

Positive Effect of Fluorine moiety on Oxygen Storage Capacity of UiO-66 Metal-Organic Frameworks

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ELECTRONIC SUPPLEMENTARY INFORMATION

1. Materials and methods

Chemicals and solvents were analytical grade, purchased from various commercial suppliers and used without further purification.

Nitrogen adsorption isotherms were measured at -77 K using a Quantachrome Quadrasorb surface area analyser. Samples were degassed in vacuum for 2 h at 200°C prior to the analysis. Relative pressure range varied between $1 \cdot 10^{-3}$ and 0.99 p/p_0 for adsorption measurements and between 0.99 and $1 \cdot 10^{-1}$ p/p_0 for desorption measurements. For the calculation of the BET surface area and total pore volume all the criteria for a correct estimation were taken into account [1,2].

Powder diffraction measurements were performed on a Bragg-Brentano Diffractometer, D8 Advance from Bruker AXS, equipped with copper tube, 2.5° Soller collimators, 0.3 mm divergence slit, anti-scatter screen, flip-stick stage and silicon strip detector (LynxEye) with 3° 2 θ detector opening. The diffraction patterns were monitored between 5° and 65° 2 θ with 0.06° 2 θ step width and 3s counting time per step.

IR spectra were recorded between 650 and 4000 cm^{-1} at a resolution of 4 cm^{-1} accumulating 64 scans using a diamond ATR/FT-IR spectrometer (Thermo Nicolet 6700; ATR-Durascope) with a MCT detector. TGA experiments were carried out on a TGA Q5000 TA Instruments device. Samples were heated under air at a heating rate of 10 K min^{-1} up to 700°C.

High pressure gas adsorption isotherms measurements were carried out employing a magnetic suspension balance from Rubotherm, type ISOSORP® HyGrA. Samples were activated at 200°C for 6 h under vacuum. Adsorption measurements with nitrogen started in vacuum, with increasing pressure up to 100 bar.

¹H-NMR spectra were recorded on a Bruker Avance 250 spectrometer (250.1 MHz). The measurements were carried out employing CDCl₃ as solvent. Chemical shifts were determined by reference to residual solvent peaks. The evaluation was done with the software MestRec.

2. Synthesis of 2-trifluoromethyl-1,4-benzodicyclohexanecarboxylic acid [3]

A mixture of 4-methyl-2-(trifluoromethyl)benzoic acid (0.496 g, 2.4 mmol), NaOH (0.192 g, 4.8 mmol), KMnO₄ (0.95 g, 6.0 mmol) and deionized water (12.5 mL) was refluxed for 2 h and then cooled down to room temperature. After filtration, the filtrate was diluted with water to 250 mL and the diluted solution was acidified with HCl (37%). The resulting white solid was collected by filtration, washed thoroughly with water and dried in an oven at 80 °C for 12 h. Yield: 0.345 g (67%).
FT-IR (cm^{-1}): 2823 (brd), 2660 (brd), 2555 (brd), 1669 (s, shp), 1418 (w), 1400 (w), 1265 (s, shp), 1128 (s, shp), 1052 (w, shp), 908 (w), 863 (w), 759 (s, shp), 685 (w, shp)

¹H NMR (d_6 -DMSO): 7.925 (1H, d), 8.24 (2H, m).

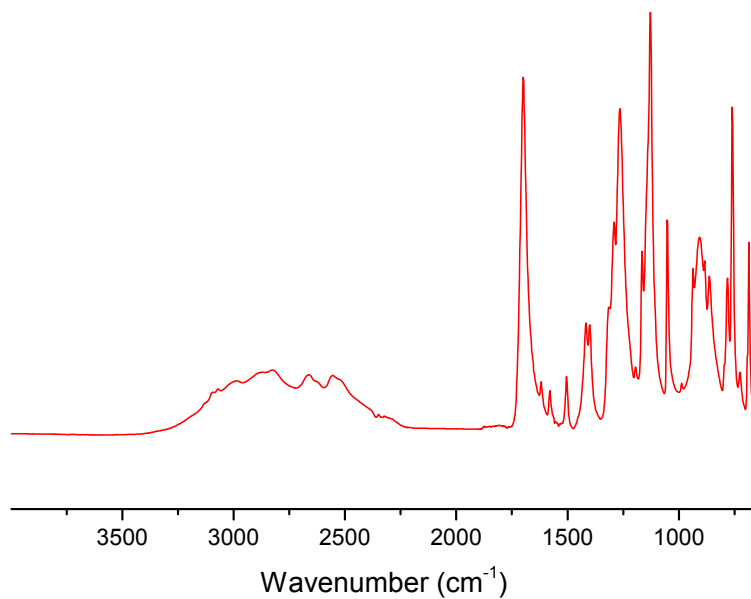


Figure S1: FT-IR spectrum of 2-trifluoromethyl-1,4-benzodicyclohexanecarboxylic acid

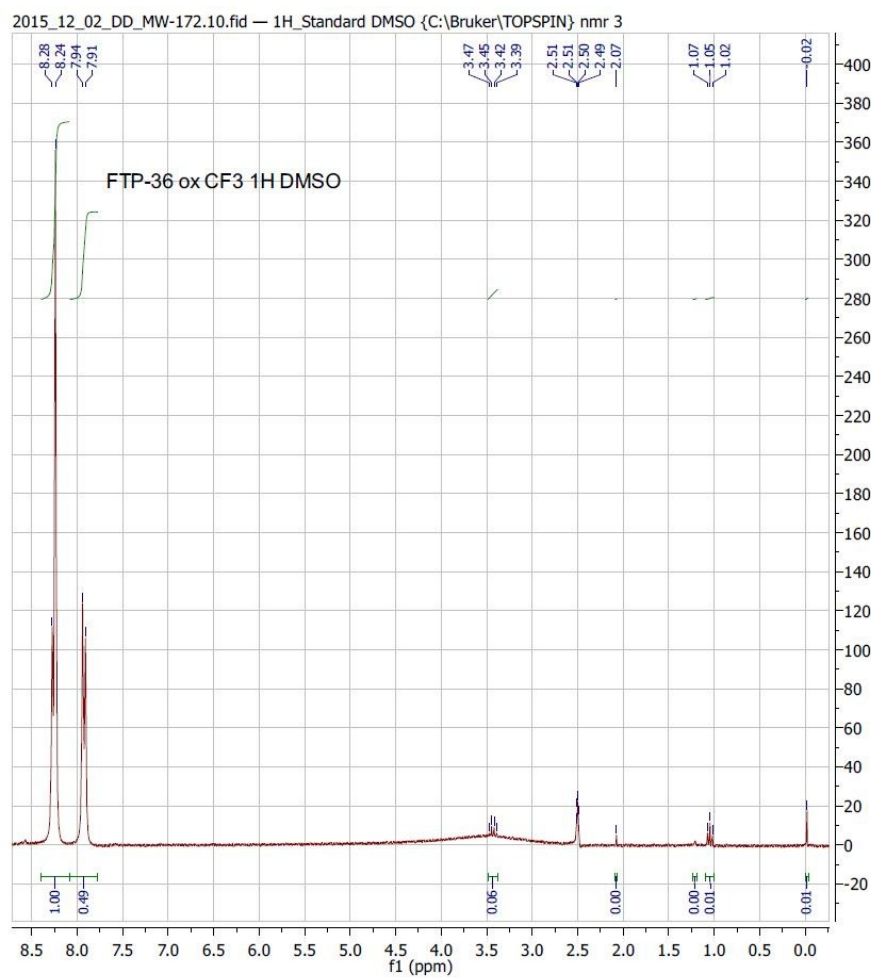


Figure S2: ¹H-NMR of 2-trifluoromethyl-1,4-benzodicyclohexanecarboxylic acid

3. Synthesis of fluorinated UiO-66 ^[4]

ZrCl₄ (0.935 g; 2.7 mmol) is suspended in DMF (50 mL), concentrated HCl (10 mL) is added and the mixture is sonicated with ultrasound for some minutes, until it becomes clear. 1,4-benzodicycloxylic acid (0.67 g; 2.7 mmol) is dissolved in DMF (100 mL) and it is poured into the ZrCl₄ solution. The final mixture is stirred at 80°C for 24 h. Afterwards the suspension is filtered off on a PTFE membrane filter; the recovered white solid is suspended in DMF and stirred at r.t. for 24h. The solid is recovered by filtration, washed with DMF (4x20 mL), suspended and stirred at r.t. for 24 h in MeOH. After this the suspension is filtered off again, washed on a polypropylene membrane filter with MeOH (3x20 mL) and dried at air.

