Supporting Information

The impact of structural defects on iodine adsorption in UiO-66

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Materials

$ZrCl_4$ (99.5%), acetone, iodine and furfuryl alcohol (99%) were purchased from Sigma Aldrich. Formic acid (98%) and dimethylformamide were purchased from Fisher Scientific. Terephthalic acid (99%) was purchased from Acros Organics.

Synthesis

The synthesis methods used were based on a previous study.[1] UiO-66 synthesised without the formic acid modulator is referred to as UiO-66. UiO-66 synthesised with formic acid modulator is referred to as UiO-66-FA.

Synthesis of UiO-66

$ZrCl_4$ (1.165 g, 5.000 mmol) was dissolved in dimethylformamide (DMF) (100 mL). Water (0.27 mL, 15.0 mmol) and terephthalic acid (0.83 g, 5.00 mmol) were then added and the solution heated to 120 °C for 24 h. The white solid produced was washed with DMF and soaked in acetone for 3 days changing the acetone twice per day. The solid was then separated via centrifugation and dried in an oven overnight at 80 ^{o}C.

Synthesis of UiO-66-FA

$ZrCl_4$ (1.165 g, 5.000 mmol) was dissolved in DMF (81 mL). Water (0.270 mL, 15.0 mmol), formic acid (18.8 mL, 500 mmol) and terephthalic acid (0.830 g, 5.00 mmol) were then added. The solution was heated to 120 °C for 24 h. The white solid produced was washed with DMF and soaked in acetone for three days changing the acetone twice per day. The solid was then separated via centrifugation and dried in an oven overnight at 80 ^{o}C.

Iodine vapour loading and cycling

Samples were activated under vacuum at a temperature of 150 °C for 24 h. The activated sample was then sealed in a Schlenk flask with an excess of solid I_2 under N_2. The flask was heated to 80 °C in an oven for 3 days. After 3 days the I_2-loaded sample was collected for further analysis. I_2-loading was cycled using a large batch of MOF that was activated at 150 °C under vacuum for 24 h and then loaded with an excess of solid I_2. A small sample was taken for TGA analysis to determine the I_2 content. The bulk sample was then washed via Soxhlet extraction using acetone for 24 h. The washed samples were analysed using PXRD and the process was then repeated using the same bulk sample.

Analysis

Powder X-ray diffraction (PXRD) patterns were collected in the 3 - 60 ° 2θ range with a Philips X'pert diffractometer. The X-ray tube was operated at 45 kV and 40 mA. For confocal fluorescence microscopy samples were prepared as follows: a 10 mg sample of MOF was immersed in furfuryl alcohol (1 mL) at 80 °C for 24 h. The MOF was collected via centrifugation and washed with acetone and dried. The fluorescence micrographs were obtained using an Olympus Fluoview FV-1000. For BET surface area analysis, samples were activated under vacuum at 150 °C for 24 h. The BET surface area and pore size distribution of the activated samples were measured using N_2 uptake. The samples were activated using a Smart Vac Prep and the surface area measurements were undertaken on a Micromeritics 3 Flex instrument. Raman spectra were collected using a Horiba Scientific Xplora plus Raman Microscope using a 514 nm laser with a grating of 1200 gr mm^{-1}. A total of 10 acquisitions with an exposure time of 10 seconds were used to collect the spectra. Thermal gravimetric analysis coupled mass spectrometry (TGA-MS) was conducted using a SDT 650 Discovery Series TGA paired with an HPR-20 QIC mass spectrometer. TGA was performed at a rate of heating of 5 °C min^{-1} to a temperature of 600 °C under N_2. I_2 uptakes were calculated using the difference in weight percent between activated and I_2-loaded samples at 300 °C.

Figure S1: Colour change observed in UiO-66-FA. Sample before loading with I_2 (left) and sample after loading with I_2 (right).

