

Supporting Information

**A novel UiO-66 analog with uncoordinated
carboxylic acid groups for the broad spectrum
removal of toxic chemicals**

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Synthesis of materials

UiO-66 was synthesized in a manner similar to that laid out by Peterson et al.¹ In short 19.07 mmol of $ZrCl_4$ and terephthalic acid were stirred in 742 mL of dimethylformamide until completely dissolved. The solution was placed in three 500 mL jars and placed in an oven preheated to 120 °C for 24 h. The resulting solution was cooled to room temperature, filtered, and washed with DMF.

UiO-66-vac was synthesized as previously reported;² briefly, $ZrCl_4$ (125 mg, 0.54 mmole) was added to an 8 dram vial. 1 mL of HCl followed by 5 mL of DMF was added to the vial. The vial was subsequently sonicated until all of the $ZrCl_4$ was dissolved (ca. 20 minutes). Terephthalic acid (123 mg, 0.75 mmole) was subsequently added to the vial followed by an additional 10 mL of DMF. The vial, roughly half full of solvent, was sonicated until all the terephthalic acid was dissolved. The vial was then heated at 80 °C overnight (ca. 15 h). The resulting solid was then filtered and washed first with DMF (2x 30 mL) and then with isopropanol (2 x 30 mL).

UiO-66-ox was synthesized from the resulting UiO-66-vac crystals. Approximately 0.12 g (1.33 mmol) of oxalic acid was dissolved in dimethylformamide. 0.25 g of UiO-66-vac was slowly added to the stirring solution, and allowed to stir for 2h at room temperature. The resulting solution was filtered and washed with DMF. All samples were solvent exchanged with methanol via Soxhlet extraction for 24h. The resulting samples were filtered and activated in a vacuum oven at 150 °C for 24h.

Powder X-ray diffraction

Each MOF was analyzed using powder X-ray diffraction (PXRD). PXRD measurements were taken using a PANalytical X'Pert X-ray powder diffractometer with an X'celerator detector. Samples were scanned at 45 kV and 40 mA, using Cu Ka radiation ($\lambda = 1.54 \text{ \AA}$), a step size of $2\theta = 0.033^\circ$ (10.08 s per step) over a 2θ range of 5 to 30° . Zero-background discs were used to minimize background

scattering. PXRD diffraction patterns were processed using the Reflex module in Material Studio 6.1 by Accelrys.

N₂ isotherms

Nitrogen adsorption isotherms were measured for each activated MOF sample using a Micromeritics TriStar 3000 analyzer at 77 K. Prior to analysis, approximately 100 mg of each MOF was activated overnight at 150 °C under a flow of dry nitrogen. BET modeling was performed to obtain the specific surface area ($\text{m}^2 \text{g}^{-1}$). The BET model was applied over the pressure range as described by Walton et al. to obtain physically meaningful parameters.³

Microbreakthrough experiments

A miniaturized breakthrough apparatus was used to evaluate milligram-scale quantities of MOF samples for the adsorption of ammonia, sulfur dioxide and cyanogen chloride as described in depth elsewhere.^{4,5} Approximately 10-15 mg of material were loaded into a nominal 4 mm i.d. fritted glass tube that was subsequently loaded into a water bath for isothermal testing. Prior to testing, each MOF was regenerated for one hour at 150 °C under flowing dry air to remove any physisorbed water. A ballast with a predetermined quantity of challenge gas was then mixed with a stream of dry (-40°C dew point) air at a rate necessary to achieve the desired challenge concentration as summarized in Table S1. The appropriate contaminated air stream was then sent through the fritted glass tube at a flow rate of 20 mL min^{-1} , equivalent to a residence time of approximately 0.16 seconds. The effluent stream was sent through the appropriate detector to monitor the analyte concentration. The corresponding breakthrough curve was integrated to determine the loading at saturation.

