

Supporting Information for:

Removal of Hydrocarbon Contaminants from Water with Perfluorocarboxylated UiO-6X Derivatives

Dante M. DeChellis, Douglas T. Genna

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I. Materials and Methods

All chemical reagents were purchased and used without further purification. Zirconium (IV) chloride, perfluorooctanoic acid, heptafluorobutyric acid, and terephthalic acid were purchased from Sigma Aldrich. All solvents were purchased from Fisher Scientific.

UiO-66 and UiO-67 were synthesized as described in the literature.¹

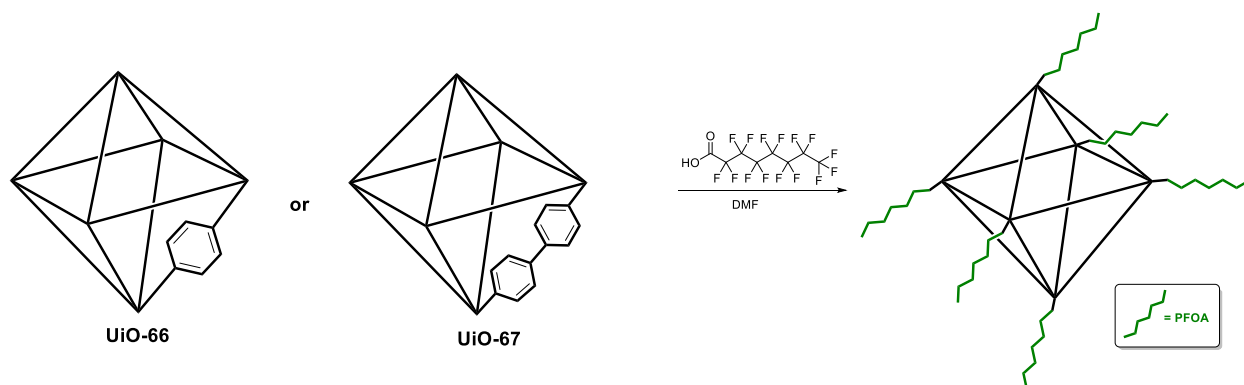
TGA data were collected on a TA Instruments TGA Q50 from 50 °C to 600 °C at a rate of 10 °C per minute.

Powder XRD patterns of small samples were collected on a Bruker AXS X8 Prospector CCD single crystal diffractometer using the “pilot” plugin for collection of multicrystalline XRD patterns. The instrument is equipped with a copper I μ S microsource with a laterally graded multilayer (Goebel) mirror for monochromatization ($\lambda = 1.54178 \text{ \AA}$, beam size 0.1-0.2 mm) and an ApexII CCD area detector. Powder samples were thoroughly ground to assure a representative number of crystallites to be present in the X-ray beam. Powder samples were mixed with small amounts of mineral oil and mounted onto a 0.4 mm diameter Mitegen micromesh mount for data collection. Samples were centered in the beam using the instrument’s mounting microscope video camera. Data were collected in an emulated theta-2theta setup using the Apex2 software package of Bruker AXS. The sample mount was aligned horizontally ($\text{Chi} = 0^\circ$) and theta angles were set to eight different angles between 12 and 96° to cover a range equivalent to a 0 to 110° range of a powder X-ray diffractometer operated in Debye Scherrer mode (omega angles of each run were set to half the theta values). Samples were rotated around the mount’s spindle axis during measurement (360 rotation around phi), typical exposure times were 30 seconds per frame collected. The eight individual patterns taken were corrected for unequal sample to detector surface distance (“unwarped”) and were combined into one continuous pattern using the “pilot plugin” software embedded in the Apex2 software package. Data were integrated over 2theta, converted in powder XRD patterns in Bruker “raw” format and were further processed with standard powder XRD software packages.

