

Supplementary Information

Rapid Spatially-Resolved Post-Synthetic Patterning of Metal-Organic Framework films

Fatimah Al-Ghazzawi,^{a,b,c} Luke Conte,^d Klaudia Wagner,^{a,b} Christopher Richardson^{*d} and Pawel Wagner^{*a,b}

^a ARC Centre of Excellence for Electromaterials Science, AIIIM Faculty, Innovation Campus, University of Wollongong, North Wollongong, NSW 2522, Australia.

^b Intelligent Polymer Research Institute, AIIIM Faculty, Innovation Campus, University of Wollongong, North Wollongong, NSW 2522, Australia.

^c Al-Nasiriyah Technical Institute, Southern Technical University, 64001, Thi-Qar, Iraq.

^d School of Chemistry and Molecular Bioscience, Faculty of Science Medicine and Health, University of Wollongong, NSW 2522, Australia.

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1 General experimental

All chemicals used were of analytical grade and purchased from either Sigma Aldrich, VWR Australia or Ajax Finechem Pty Ltd. Films of UiO-66-NH₂ were prepared following the method described by Li et al.¹

Inkjet printing was performed using a PixDro LP50 piezo-controlled drop-on-demand printer with a single printhead. The printhead was assembled with the ink bottle connected to the pressure tube and voltage cable and computer controlled. The substrate stage was moved only in the XY domain at 200 mm/s during printing. Patterns were printed using a 128 nozzle printhead (Type SE 128 AA) with nozzle spacing of 502 microns and nozzle diameter 35 microns. When one nozzle was selected for printing, the efficiency was checked by the drop-watcher camera. The pressure and voltage of inks were 18-21 mbar and 58-60 V, respectively. The ejection speed and drop size from the nozzle were 0.76 ± 0.1 m/s and 30 ± 1.8 pL, respectively. After every 10 layers, the active nozzle was checked for blockage. After completing the pattern, the film samples were washed two times using the print solvent, two times with EtOH and multiple times with acetone. The ink was prepared by dissolving ferrocene carboxaldehyde (214 mg, 1 mmol) in 10 mL of 1,4-dioxane. After storage for 24 h, the ink was filtered ($45 \mu\text{m}$) to remove any particles that may lead to blocking the printhead.

Leica M205A and Leica DM6000 microscopes fitted with CCD cameras were used to obtain images of the morphology of the samples and resolution of the patterns. The Leica M205A was used at scales from 10 mm to 1 mm and the Leica DM6000 at scales from $500 \mu\text{m}$ to $25 \mu\text{m}$.

A JEOL JSM-7500 was used to study morphologies of all the samples at 15 kV. Energy-Dispersive X-Ray Spectroscopy (EDS) data was recorded on a JEOL JSM-6490LV at 15 kV accelerating voltage. Samples were prepared by attaching the printed material onto a copper heel by a conductive carbon tape and silver paint. Samples for imaging were coated by thin platinum layer. Samples for EDS analysis were not coated.

TG-DSC traces were obtained using a NETZSCH STA 449 F3 Jupiter simultaneous thermogravimetric and differential scanning calorimeter. Data was processed using NETZSCH Proteus Thermal Analyser software, version 6.1.0. Traces were recorded by placing the sample (~ 5 -10 mg) in a Pt pan and subjecting the material to the specified heating protocols reported. This was usually 35-1000 °C at 10 °C/min under a flow of O₂/N₂ (20:80) of 20 cm³/min.

Powder X-ray diffraction (PXRD) patterns were recorded on a GBC-MMA X-ray diffractometer with samples mounted on the borosilicate glass substrate 2θ angle range of 5°-45° in 2θ with a step size of 0.05° at 1° per minute.

Gas adsorption studies were carried out at the Wollongong Isotope and Geochronology Laboratory using a Quantachrome Autosorb MP instrument and high purity nitrogen (99.999 %) gas. Surface areas were determined using Brunauer-Emmett-Teller (BET) calculations.

ICP-MS was performed at the University of Sydney by Dr Nicholas Proschogo on a PerkinElmer NexION 2000B Inductively Coupled Plasma-Mass Spectrometer. Samples were digested in trace metal free concentrated HF ($\sim 200 \mu\text{L}$ for ~ 2 mg samples). The samples were centrifuged and $40 \mu\text{L}$ of the supernatant taken, diluted to a volume of 10 mL in 0.4 M trace metal free HNO₃ and subjected to analysis in triplicate.

The electrochemical measurements were acquired using a CHI instrument, model 660D, and data was analysed using CHI software. For cyclic voltammetry the potential was applied in positive direction at a scan rate 50 mV/s between 0 and 1.3 V. The working electrode was FTO coated glass with or without UiO-66-NH₂ and UiO-66-N=CHFc films. The counter electrode was Pt mesh. The reference electrode was Ag/Ag⁺ (silver wire and 0.005 M AgNO₃ in 0.1 M tetrabutylammonium perchlorate in dry acetonitrile) and the measurements were performed in dry acetonitrile containing 0.1 M LiClO₄ as an electrolyte.

¹ J. Li, F. Wu, L. Lin, Y. Guo, H. Liu and X. Zhang, *Chem. Eng. J.*, 2018, **333**, 146-152.

2 Preparative chemistry

2.1 Preparation of UiO-66-NH₂ films

A typical preparation consisted of immersing a section of an O₂ plasma treated glass slide in a vial containing 139 mg of ZrCl₄ (0.5 mmol) and 108 mg of 2-aminoterephthalic acid (0.5 mmol) dissolved in 10 mL of DMF, 1 mL of acetic acid and 0.2 mL of H₂O. The vial was capped and heated in the oven at 120 °C for 24 h. After cooling, the glass slide coated with UiO-66-NH₂ was removed and washed twice with fresh DMF and multiple times with EtOH.

2.2 Preparation of UiO-66-N=CHFc(*p*-46)

Ferrocene carboxaldehyde (536 mg, 2.5 mmol) was dissolved in 25 mL of 1,4 dioxane to give a 0.1 M solution and added to UiO-66-NH₂ (250 mg, 0.14 mmol*). The reaction solution was heated at 70 °C overnight. The dark brown crystals of PSM-UiO-66-N=CHFc(*p*-46) were recovered by centrifugation and washed with fresh 1,4-dioxane solution (three times) and CH₂Cl₂ (three times). The supernatant DCM solution was colourless indicating no leaching of ferrocene species into solution. The mass recovery was essentially quantitative.

*Based on the formula Zr₆O₄(OH)₄(O₂C-C₆H₃NH₂-CO₂)₆ (1754.09 g·mol⁻¹).

3 PXRD Patterns

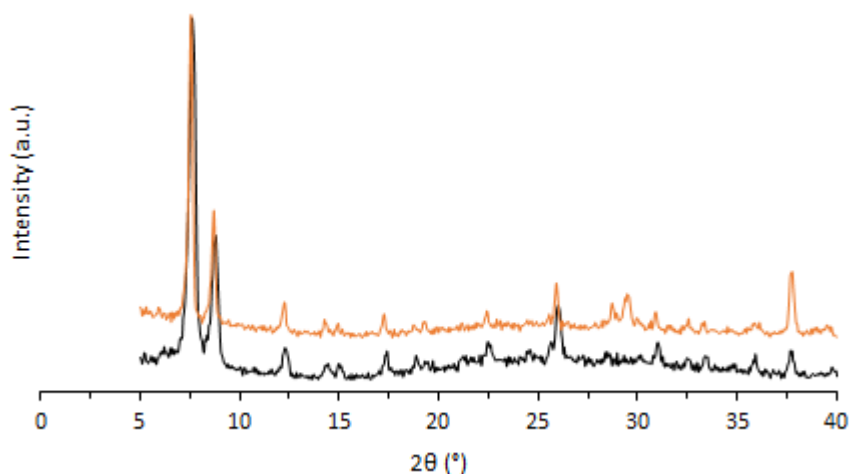


Figure S 1 PXRD patterns of UiO-66-NH₂ film on a glass slide (black) and UiO-66-N=CHFc(*f*-8) (orange). No background subtraction has been performed.