1,4-benzodicycloxylic acid is (H₂BDC) partially replaced by increasing amount of 2-fluoro-1,4-benzodicycloxylic acid (2F-H₂BDC) or 2-trifluoromethyl-1,4-benzodicycloxylic acid (2CF₃-H₂BDC), as reported in Table 1.

Eight fluorine containing MOFs, were synthesized and fully characterized. Each MOF contains respectively 25%, 50%, 75 % and 100% mol/mol of the fluorine containing linker; 2F-H₂BDC for the UiO-66-F series and 2CF₃-H₂BDC in the case of the UiO-66-CF₃ series.

Table 1. Amount of metal precursor and organic linker utilized for the syntheses of fluorine containing UiO-66

Entry	ZnCl ₄ (g)	H ₂ BDC (g)	2F-H ₂ BDC (g)	2CF ₃ -H ₂ BDC (g)
UiO-66-F 25	0.635	0.336	0.126	-
UiO-66-F 50	0.631	0.227	0.251	-
UiO-66-F 75	0.626	0.119	0.373	-
UiO-66-F 100	0.632	-	0.505	-
UiO-66-CF ₃ 25	0.637	0.334	-	0.161
UiO-66-CF ₃ 50	0.517	0.186	-	0.257
UiO-66-CF ₃ 75	0.528	0.105	-	0.370
UiO-66-CF ₃ 100	0.521	-	-	0.517

4. Surface and Pores analysis

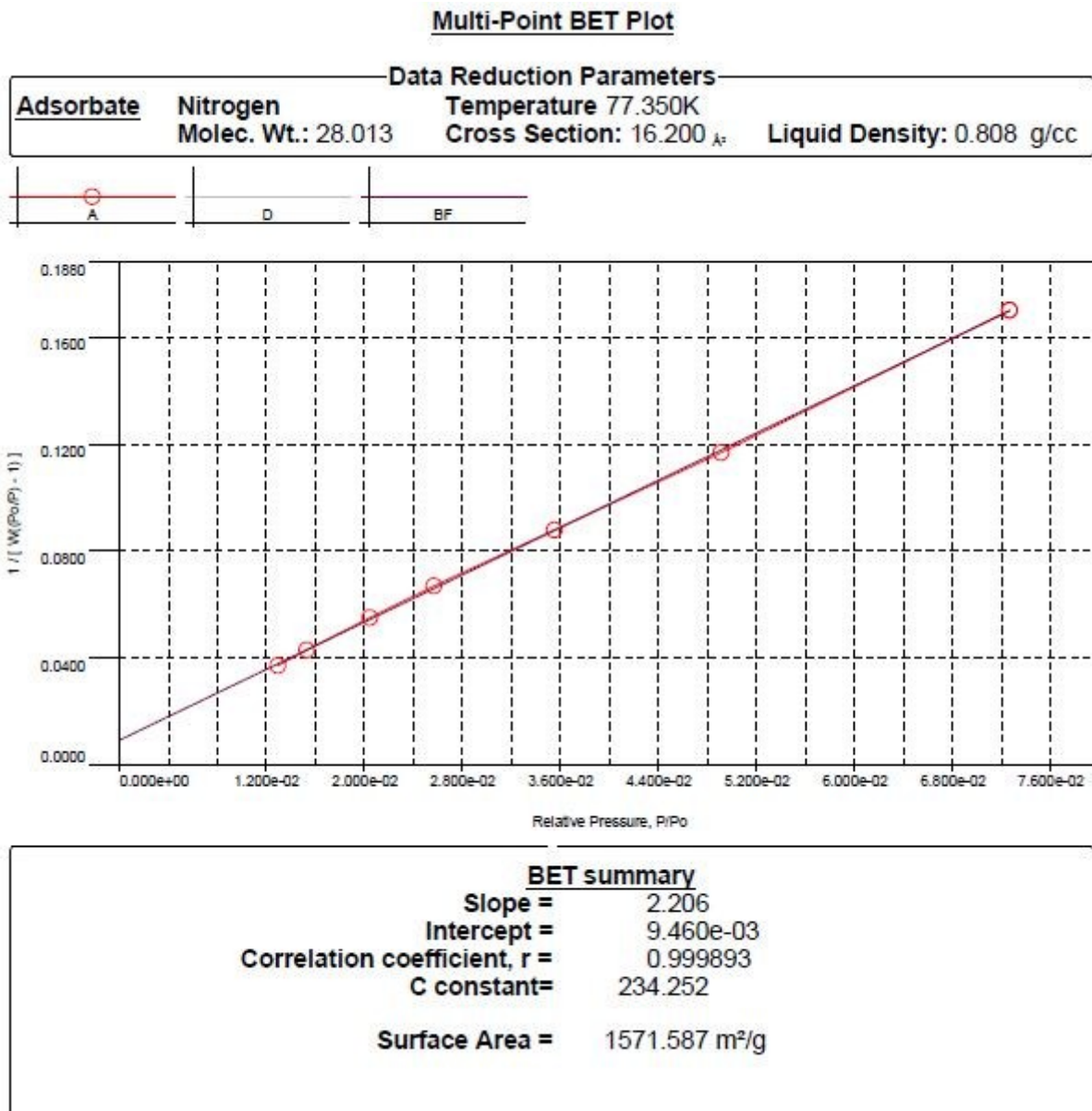


Figure S3: B.E.T. N₂ adsorption isotherm of UiO-66

Multi-Point BET Plot



Figure S4: B.E.T. N₂ adsorption isotherm of UiO-66-F 25.

Multi-Point BET Plot



Figure S5: B.E.T. N₂ adsorption isotherm of UiO-66-F 50.