Table S1. Parameters used in microbreakthrough experiments

	NH ₃	CK	SO ₂	NO ₂	C ₈ H ₁₈
Challenge Concentration (mg m ⁻³)	2000	4000	1000	2138	4000
Temperature (K)	293				
Dew Point (K)	233				
Bed height mm	4				
Bed Volume (mm ³)	50				
Flow rate (mL min ⁻¹)	20				
Detector	GC/PID	GC/FID	GC/FPD	FTIR	GC/FID

Attenuated total reflectance Fourier-transform infrared spectroscopy

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of each MOF were taken using a Bruker Tensor 27 FTIR with a Bruker Platinum ATR accessory equipped with a single reflection diamond crystal. Sixteen scans were averaged over a range of 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹.

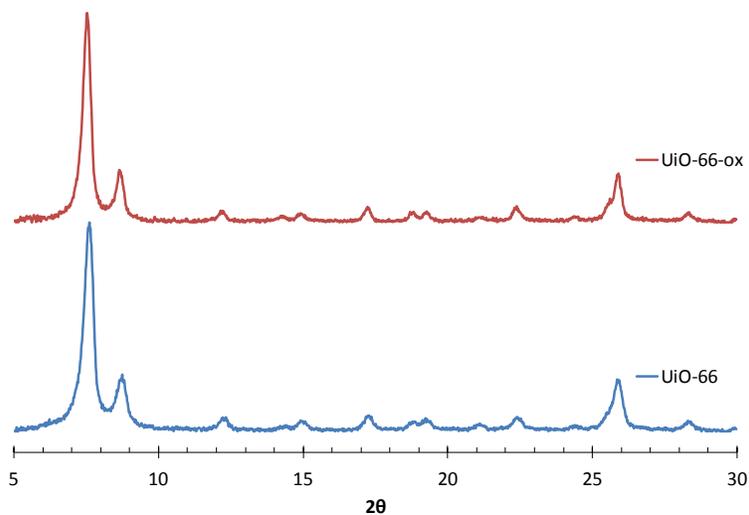


Figure S1. PXRD patterns of UiO-66, and UiO-66-ox.

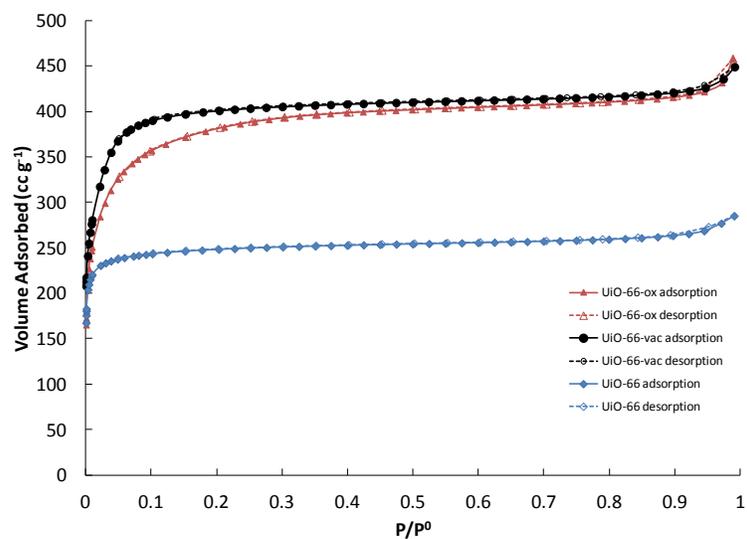


Figure S2. N₂ isotherms measured at 77K of UiO-66, UiO-66-vac, and UiO-66-ox.

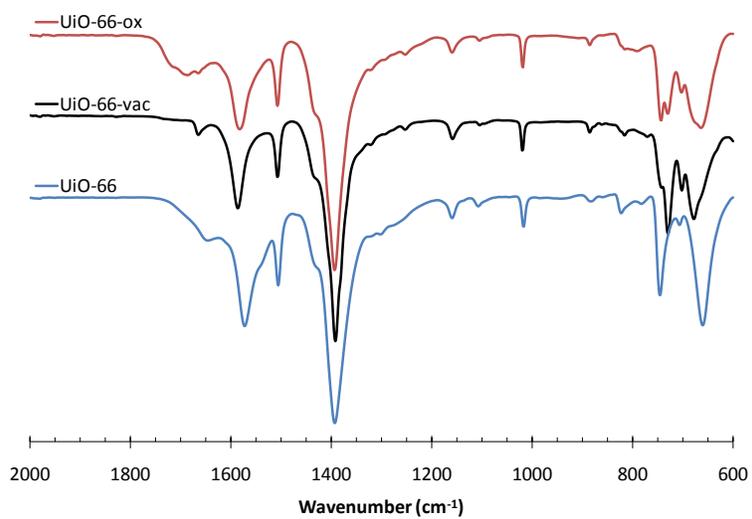


Figure S3. ATR-FTIR spectra from 2000 to 600 cm⁻¹ for UiO-66, UiO-66-vac, and UiO-66-ox.