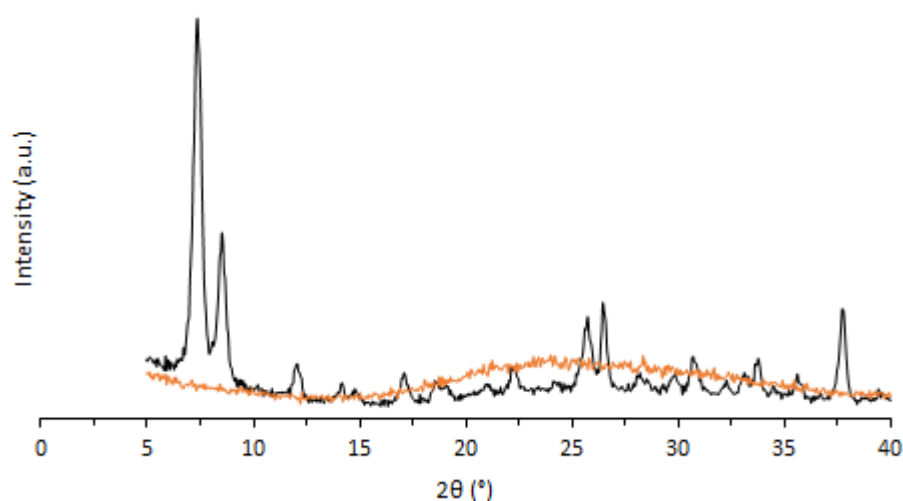


Figure S 2 PXRD patterns of UiO-66-NH₂ film grown on FTO (black) and a trace of the FTO substrate (orange). No background subtraction has been performed.

4 Images

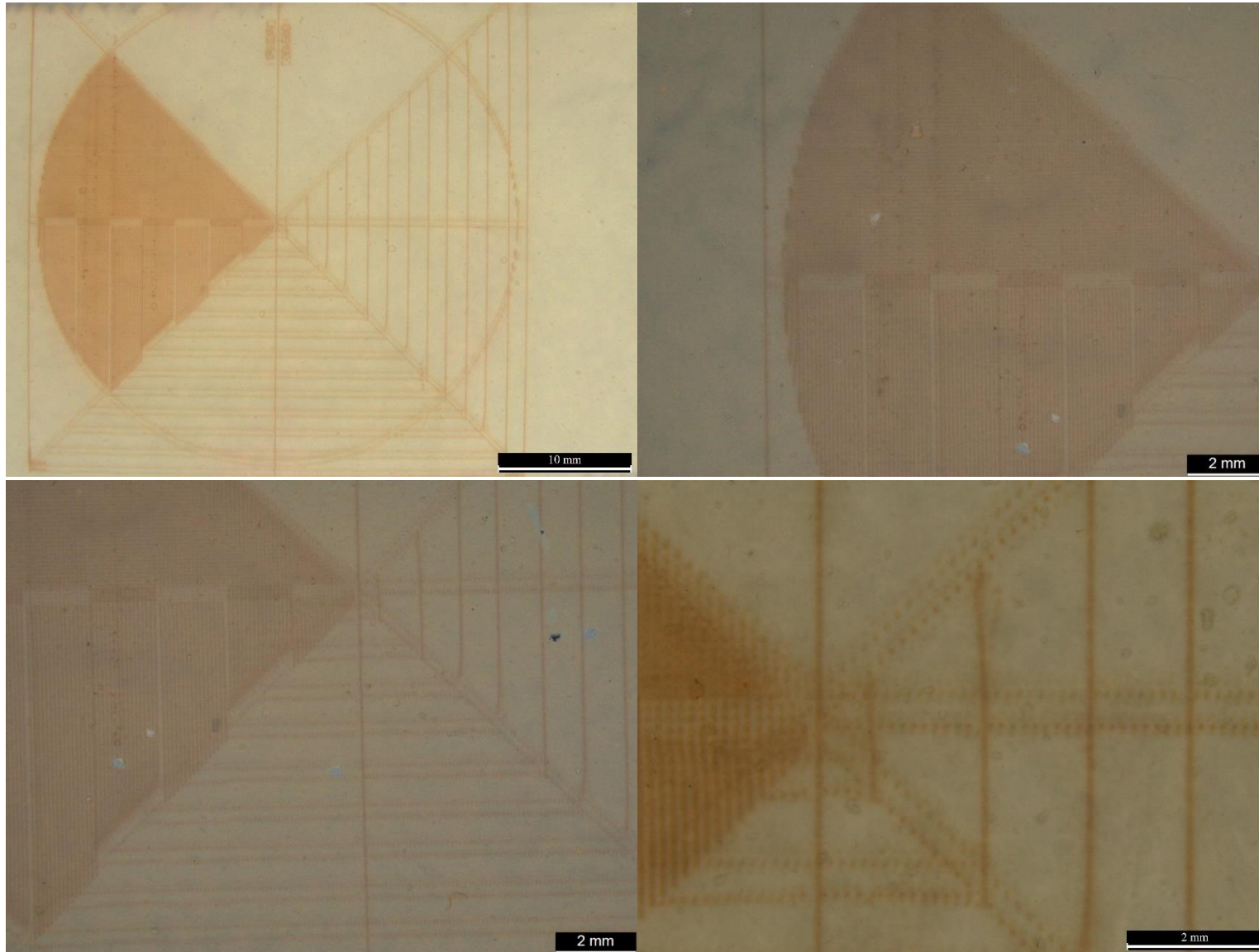


Figure S 3 A complex pattern shown in several areas and magnifications.

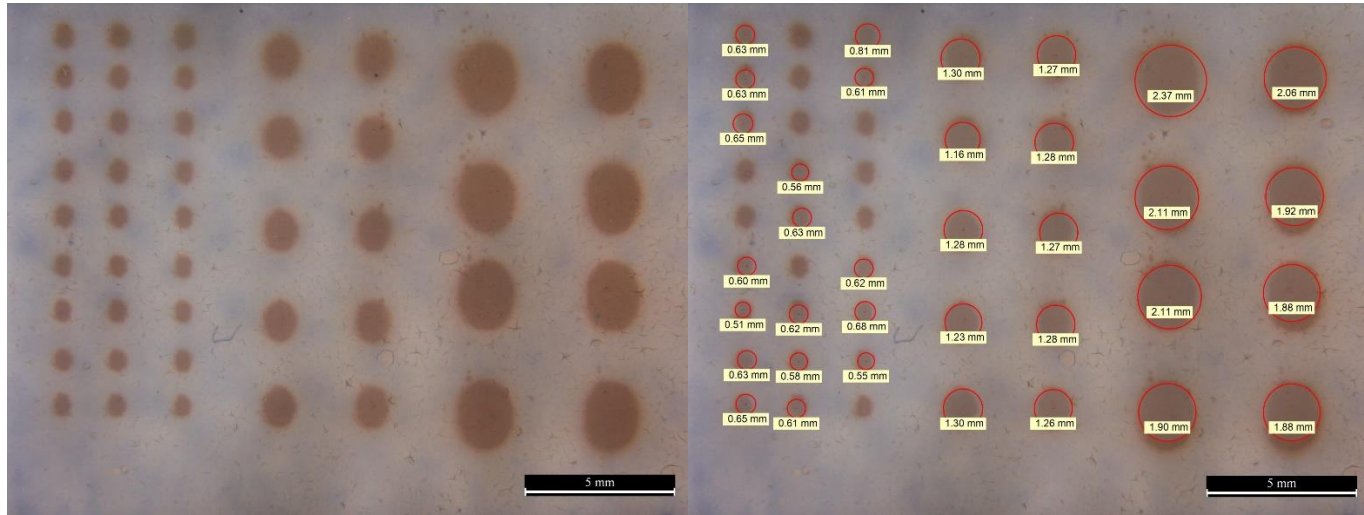


Figure S 4 A series of printed dots of varying sizes. The image at right is identical but has several of the dots measured.