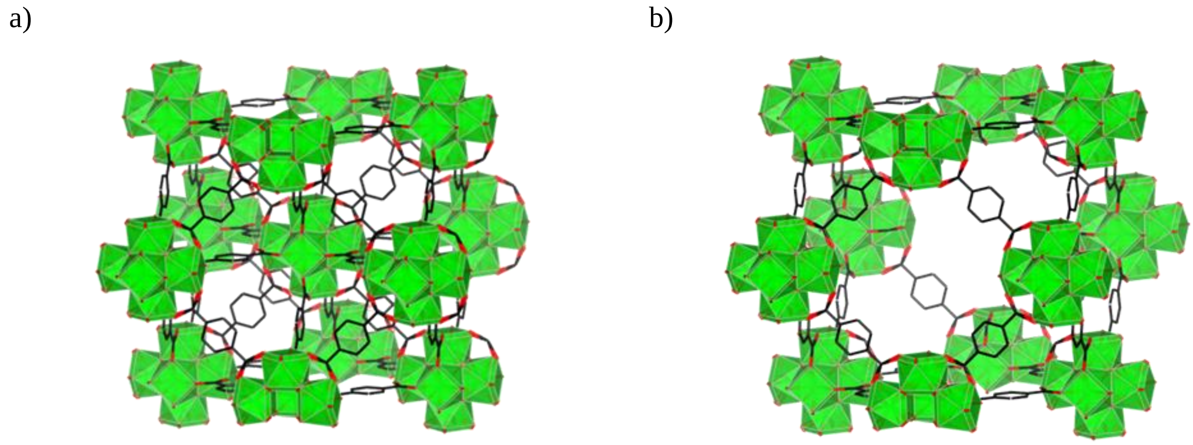

Figure S2: Structure of (a) UiO-66 and of (b) UiO-66-FA showing a missing cluster defect.

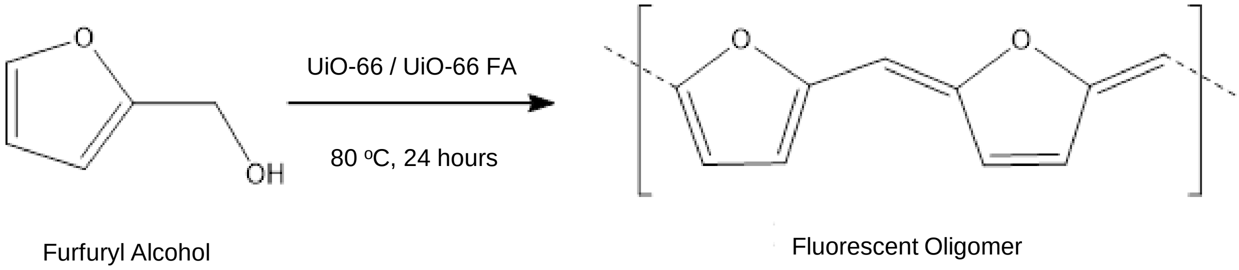

Figure S3: Reaction scheme for the synthesis of the fluorescent oligomer from furfuryl alcohol.

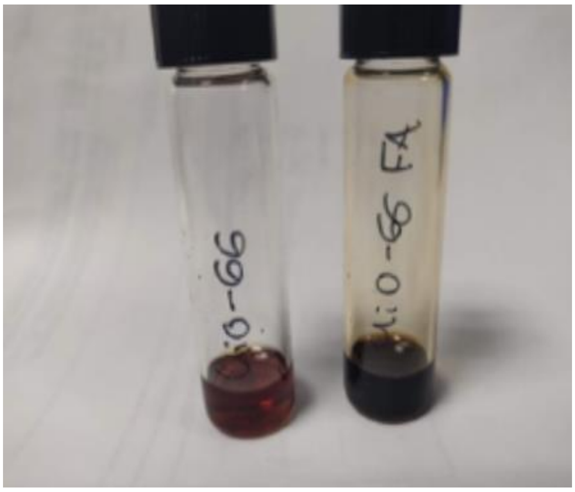

Figure S4: Sample of UiO-66 (left) and UiO-66-FA (right) in furfuryl alcohol after oligomerization reaction. Furfuryl alcohol is a clear compound while the furfuryl alcohol oligomer is brown/black.