Multi-Point BET Plot

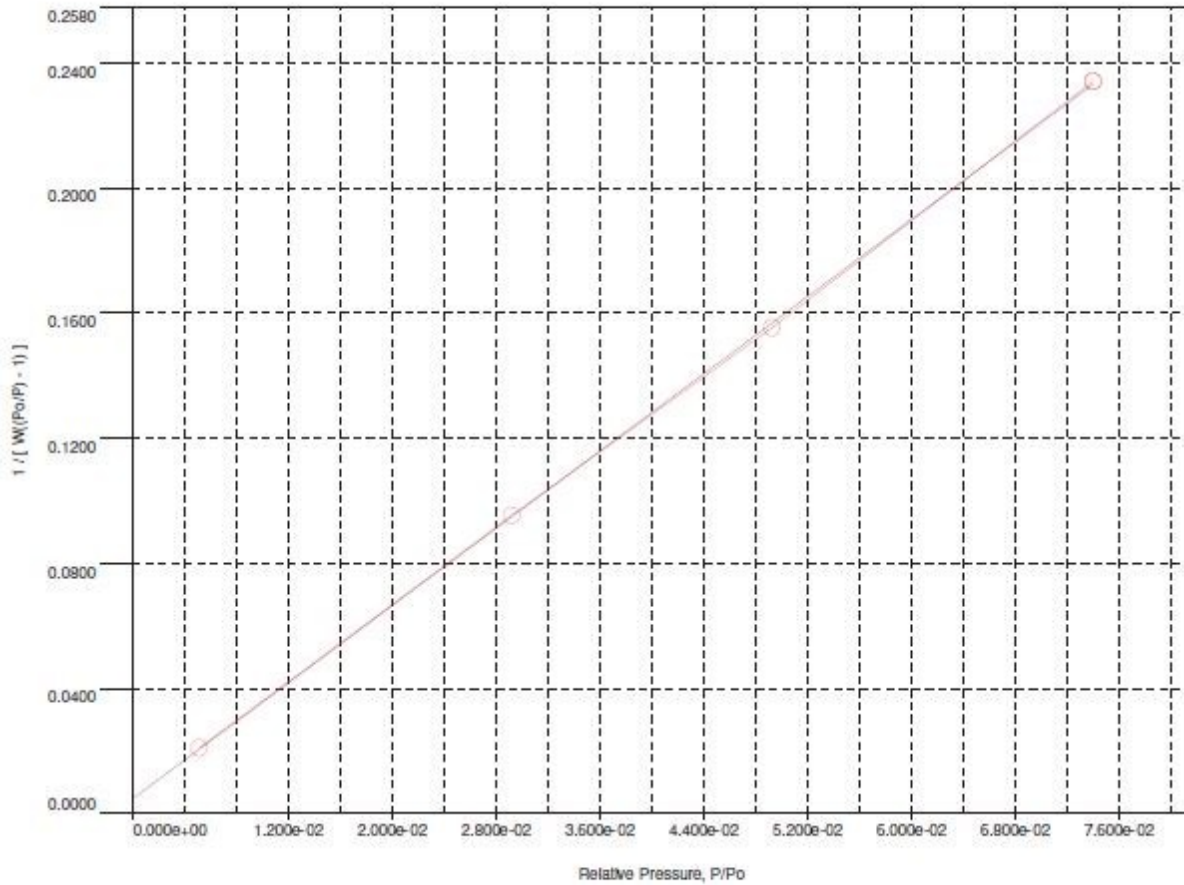


Figure S6: B.E.T. N₂ adsorption isotherm of UiO-66-F 75.

Multi-Point BET Plot

Adsorbate		Data Reduction Parameters			
Nitrogen	Molec. Wt.: 28.013	Temperature	77.350K	Liquid Density:	0.806 g/cc
		Cross Section:	16.200 Å ²		

A	BF
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<u>BET summary</u>	
Slope =	3.089
Intercept =	4.731e-03
Correlation coefficient, r =	0.999932
C constant =	653.929
Surface Area =	1125.557 m ² /g

Figure S7: B.E.T. N₂ adsorption isotherm of UiO-66-F 100.

Multi-Point BET Plot

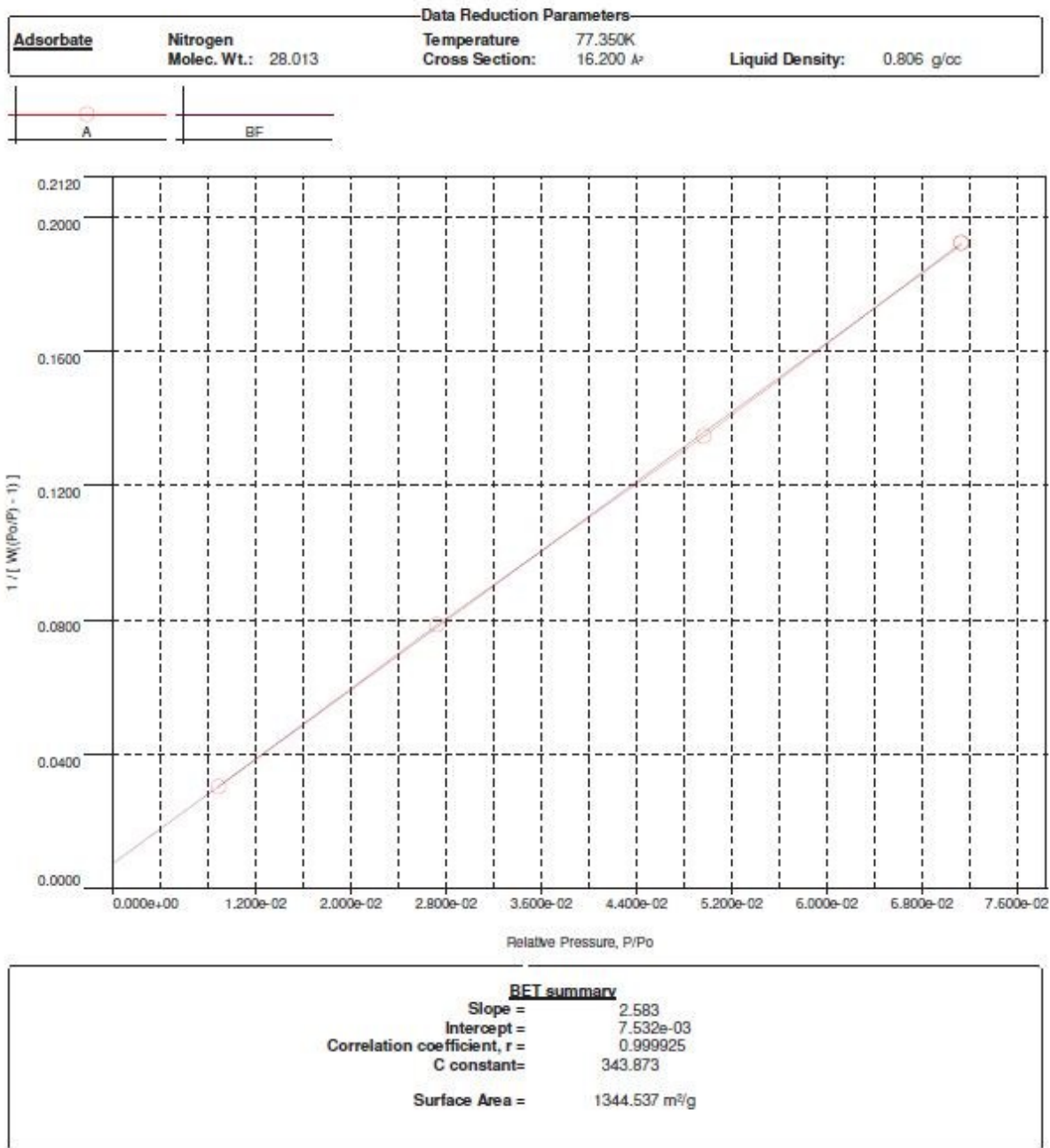
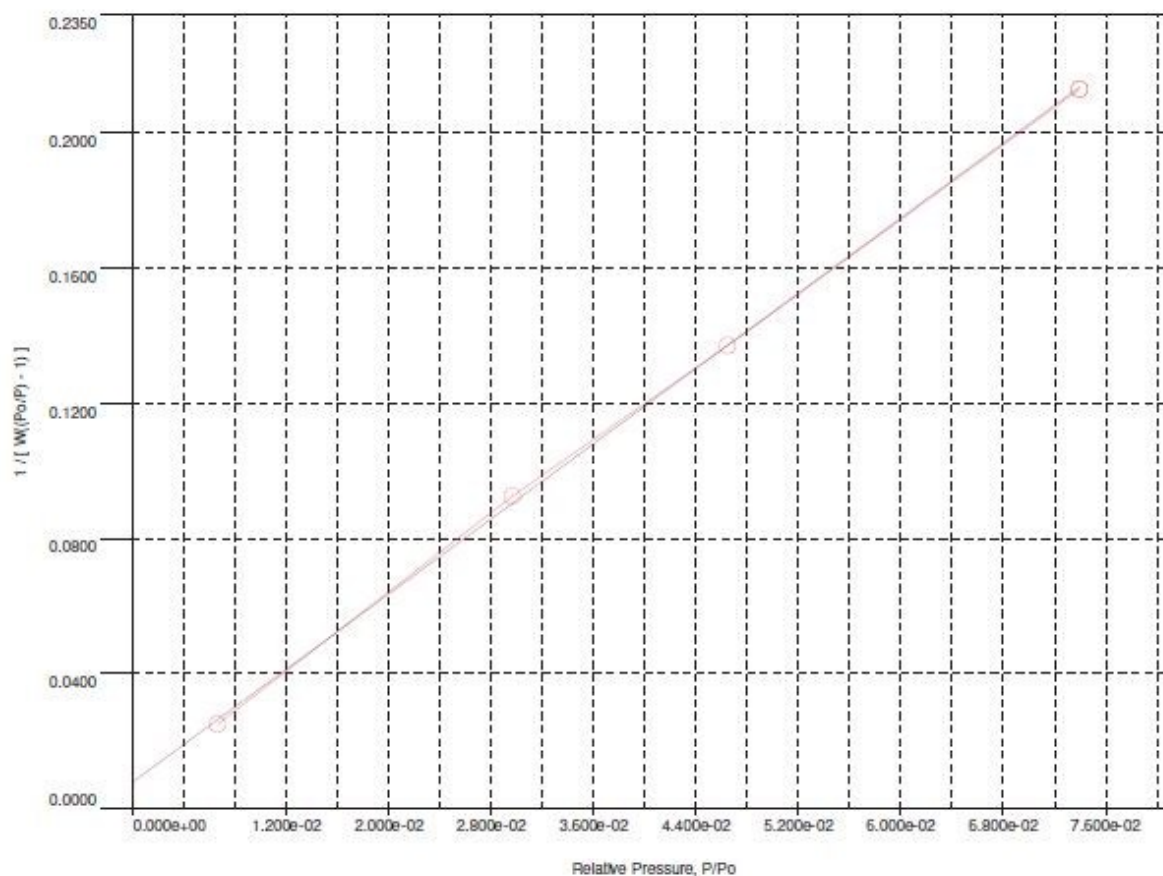