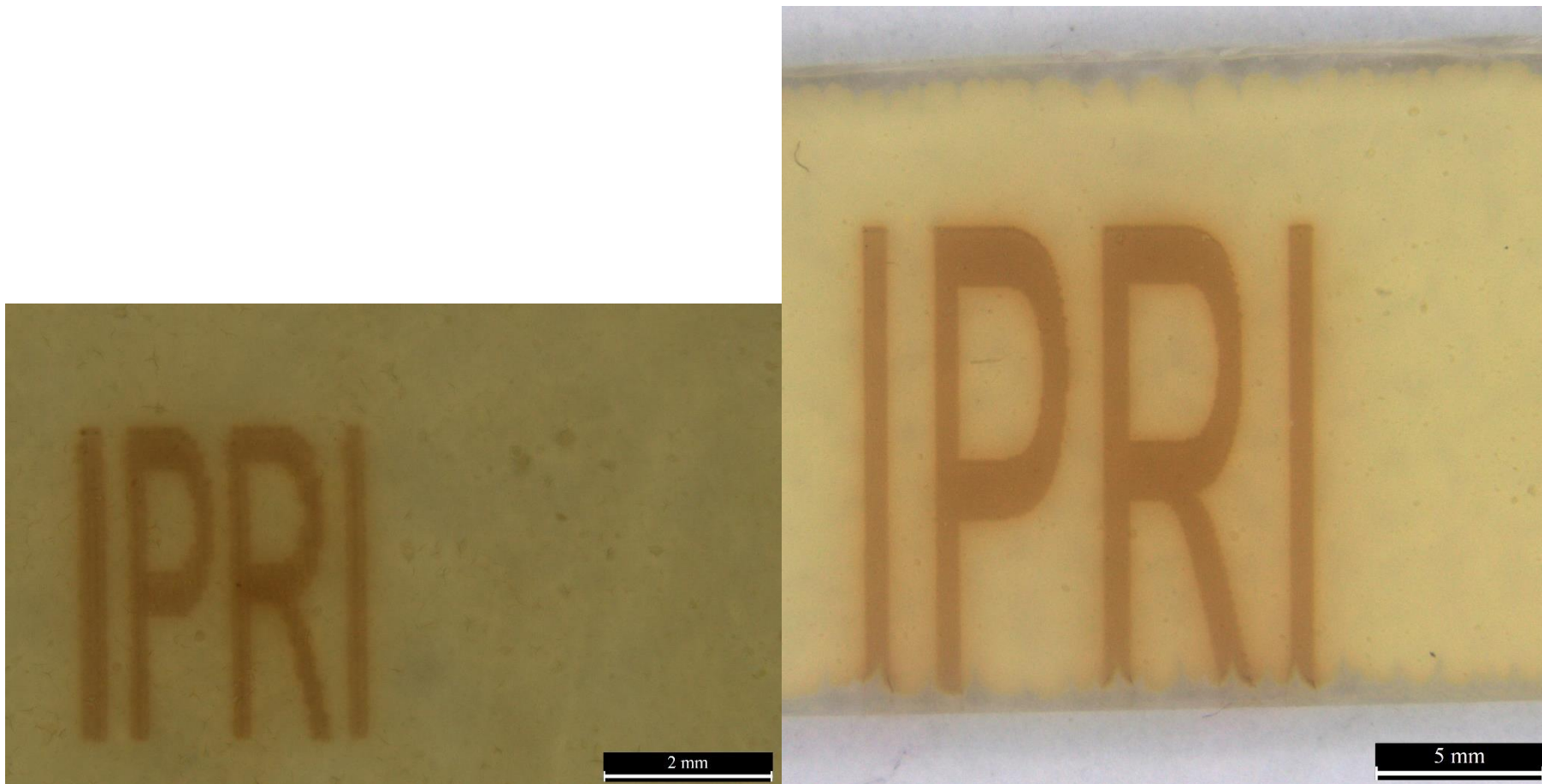


Figure S 5 Two sizes of printing IPRI. The acronym stands for the Intelligent Polymer Research Institute.

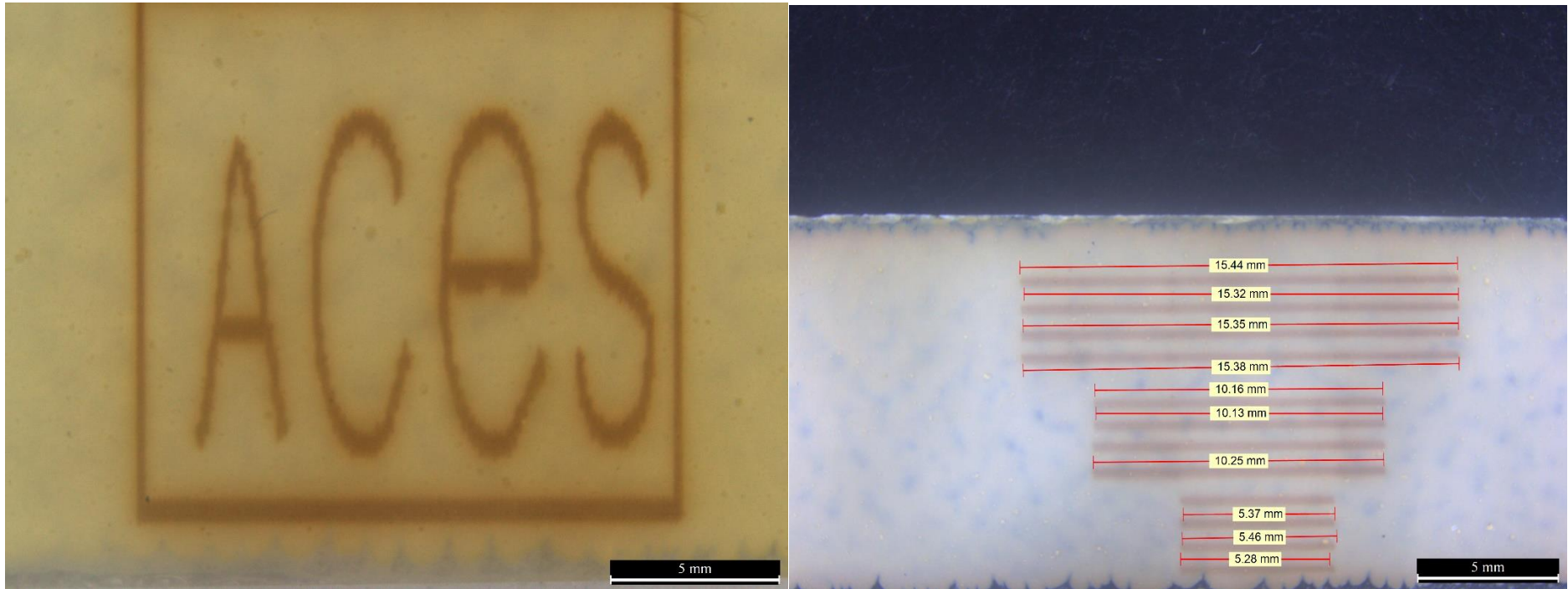


Figure S 6 The acronym ACES (ARC Centre of Excellence in Electromaterials Science) and a series of printed lines.

5 SEM-EDS area scans of films

This series of scans analysed all the elements were analysed. The signals of glass were removed from all subsequent spectra.