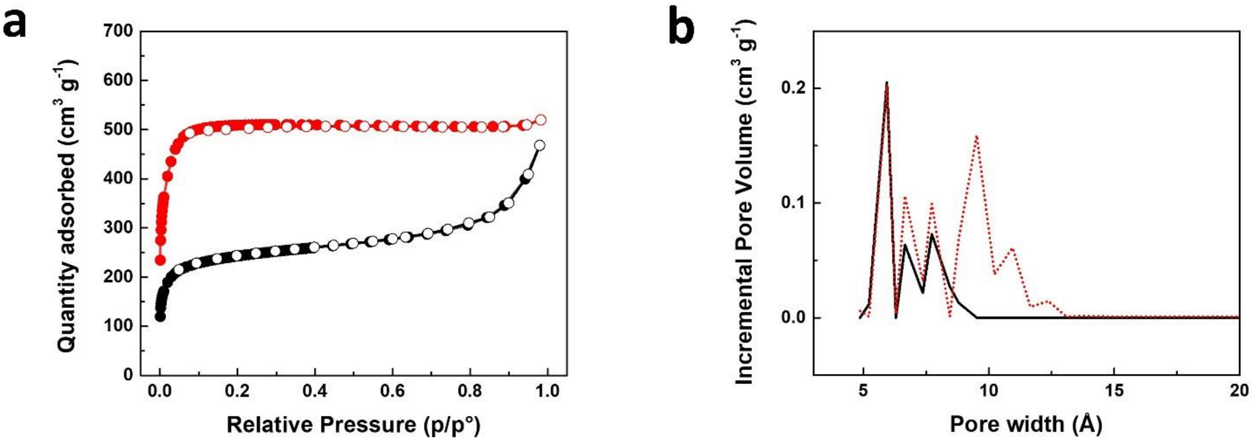

Figure S5: (a) N_2 adsorption isotherm and (b) pore size distribution of UiO-66 (black) and UiO-66-FA (red).