Figure S8: B.E.T. N₂ adsorption isotherm of UiO-66-CF₃ 25.

Multi-Point BET Plot

Adsorbate		Nitrogen		Data Reduction Parameters	
		Molec. Wt.:	28.013	Temperature	77.350K
				Cross Section:	16.200 Å ²
				Liquid Density:	0.806 g/cc

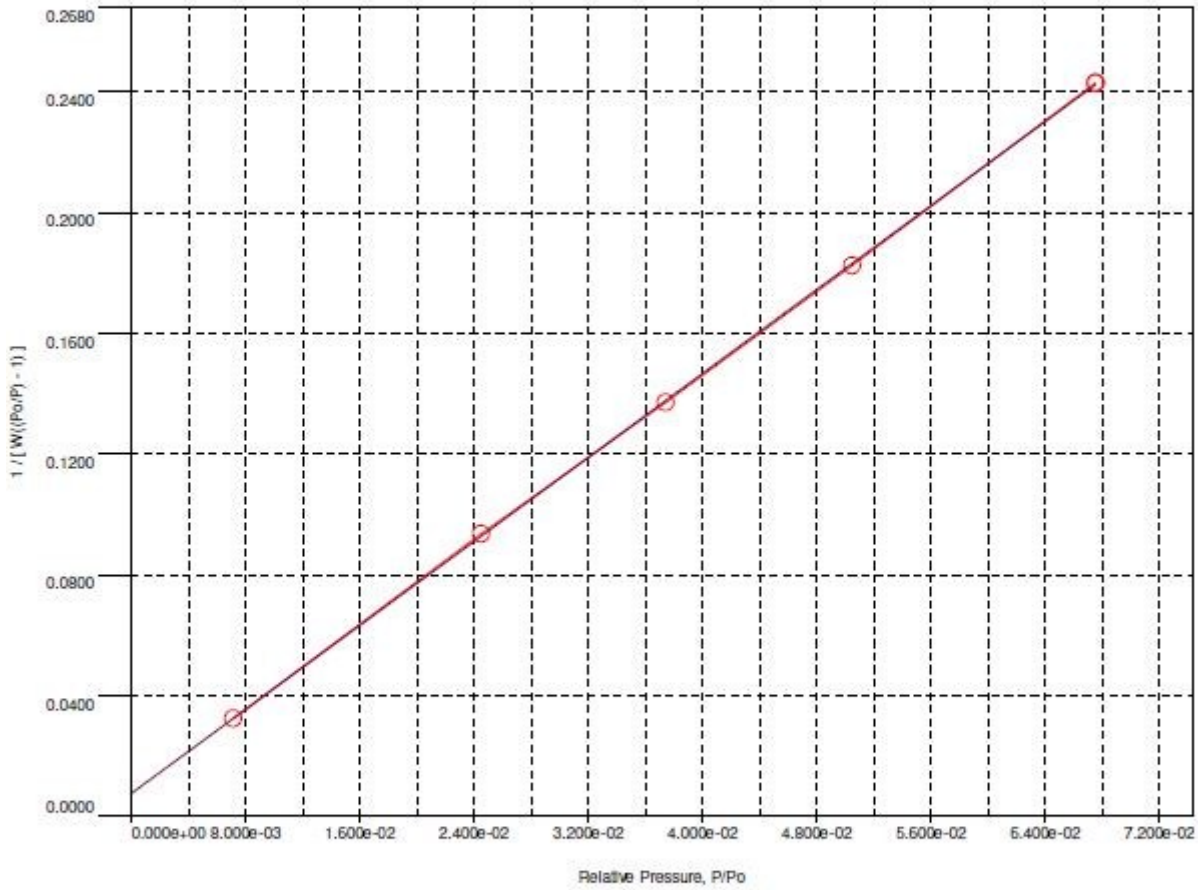
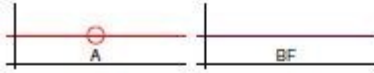


<u>BET summary</u>	
Slope =	2.779
Intercept =	8.009e-03
Correlation coefficient, r =	0.999825
C constant =	348.008
Surface Area =	1249.495 m ² /g

Figure S9: B.E.T. N₂ adsorption isotherm of UiO-66-CF₃ 50.

Multi-Point BET Plot

Adsorbate		Data Reduction Parameters			
Nitrogen	Molec. Wt.: 28.013	Temperature	77.350K	Liquid Density:	0.806 g/cc
		Cross Section:	16.200 Å ²		