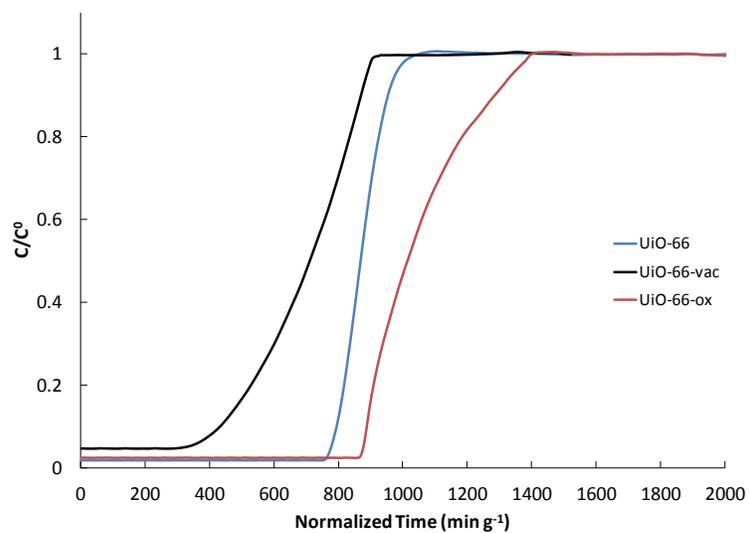


Figure S4. Microbreakthrough plot for UiO-66, UiO-66-vac, and UiO-66-ox against NH₃.

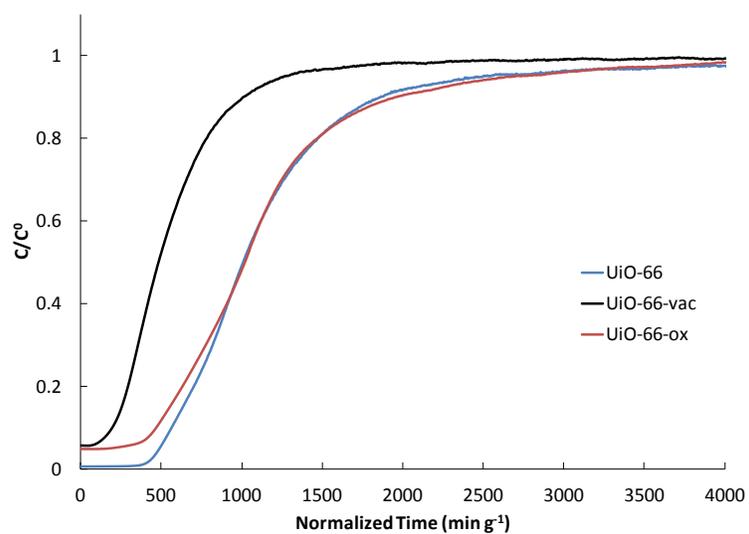


Figure S5. Microbreakthrough plot for UiO-66, UiO-66-vac, and UiO-66-ox against ClCN.

