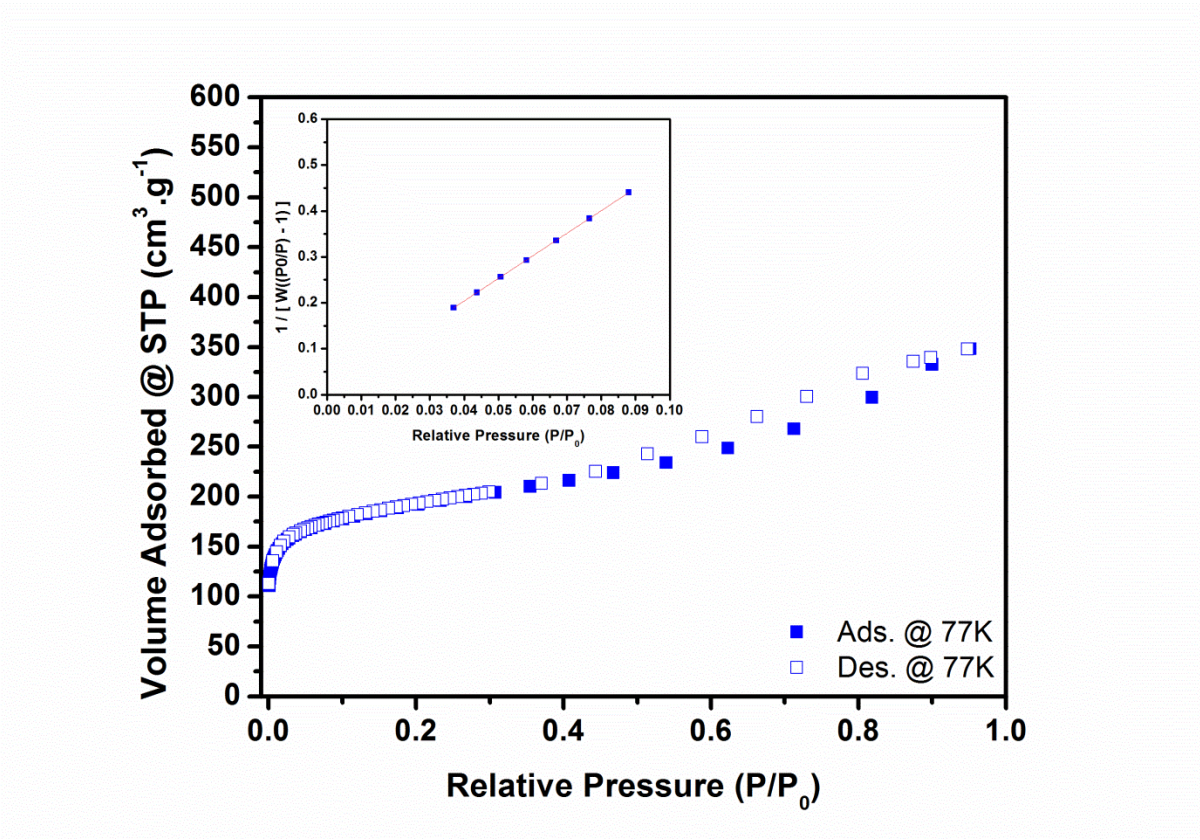


FIGURE S25: [1]H NMR spectra of the digested sample[a] of the MTV-UiO-66 prepared by mixing BDC, BDC-Br and BDC-NH_2 ligands.



[a] Approximately, 10 mg of the dried samples were digested in a mixture of 48% HF (20 µL) and DMSO-d_6 (600 µL).

FIGURE S26: N_2 adsorption isotherm and BET linear fit for the synthesised MTV-UiO-66 with BDC:BDC-Br:BDC-NH_2 molar ratio of 1:1.1:0.6.



BET surface area: 706.923 m²/g

Slope: 4.919 g/cm^3 STP

Intercept: 7.094e-03 g/cm^3 STP

Correlation coefficient: 0.999988

C constant: 694.452

Molecular cross-sectional area: 0.1620 nm²