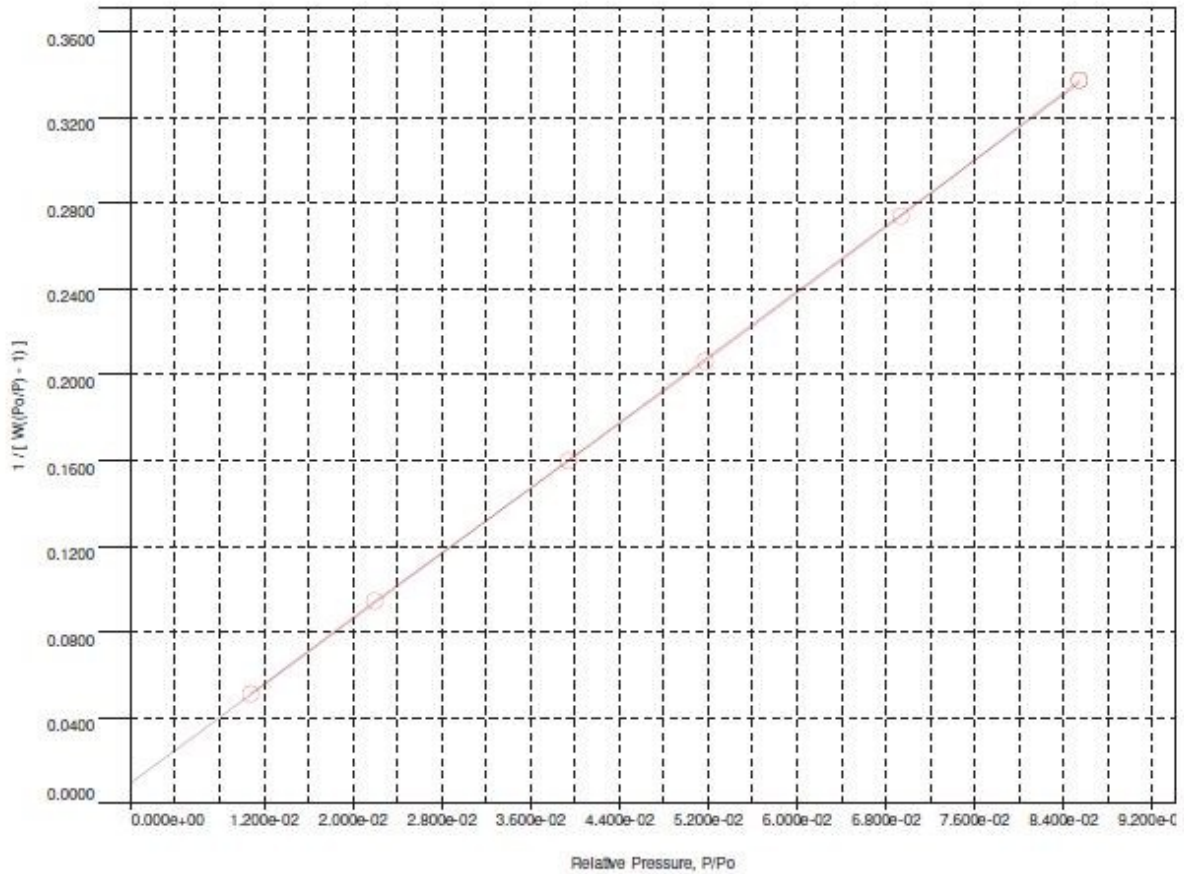
BET summary	
Slope =	3.477
Intercept =	7.598e-03
Correlation coefficient, r =	0.999966
C constant =	458.565
Surface Area =	999.527 m ² /g

Figure S10: B.E.T. N₂ adsorption isotherm of UiO-66-CF₃ 75.

Multi-Point BET Plot

Data Reduction Parameters			
Adsorbate	Nitrogen	Temperature	77.350K
	Molec. Wt.: 28.013	Cross Section:	16.200 Å ²
		Liquid Density:	0.806 g/cc

A	BF
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BET summary	
Slope =	3.820
Intercept =	9.545e-03
Correlation coefficient, r =	0.999965
C constant =	401.221
Surface Area =	909.382 m ² /g

Figure S11: B.E.T. N₂ adsorption isotherm of UiO-66-CF₃ 100.