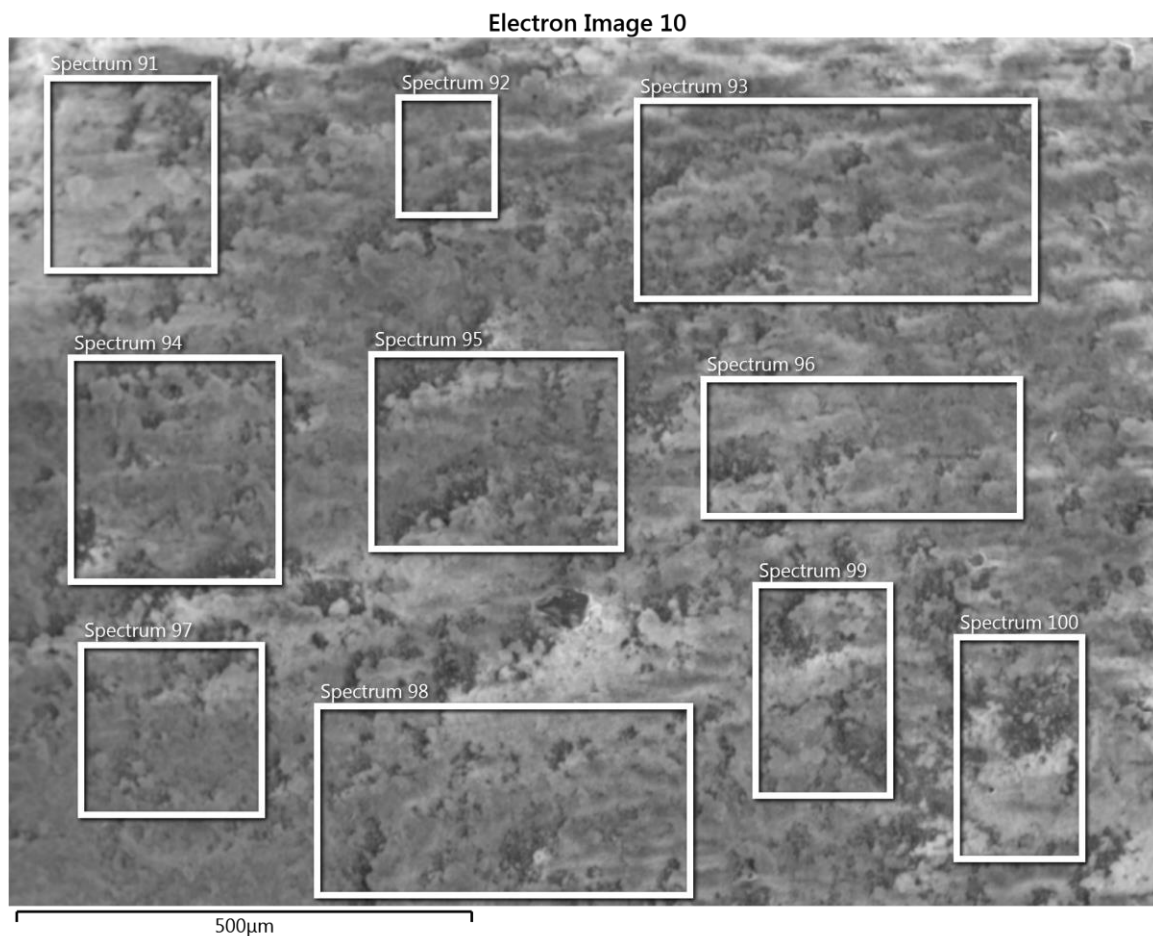


Figure S 7

Table S 1 Elemental analyses obtained from SEM-EDS scans of a representative film of UiO-66-NH₂.

Spectrum Label	Spectrum 100	Spectrum 91	Spectrum 92	Spectrum 93	Spectrum 94	Spectrum 95	Spectrum 96	Spectrum 97	Spectrum 98	Spectrum 99
C	39.33	41.96	40.05	42.29	37.11	37.70	39.08	40.51	42.08	40.64
O	28.80	28.15	28.49	27.81	29.76	29.79	29.20	28.37	28.15	28.78
Na	2.77	1.87	1.45	1.80	2.39	2.36	1.87	2.43	1.96	2.52
Mg	0.82	0.51	0.47	0.53	0.68	0.69	0.54	0.72	0.57	0.76
Al	0.28	0.20	0.17		0.24	0.23	0.19		0.20	0.19
Si	12.39	8.97	7.79	8.94	10.88	10.67	9.03	11.31	9.37	11.56
K	0.13	0.10		0.08				0.11	0.10	0.11
Ca	1.94	1.37	1.32	1.35	1.76	1.66	1.38	1.84	1.47	1.77
Br				0.45				0.45		
Zr	13.53	16.88	20.24	16.75	17.19	16.91	18.71	14.26	16.11	13.67
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Statistics	C	O	Na	Mg	Al	Si	K	Ca	Br	Zr
Max	42.29	29.79	2.77	0.82	0.28	12.39	0.13	1.94	0.45	20.24
Min	37.11	27.81	1.45	0.47	0.17	7.79	0.08	1.32	0.45	13.53
Average	40.07	28.73	2.14	0.63		10.09		1.59		16.43
Standard Deviation	1.79	0.68	0.41	0.12		1.47		0.23		2.15

5.1 UiO-66-NH₂

This scan is UiO-66-NH₂ film with elements of glass removed from the analyses.

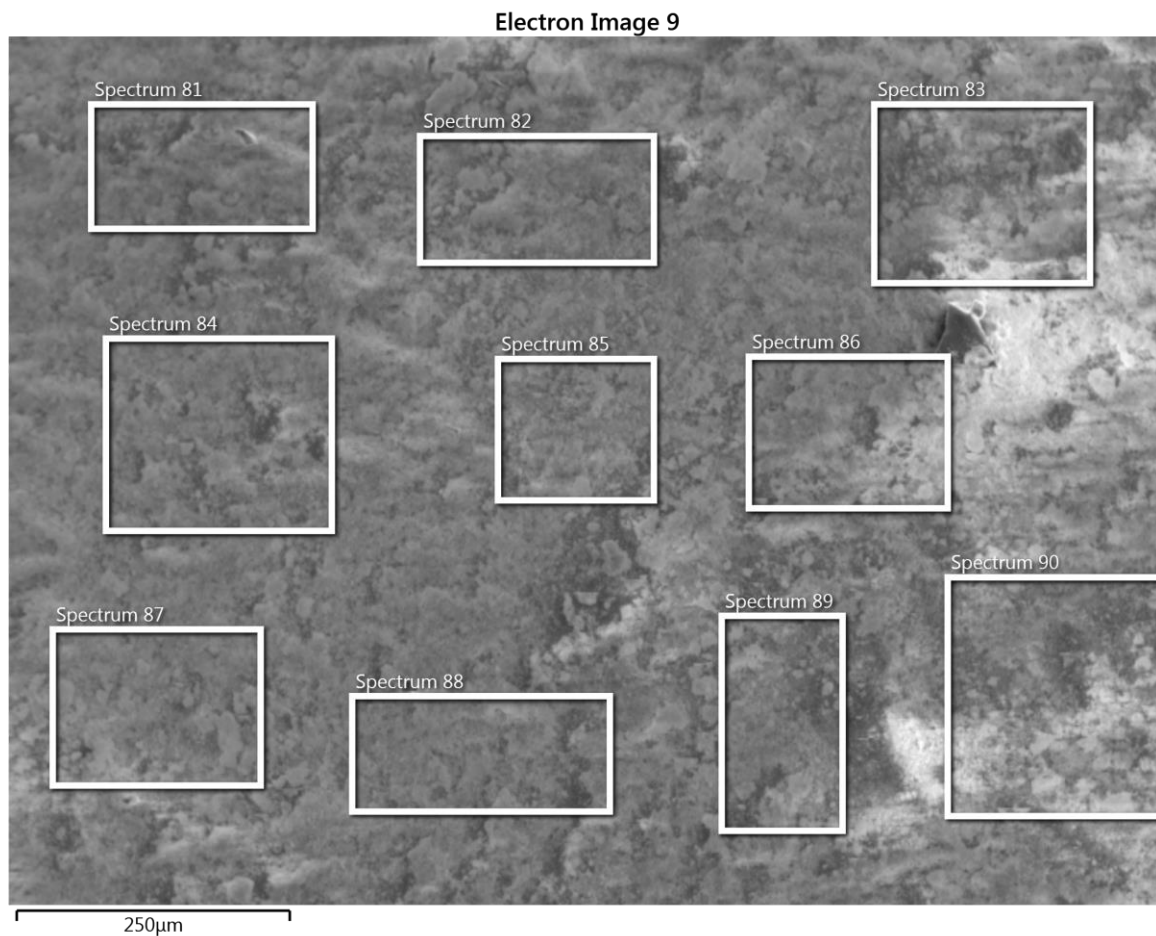


Figure S 8

Table S 2 Elemental analyses obtained from SEM-EDS scans of a representative film of UiO-66-NH₂.