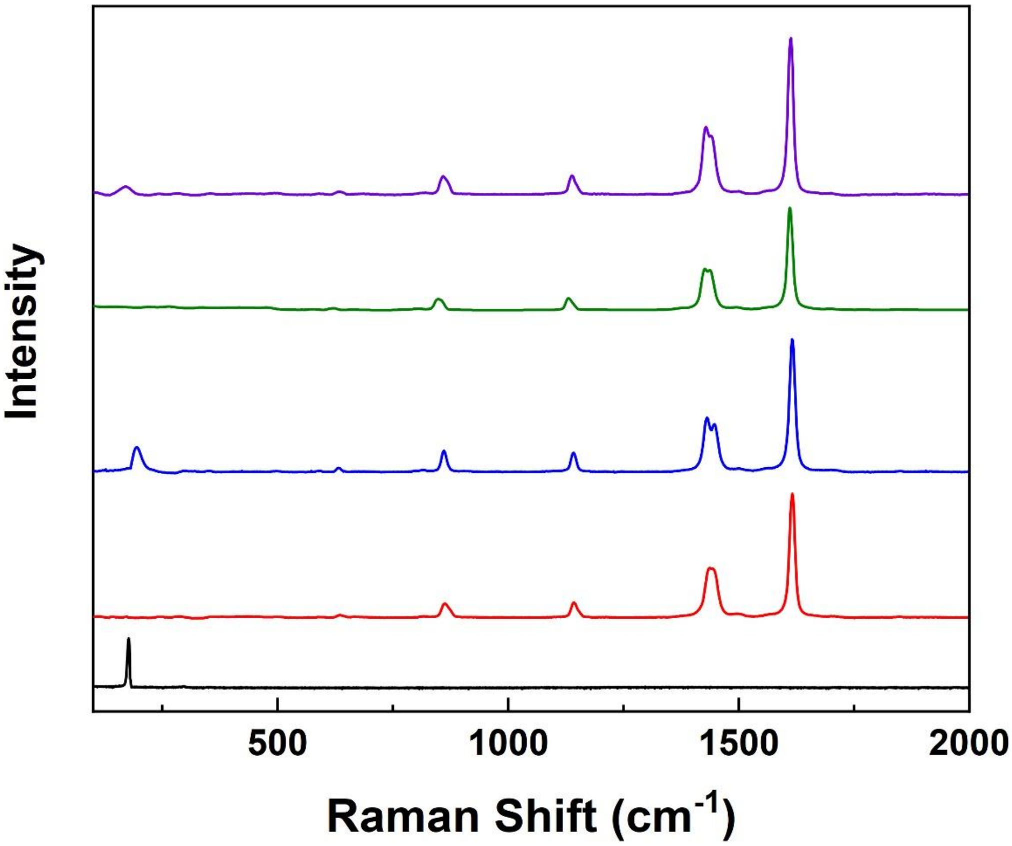

Figure S6: Raman spectra of I_2 (black), UiO-66 (blue), I_2-loaded UiO-66 (red), UiO-66-FA (green), and I_2-loaded UiO-66-FA (purple).

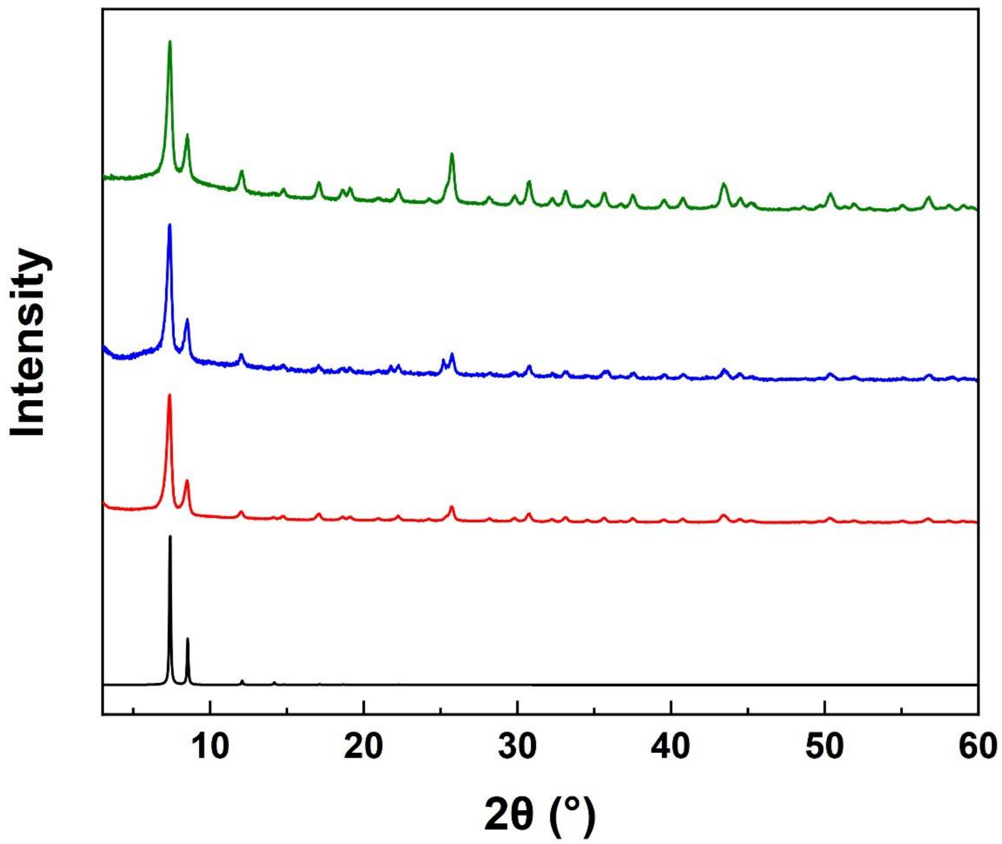

Figure S7: PXRD of UiO-66 after removal of captured I_2. First cycle (blue), second cycle (red), third cycle (green) and simulated PXRD pattern (black).[2]