5. XRD patterns

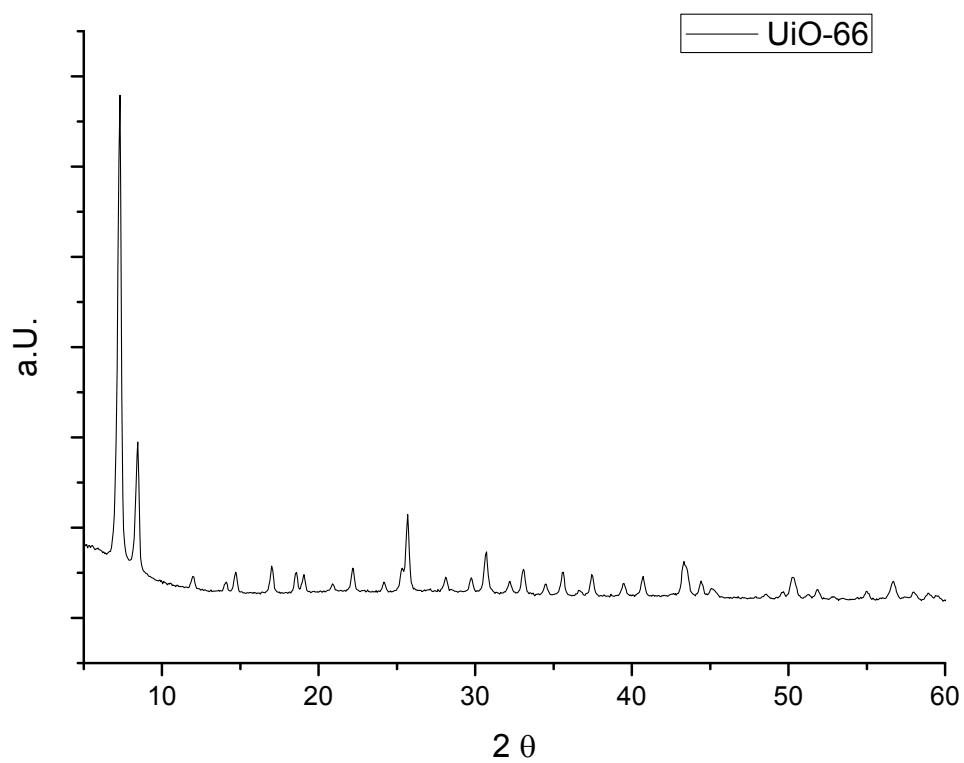


Figure S12. XRD pattern of UiO-66

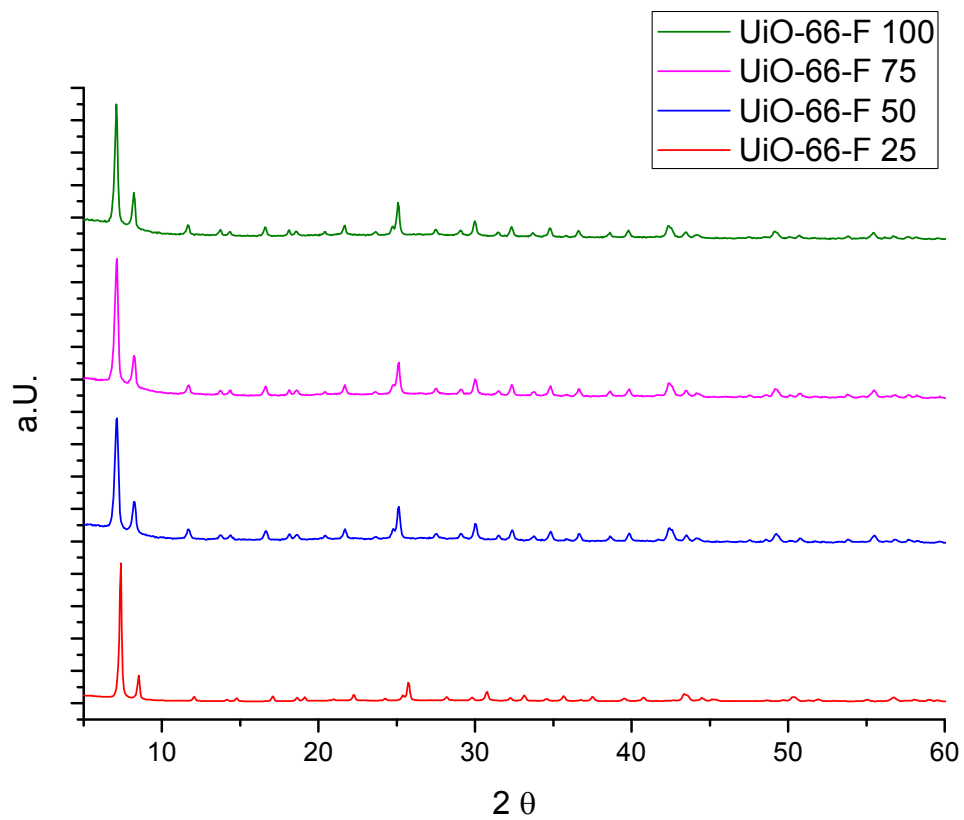


Figure S13. XRD pattern of UiO-66-F series

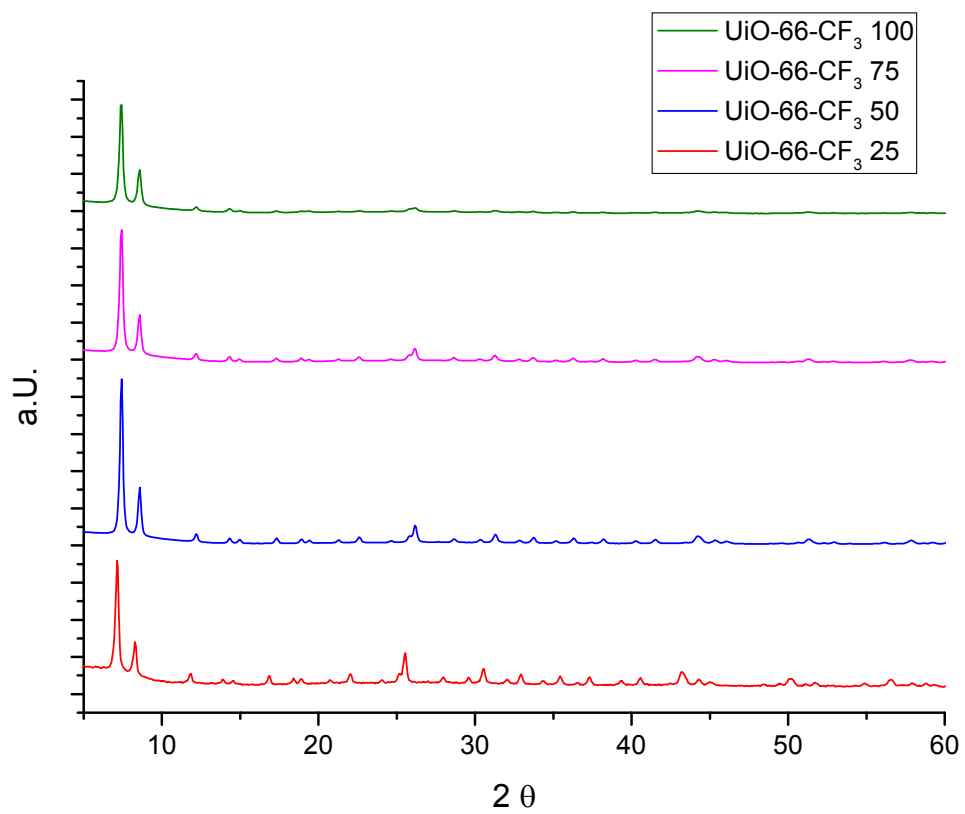


Figure S14. XRD pattern of UiO-66-CF₃ series

6. FT-IR spectra

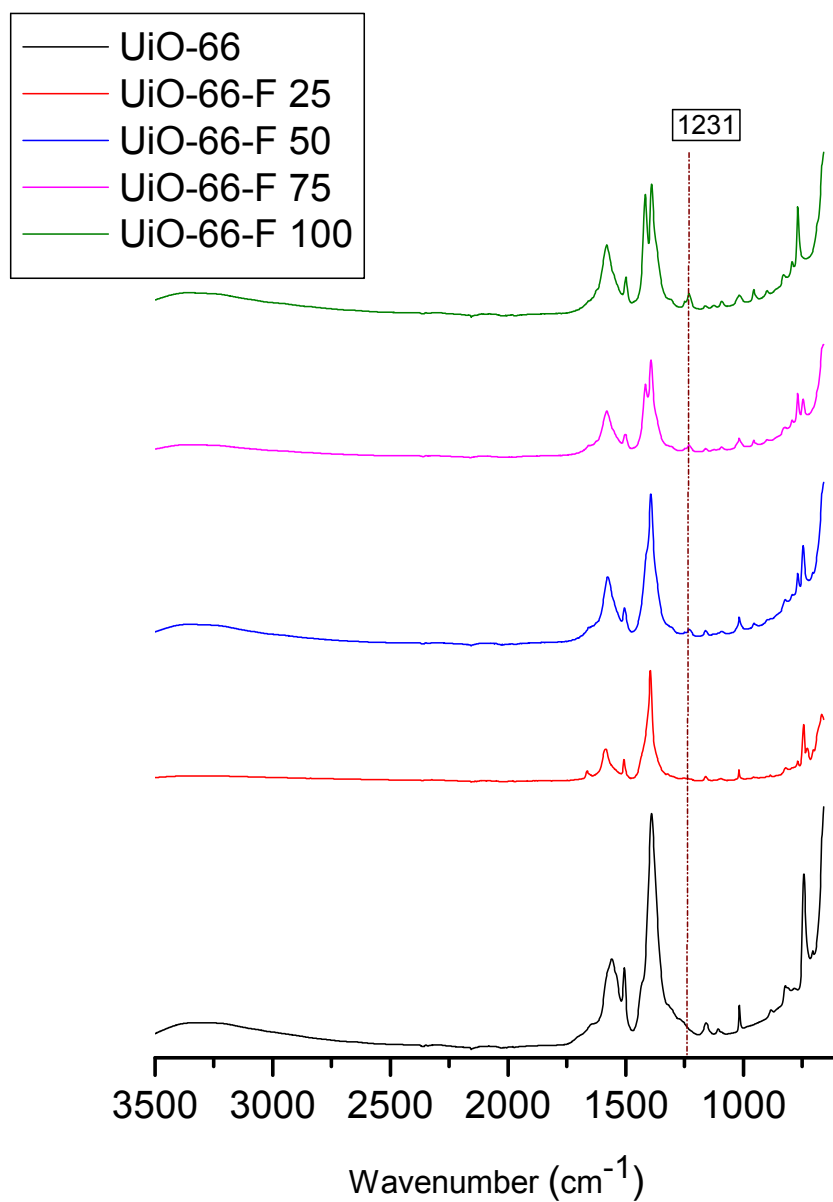


Figure S15. FT-IR spectra of UiO-66-F series compared with standard UiO-66. The formation of the band at 1231 cm⁻¹, relative to the Ar-F bond is highlighted.