Spectrum Label	Spectrum 90	Spectrum 81	Spectrum 82	Spectrum 83	Spectrum 84	Spectrum 85	Spectrum 86	Spectrum 87	Spectrum 88	Spectrum 89
C	37.69	39.34	40.08	37.30	39.42	38.64	40.51	39.53	39.07	38.82
O	40.29	36.59	34.71	40.25	36.43	37.83	33.76	36.24	37.02	37.75
Zr	22.02	24.07	25.21	22.46	24.15	23.54	25.73	24.23	23.92	23.43
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Statistics	C	O	Zr
Max	40.51	40.29	25.73
Min	37.30	33.76	22.02
Average	39.04	37.09	23.87
Standard Deviation	0.99	2.09	1.12

5.2 UiO-66-NH=CHFc printed at ink temperature 25 °C; time before analysis 1 day.

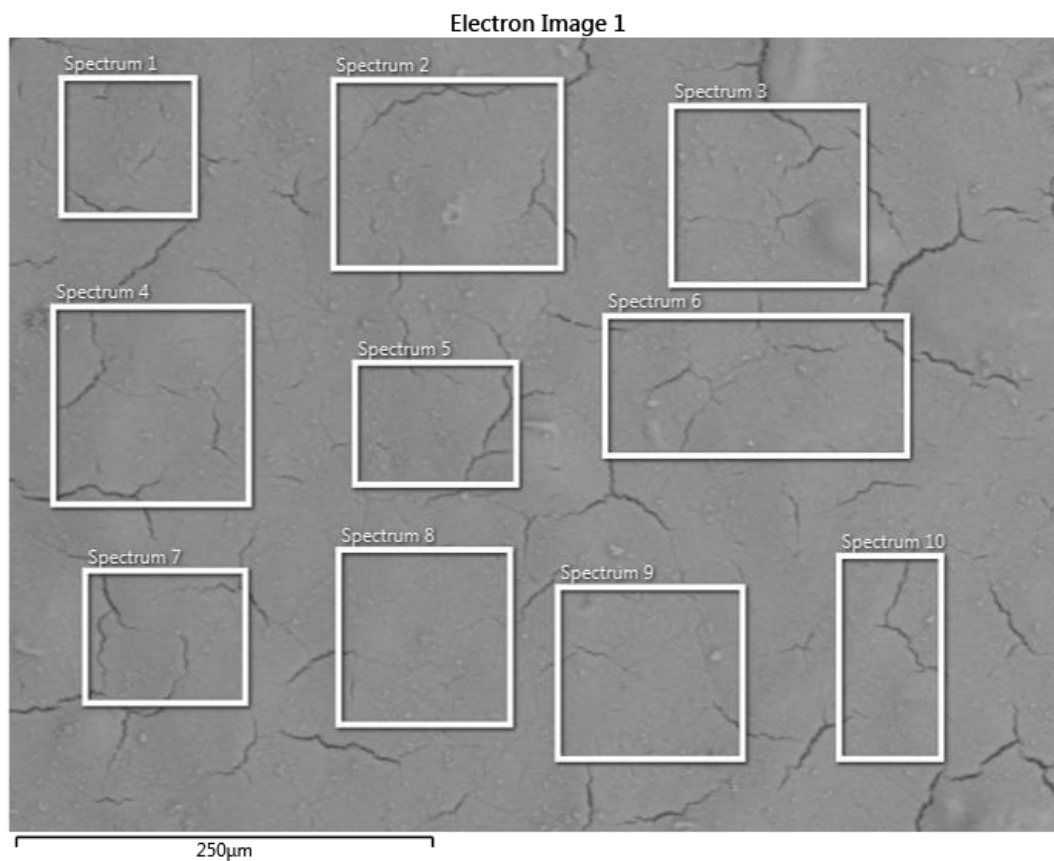


Figure S 9

Table S 3 Elemental EDS vales for the sections examined in the film shown in Figure S9.

Spectrum Label	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8	Spectrum 9	Spectrum 10
C	46.18	46.41	46.29	46.38	46.69	46.26	46.12	46.24	46.41	46.74
O	25.50	25.06	25.40	25.19	25.84	25.50	25.46	25.36	25.12	24.85
Si	0.32	0.25	0.24	0.37	0.27	0.23	0.41	0.31	0.26	0.28
Cl	1.28	1.32	1.29	1.29	1.24	1.29	1.26	1.26	1.24	1.29
Ca				0.11						
Fe	4.26	4.42	4.35	4.10	4.07	4.15	4.15	4.30	4.39	4.26
Zr	22.46	22.55	22.43	22.55	21.88	22.57	22.61	22.55	22.58	22.58
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Statistics	C	O	Si	Cl	Ca	Fe	Zr
Max	46.74	25.84	0.41	1.32	0.11	4.42	22.61
Min	46.12	24.85	0.23	1.24	0.11	4.07	21.88
Average	46.37	25.33	0.29	1.28		4.24	22.48
Standard Deviation	0.21	0.28	0.06	0.03		0.12	0.22

5.3 UiO-66-NH=CHFc printed at ink temperature 25 °C; time before analysis 2 days.

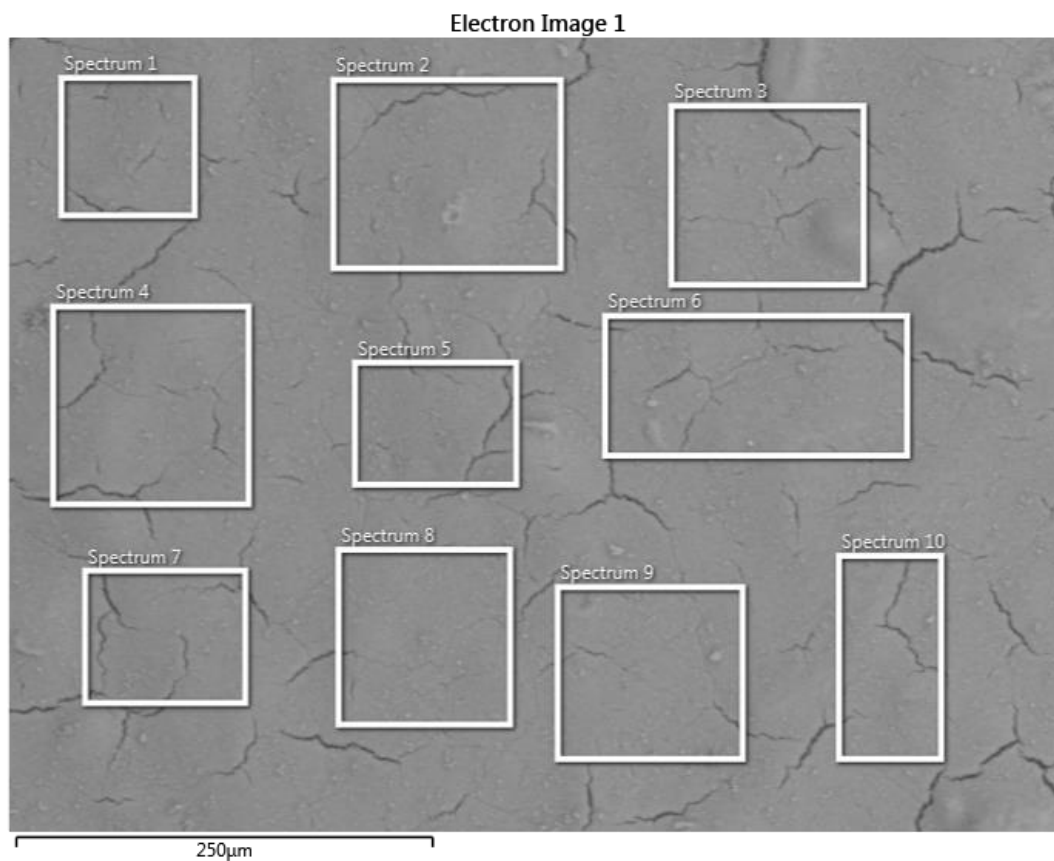


Figure S 10

Table S 4 Elemental EDS vales for the sections examined in the film in Figure S10.