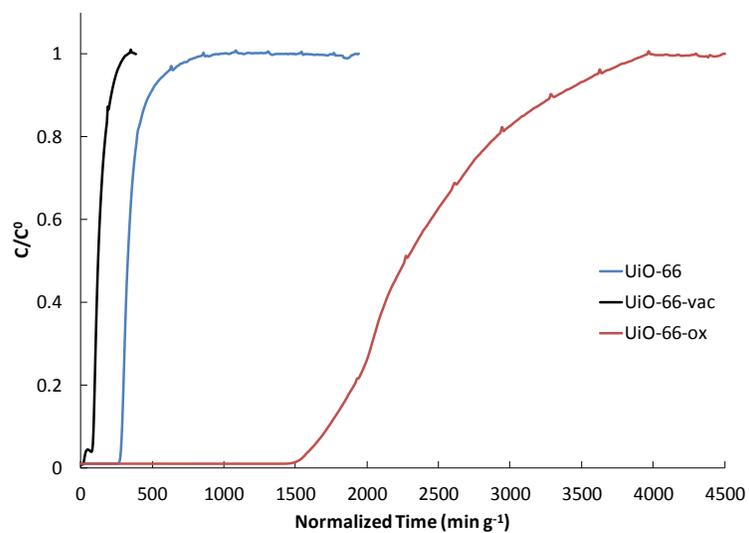


Figure S6. Microbreakthrough plot for UiO-66, UiO-66-vac, and UiO-66-ox against SO₂.

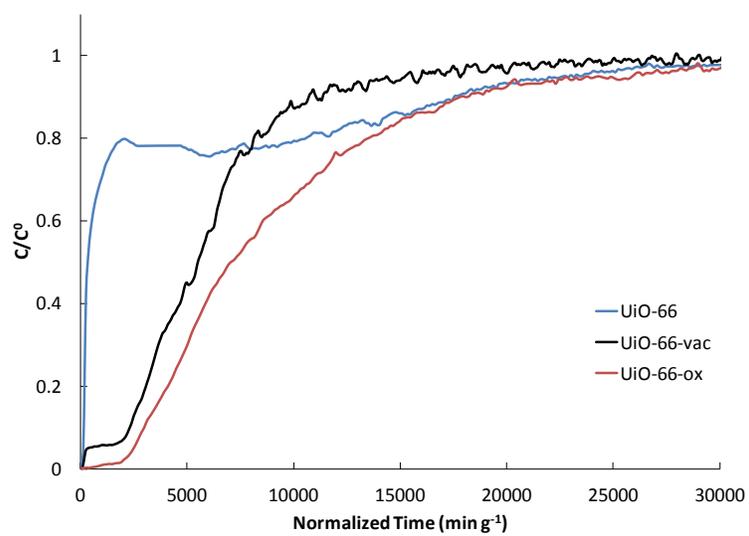


Figure S7. Microbreakthrough plot for UiO-66, UiO-66-vac, and UiO-66-ox against NO₂.

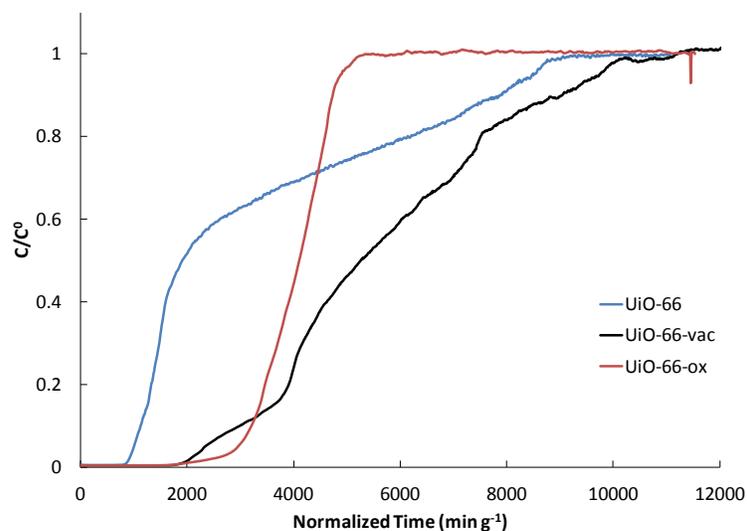


Figure S8. Microbreakthrough plot for UiO-66, UiO-66-vac, and UiO-66-ox against octane.

Table S2. Measured microbreakthrough capacities (mmol SBU^{-1}) of each MOF for ammonia, cyanogen chloride, sulphur dioxide, nitrogen dioxide, and octane.

	NH_3	ClCN	SO_2	NO_2	C_8H_{18}
UiO-66	3.3	2.8	0.16	6.2	3.7
UiO-66-vac	2.3	1.1	0.0	5.6	5.7
UiO-66-ox	3.7	2.4	1.2	12.5	4.2

Table S3. Measured microbreakthrough capacities (mmol nm^{-3}) of each MOF for ammonia, cyanogen chloride, sulphur dioxide, nitrogen dioxide, and octane.