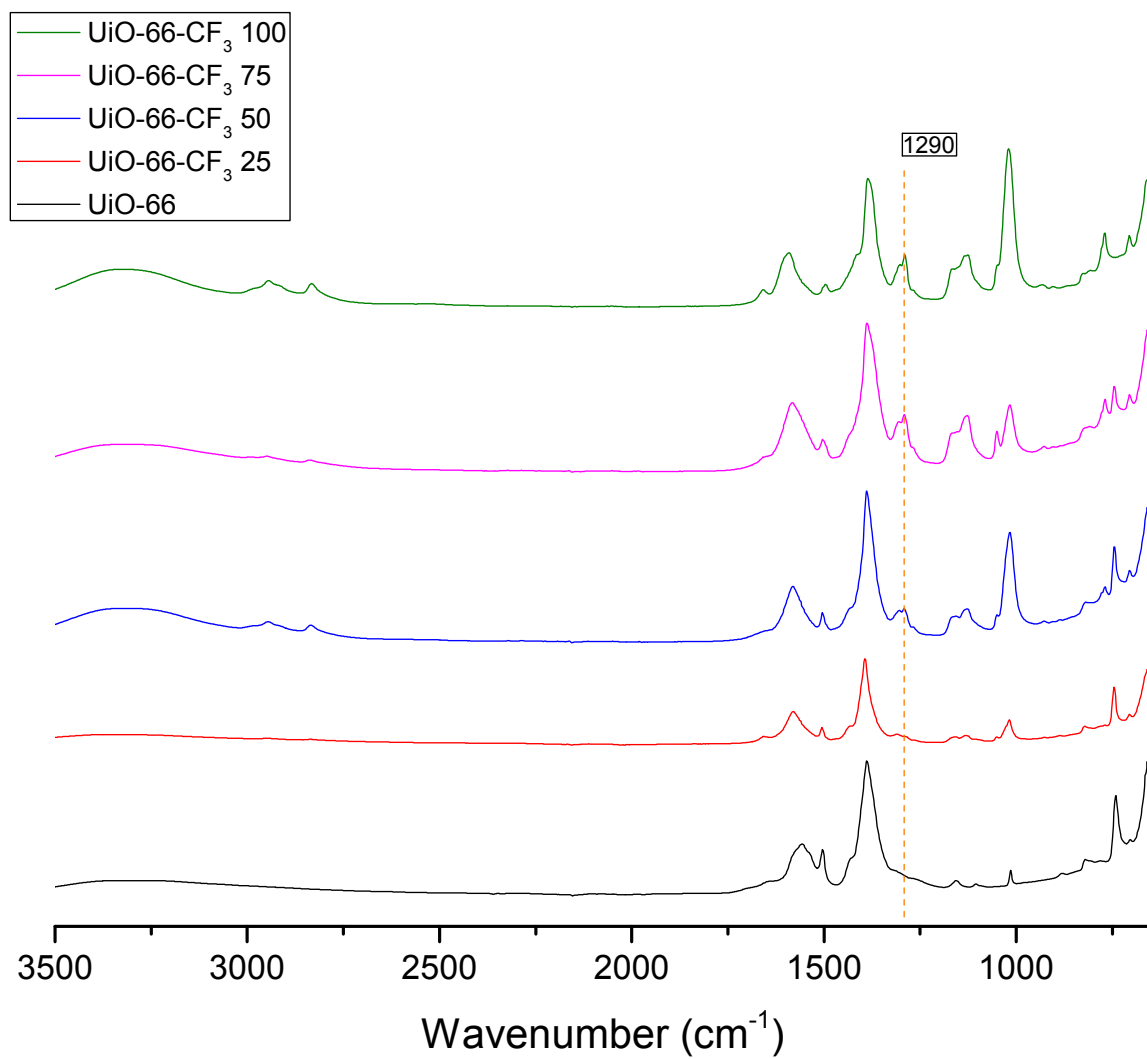


Figure S16. XRD pattern of UiO-66-CF₃ series compared with standard UiO-66. The formation of the band at 1290 cm⁻¹, relative to the Ar-CF₃ bond is highlighted.