Spectrum Label	Spectrum 10	Spectrum 1	Spectrum 2	Spectrum 3	Spectrum 4	Spectrum 5	Spectrum 6	Spectrum 7	Spectrum 8	Spectrum 9
C	45.11	44.62	44.84	44.74	44.60	45.11	44.72	44.65	44.66	44.93
O	26.12	26.78	26.30	26.64	26.73	27.12	26.74	26.72	26.62	26.30
Fe	4.55	4.54	4.71	4.64	4.39	4.34	4.42	4.42	4.58	4.66
Zr	24.22	24.07	24.14	23.98	24.28	23.43	24.13	24.21	24.15	24.10
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Statistics	C	O	Fe	Zr
Max	45.11	27.12	4.71	24.28
Min	44.60	26.12	4.34	23.43
Average	44.80	26.61	4.52	24.07
Standard Deviation	0.19	0.29	0.13	0.24

5.4 UiO-66-NH=CHFc printed at ink temperature 70 °C; time before analysis 1 day.

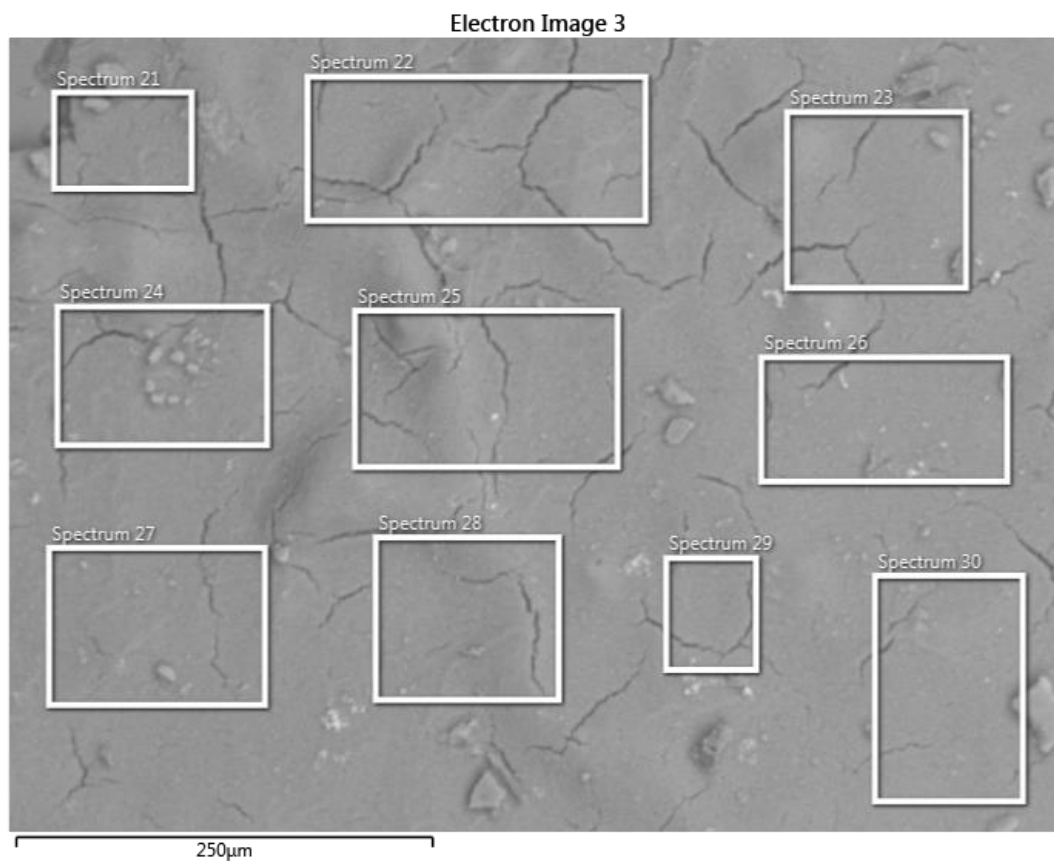


Figure S 11

Table S 5 Elemental EDS vales for the sections examined in the film in Figure S11.

Spectrum Label	Spectrum 21	Spectrum 22	Spectrum 23	Spectrum 24	Spectrum 25	Spectrum 26	Spectrum 27	Spectrum 28	Spectrum 29	Spectrum 30
C	44.33	45.45	45.07	45.88	45.78	45.40	46.24	46.08	46.02	46.19
O	30.62	27.51	27.33	27.07	26.71	27.26	26.64	26.72	26.38	26.13
Fe	4.66	5.08	5.28	5.04	5.36	5.25	5.33	5.28	5.39	5.34
Zr	20.40	21.96	22.31	22.02	22.15	22.09	21.79	21.92	22.21	22.34
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Statistics	C	O	Fe	Zr
Max	46.24	30.62	5.39	22.34
Min	44.33	26.13	4.66	20.40
Average	45.64	27.23	5.20	21.92
Standard Deviation	0.60	1.27	0.22	0.56