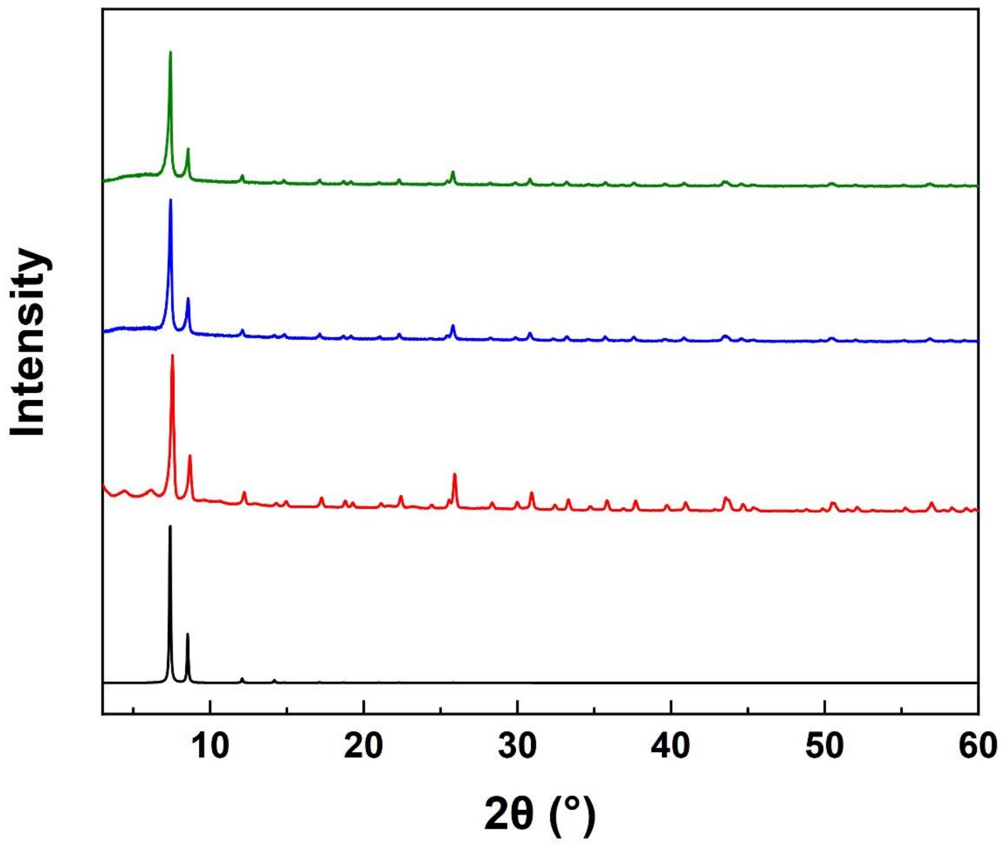

Figure S8: PXRD of UiO-66-FA after removal of captured I_2. First cycle (blue), second cycle (red), third cycle (green) and simulated PXRD pattern (black).[2]

References

1. Koutsianos, A.; Kazimierska, E.; Barron, A.R.; Taddei, M.; Andreoli, E. A new approach to enhancing the CO_2 capture performance of defective UiO-66 via post-synthetic defect exchange. *Dalton Trans.* **2019**, *48*, 3349–3359.
2. Cavka, J.H.; Jakobsen, S.; Olsbye, U.; Guillou, N.; Lamberti, C.; Bordiga, S.; Lillerud, K.P. A new zirconium inorganic building brick forming metal organic frameworks with exceptional stability. *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.