7. TGA analyses

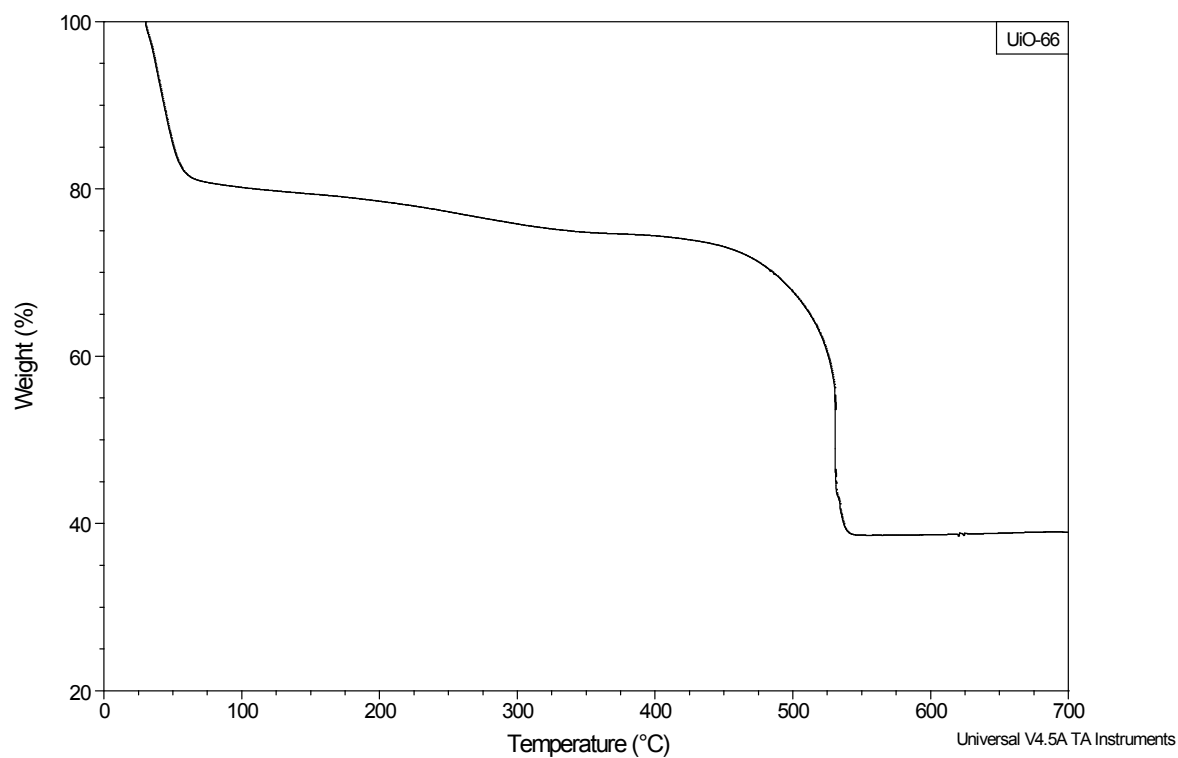


Figure S17. TGA analysis of UiO-66

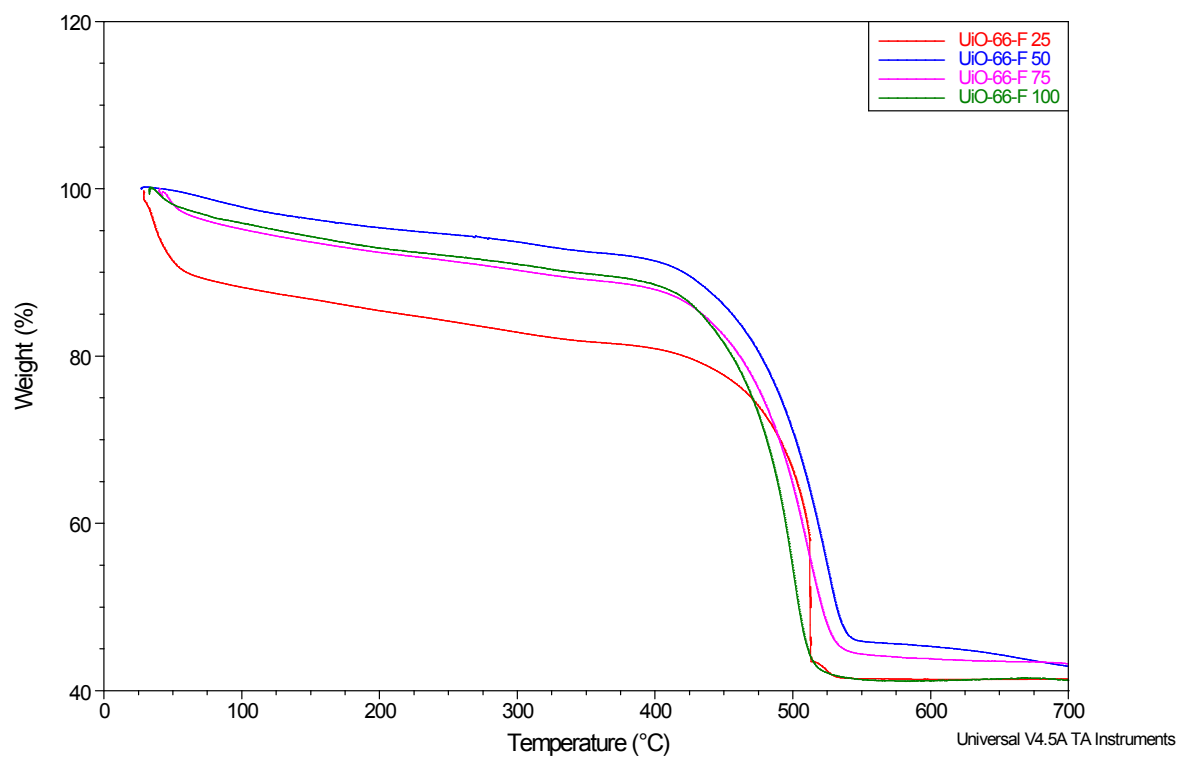


Figure S18. Overlay of TGA analyses of UiO-66-F series

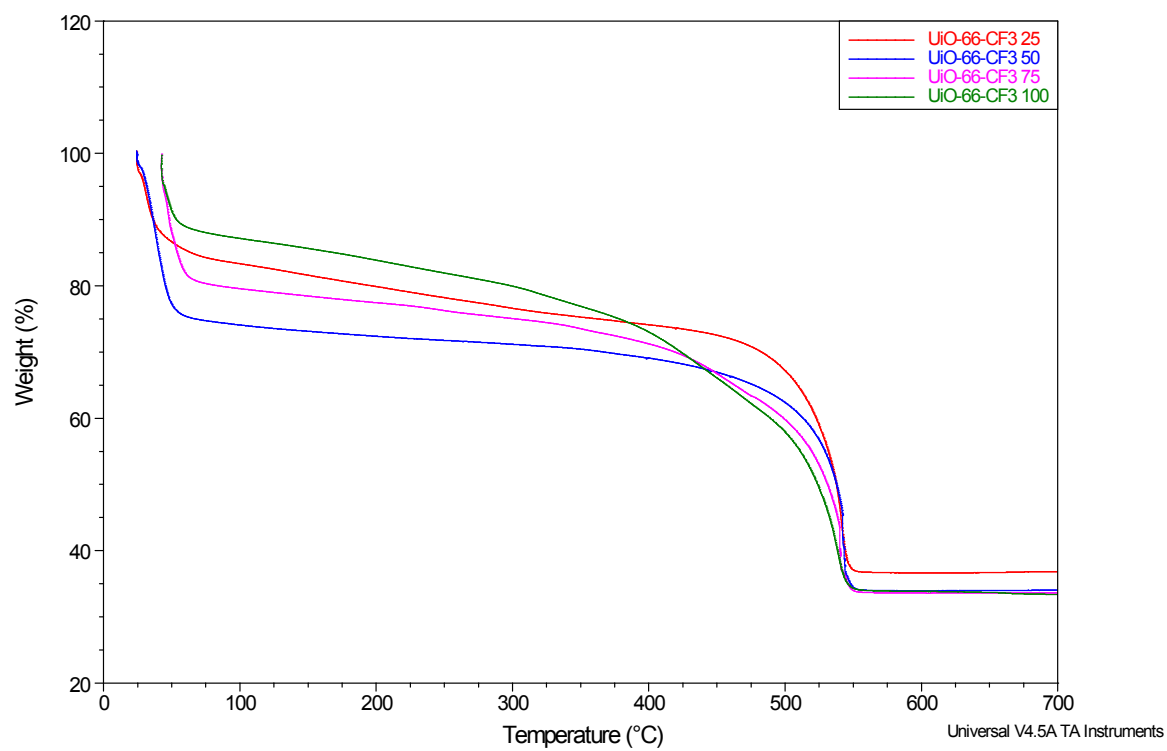


Figure S19. Overlay of TGA analysis of UiO-66-CF₃ series

8. High pressure oxygen adsorption isotherms of UiO-66-F series

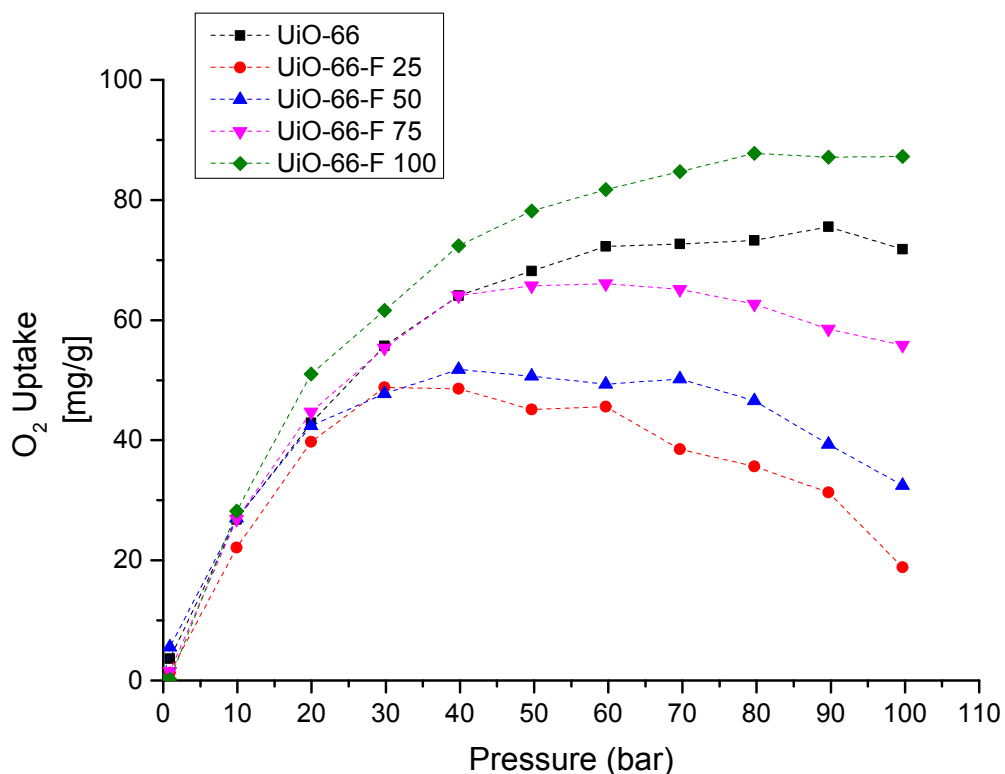


Figure S20. Oxygen adsorption isotherms for UiO-66 and UiO-66-F series up to 100 bar.

9. References

- [1] T. Düren, F. Millange, G. Férey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C*, 2007, **111**, 15350.
- [2] I. Senkovska and S. Kaskel, *Chem. Commun.*, 2014, **50**, 7089.
- [3] S. Biswas, D. E. P. Vanpoucke, T. Verstraelen, M. Vandichel, S. Couck, K. Leus, Y.-Y. Liu, M. Waroquier, V. Van Speybroeck, J.F.M. Denayer and P. Van Der Voort, *J. Phys. Chem. C*, 2013, **117**, 22784.
- [4] M. J. Katz, Z. J. Brown, Y. J. Colon, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449.