6 SEM-EDS analyses of film cross sections

6.1 UiO-66-NH=CHFc printed at ink temperature 25 °C; time before analysis 1 day.

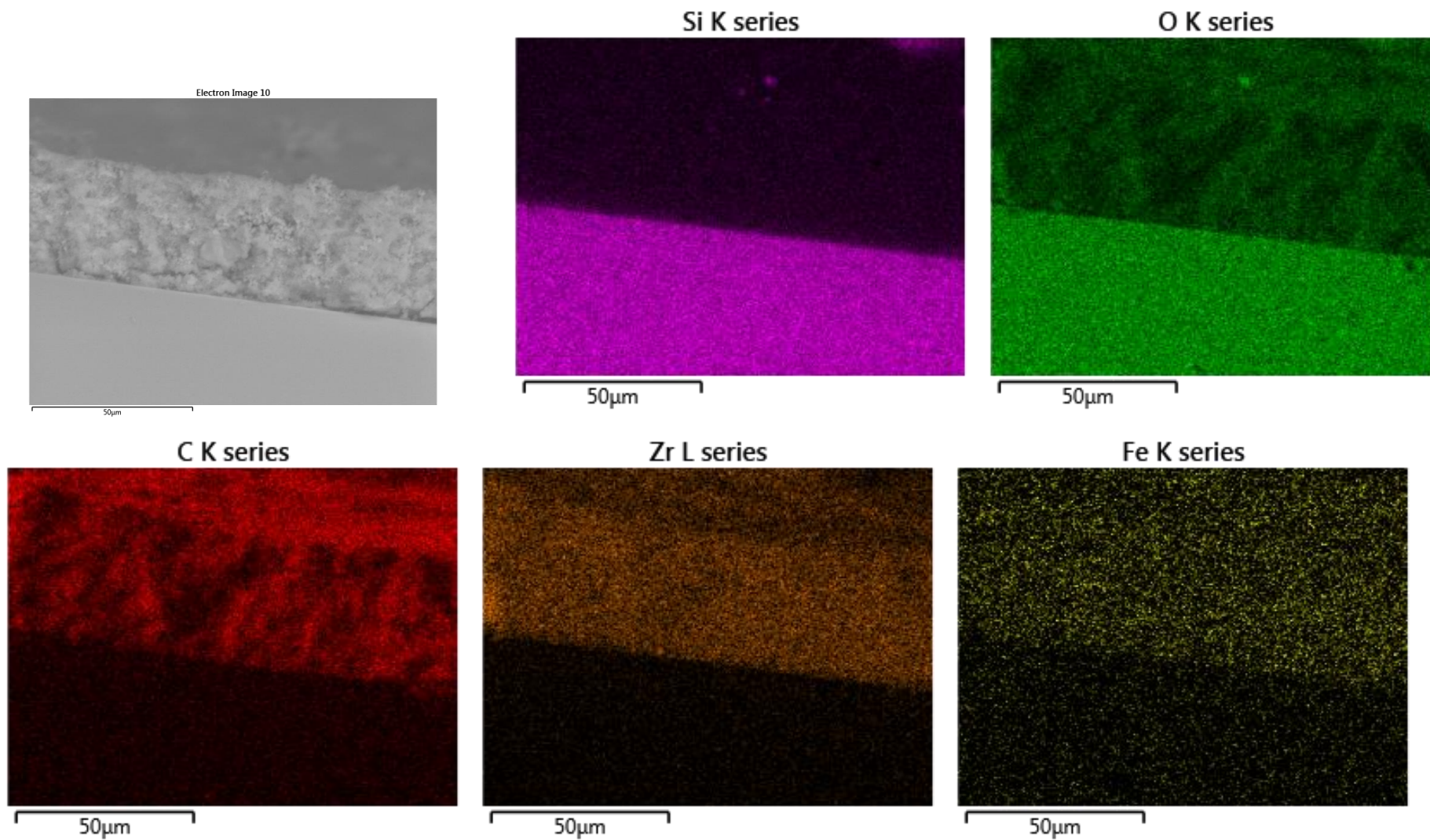


Figure S 12

6.2 UiO-66-NH=CHFc printed at ink temperature 70 °C; time before analysis 0 day.

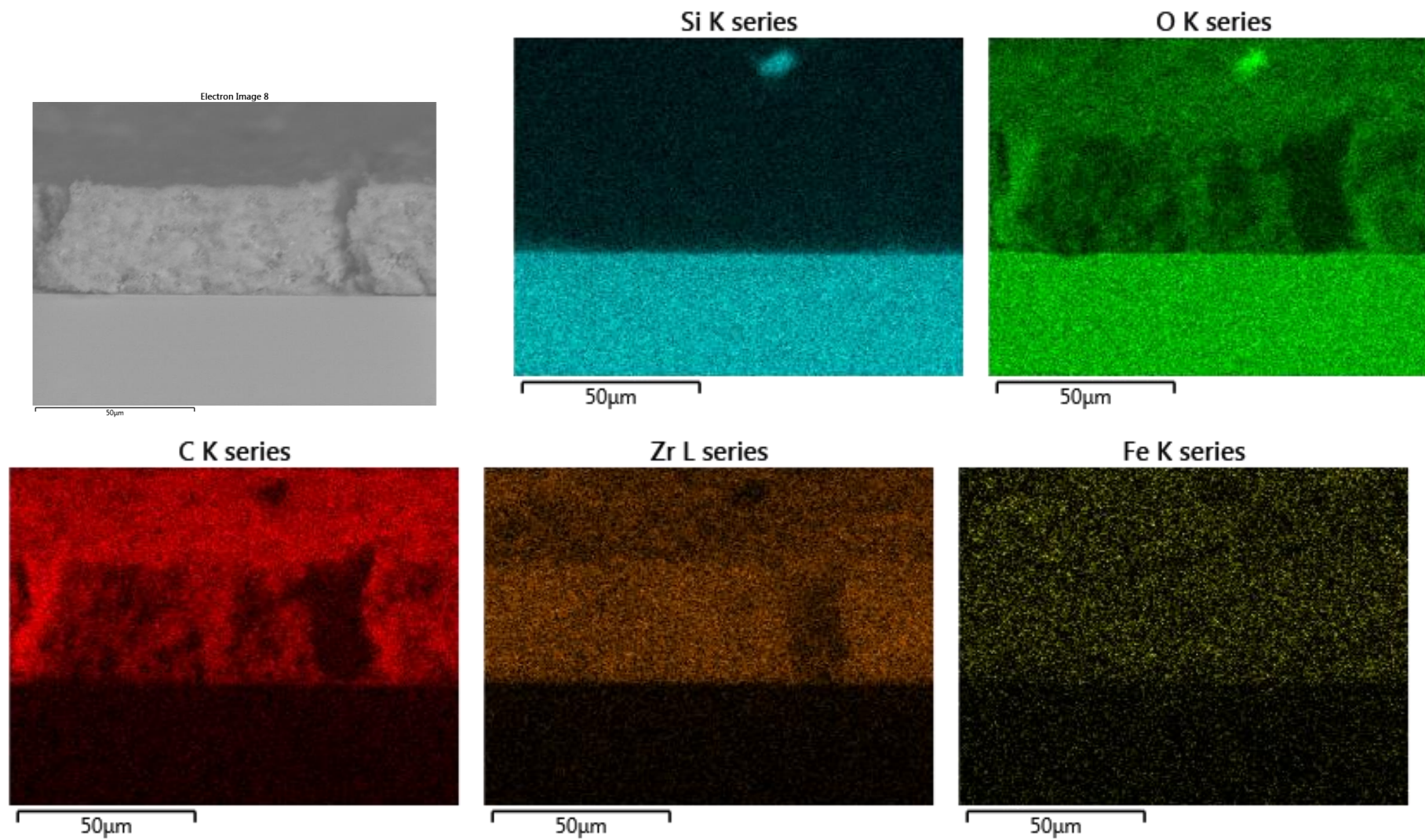


Figure S 13

6.3 UiO-66-NH=CHFc printed at ink temperature 70 °C; time before analysis 1 day.

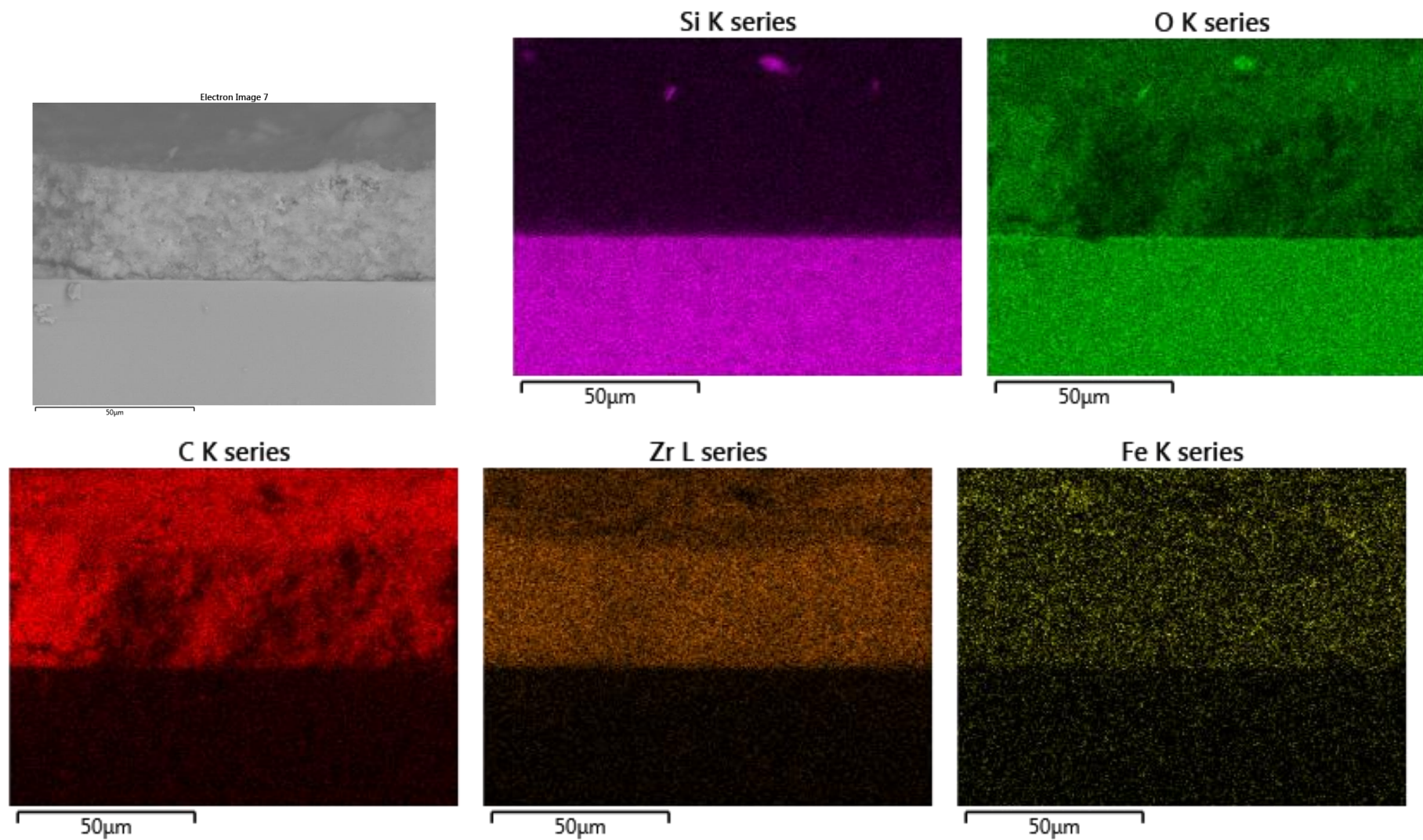


Figure S 14

Inductively Coupled Plasma-Mass Spectrometry

The ratio of Fe:Zr in the samples was determined by ICP-MS in triplicate. The conversion was based on this ratio understanding a 1:1 ratio of Zr to linkers from the formula $Zr_6O_4(OH)_4(\text{linkers})_6$. The linkers are $O_2C-C_6H_3NH_2-CO_2$ (bdc-NH₂) or $O_2C-C_6H_3N=CHFc-CO_2$ (bdc-N=CHFc)

Table S 6 ICP-MS values for analysis of UiO-66-N=CHFc(*p*-45) (lab code PSM-Lab) and UiO-66-N=CHFc(*f*-8) (lab code PrintFC).

	Fe-1 57 (ppb)	Zr 90 (ppb)	Conversion	Formula
PSM-Lab-1-1	62756606.141	140630386.308	0.4462521	$Zr_6O_4(OH)_4(\text{bdc-NH}_2)_{3.3}(\text{bdc-N=CHFc})_{2.7}$
PSM-Lab-1-2	78296385.626	172182529.721	0.454729	As above
PSM-Lab-1-3	67464193.743	149352810.233	0.4517102	As above
PrintFC-2-1	17676075.839	220478940.445	0.0801713	$Zr_6O_4(OH)_4(\text{bdc-NH}_2)_{5.52}(\text{bdc-N=CHFc})_{0.48}$
PrintFC-2-2	17872196.013	241202694.001	0.0740962	As above
PrintFC-2-3	15423709.592	222980763.006	0.0691706	As above

7 Thermogravimetric-differential scanning calorimetry

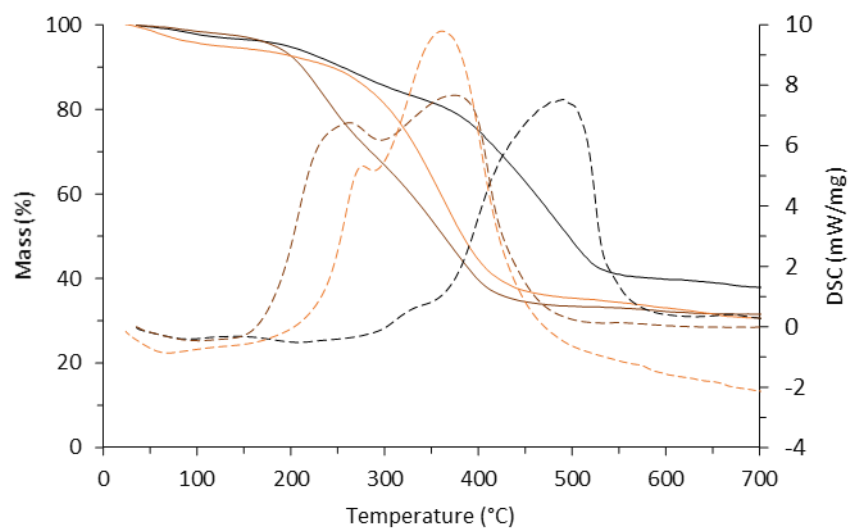


Figure S 15 TG—DSC traces for UiO-66-NH₂ (black), UiO-66-N=CHFc(*f*-8) (orange) and UiO-66-N=CHFc(*p*-45) (brown); solid lines represent the TGA; dashed lines represent the DSC.