	NH_3	ClCN	SO_2	NO_2	C_8H_{18}
UiO-66	1.5	1.2	0.072	2.8	1.7
UiO-66-vac	1.0	0.52	0.00	2.5	2.6
UiO-66-ox	1.7	1.1	0.53	5.6	1.9

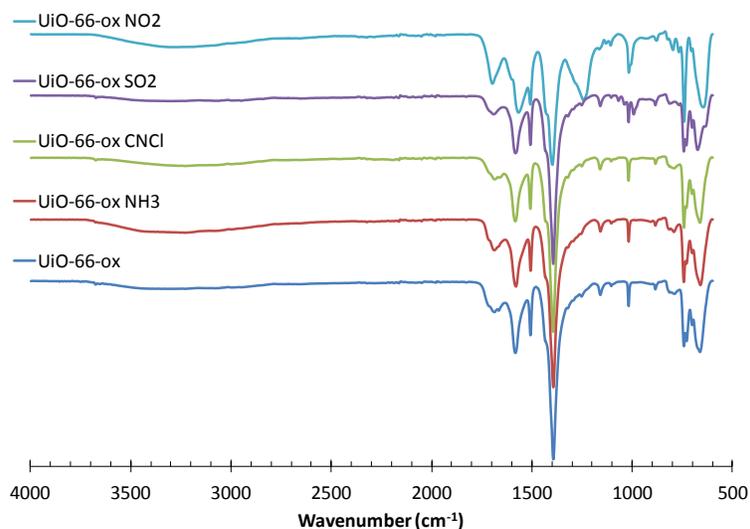


Figure S9. ATR-FTIR spectra of UiO-66-ox exposed to NH₃, CNCl, SO₂, and NO₂, from 4000 to 600 cm⁻¹; compared to UiO-66-ox spectrum.

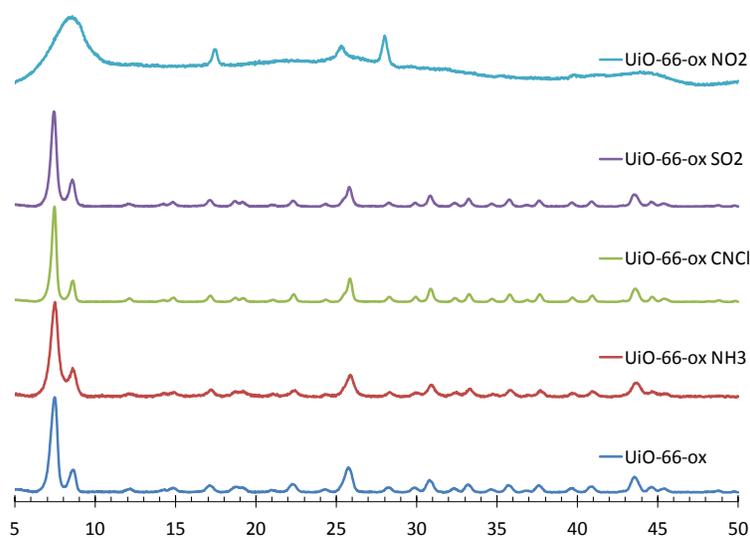


Figure S10. XRD patterns of UiO-66-ox exposed to NH₃, CNCl, SO₂, and NO₂, from 2θ = 5 to 50°; compared to UiO-66-ox pattern.

References

1. G. W. Peterson, J. B. DeCoste, T. Grant Glover, Y. Huang, H. Jasuja and K. S. Walton, *Microporous Mesoporous Mater.*, 2013, **179**, 48-53.
2. 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. (Cambridge, U. K.)*, 2013, **49**, 9449-9451.
3. K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552-8556.

4. J. B. Decoste and G. W. Peterson, *Journal of Visualized Experiments*, 2013, e51175.
5. T. G. Glover, G. W. Peterson, B. J. Schindler, D. Britt and O. Yaghi, *Chem. Eng. Sci.*, 2011, **66**, 163-170.