8 Gas adsorption

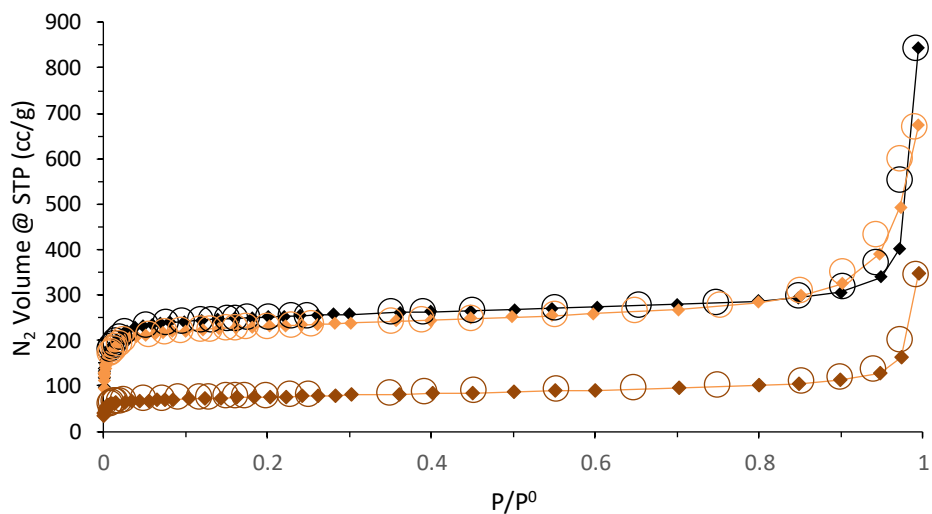


Figure S 16 N₂ adsorption-desorption isotherms at 77 K of UiO-66-NH₂ (black), UiO-66-N=CHFc(*f*-8) (orange) and UiO-66-N=CHFc(*p*-45) (brown). Adsorption points are shown as filled diamonds and desorption points as unfilled circles. A line on the adsorption legs of the isotherms are shown as a guide for the eye.

Table S 7 BET Summary table for UiO-66-NH₂ film.

Slope =		3.448
Intercept =		8.64E-03
Correlation coefficient, r =		0.999868
C constant =		400.168
Surface Area =		1007.567 m ² /g
Relative Pressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) - 1)]
0.012021	191.4906	0.050841
0.015032	199.0806	0.061339
0.025186	217.957	0.094848
0.027952	221.0841	0.10407
0.038613	228.3483	0.14073
0.047382	231.7867	0.1717
0.058198	234.812	0.21056

Table S 8 BET Summary table for UiO-66-N=CHFc(*f*-8).

Slope =		3.84
Intercept =		6.99E-03
Correlation coefficient, r =		0.999907
C constant =		550.342
Surface Area =		905.387 m ² /g
Relative Pressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) - 1)]
0.012102	180.2883	0.054367
0.015092	186.5443	0.065726
0.025826	201.3014	0.10537
0.03065	204.6244	0.12364
0.039666	208.7056	0.15835
0.050684	212.0586	0.20145
0.061625	214.6594	0.24479

Table S 9 BET Summary table for UiO-66-N=CHFc(*p*-45).

Slope =		12.473
Intercept =		8.45E-03
Correlation coefficient, r =		0.999999
C constant =		1477.216
Surface Area =		279.030 m ² /g
Relative Pressure (P/Po)	Volume @ STP (cc/g)	1 / [W((Po/P) - 1)]
0.015054	62.2557	0.19644
0.025703	64.13	0.32914
0.034163	65.1253	0.43457
0.044133	66.1331	0.5586
0.054173	67.0332	0.68366
0.064407	67.8661	0.81161
0.074331	68.6359	0.93609