¹ Katz, M. J.; Brown, Z. J.; Colon, Y. J.; Siu, P. W.; Scheidt, K. A.; Snurr, R. Q.; Hupp, J. T.; Farha, O. K. *Chem. Commun.* **2013**, 49, 9449-9451

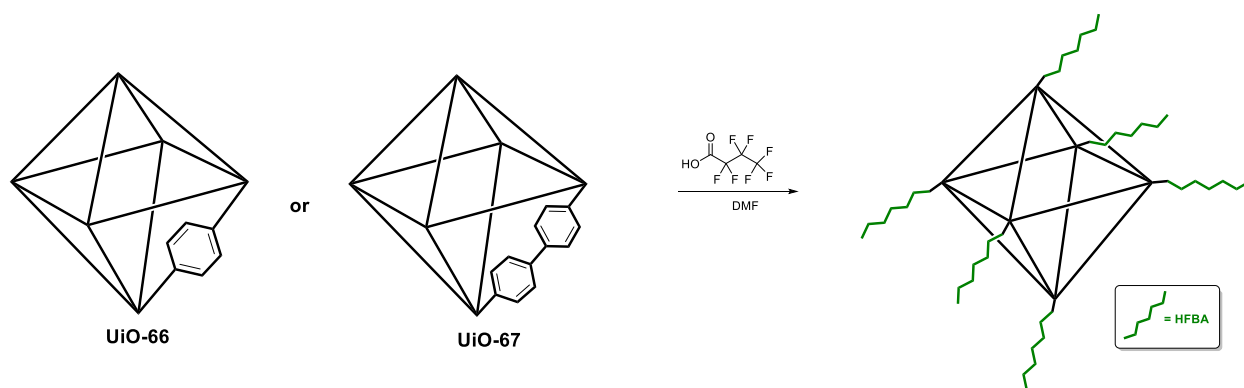
II. Experimental Procedures

Synthesis of PFOA@UiO-6X



To a 50 mL Erlenmeyer flask containing 33.5 mL of DMF, perfluorooctanoic acid (PFOA) (0.140 g, 0.338 mmol) was added. The solution was shaken manually until all PFOA had dissolved. Then 0.200 g of UiO-66 or UiO-67 was suspended in the solution. The suspension sat at room temperature for 24 hours, after which the liquid and solid components were separated by centrifugation (5 min at 5000 rpm). The liquid was decanted, and the MOF was suspended in fresh DMF (20 mL) and soaked for one hour, after which the liquid and solid components were separated by centrifugation (5 min at 5000 rpm). The liquid was decanted and the MOF was then transferred to a 20 mL vial activated at 150 °C for 24 hours *in vacuo*.

Synthesis of HFBA@UiO-6X



Heptafluorobutyric acid (HFBA) (0.140 g, 0.654 mmol) was syringed into a 125 mL Erlenmeyer flask inside a nitrogen filled glove box. The flask was removed from the glove box and DMF (65 mL) was poured into the flask as rapidly as possible. Then 0.200 g of UiO-66 or UiO-67 was suspended in the solution. The suspension sat at room temperature for 24 hours, after which the liquid and solid components were separated by centrifugation (5 min at 5000 rpm). The liquid was decanted, and the MOF was suspended in fresh DMF (20 mL) and soaked for one hour, after which the liquid and solid components were separated by centrifugation (5 min at 5000 rpm). The

liquid was decanted and the MOF was then transferred to a 20 mL vial activated at 150 °C for 24 hours *in vacuo*.

Adsorption Experiments via Column

A Pasteur pipette column was prepared by packing a small piece of Kimwipe into the taper point of the pipette (see Figure S11 for setup). Then 0.050 g of MOF was packed into the column on top of the Kimwipe. In a 4 mL vial, 2.0 mL of water and between 0.2 mL – 0.5 mL of contaminant was mixed together. The whole mixture was pipetted into the column. The cap to a 4 mL vial was placed atop the column to avoid evaporation. Small amounts of pressure were applied to the column depending on the viscosity of the liquid within the column by way of pipette bulb. The volume of the un-adsorbed liquid was measured using a graduated syringe. The amount adsorbed was determined using the following equation:

Amount adsorbed = (total mL of contaminant exposed to the column) – (mL of contaminant collected beneath)

Column Recycling for benzene adsorption

After the adsorption test, the column was placed in a 120 °C oven for 1 hour to remove any adsorbed benzene. The column was removed from the oven and allowed to cool to room temperature (approximately 20 minutes). A fresh benzene:water mixture was added as described in the general procedure. This whole process was repeated a total of five times.

Spill test experiments

To a 740 mL 125 mm x 65 mm crystallizing dish filled halfway with d.i. water was added the contaminant² (see table S1 for amounts). The contaminant was added via syringe in which the tip of the needle was placed just below the water surface and slowly dispensed to limit dispersion of the contaminant and to replicate a solvent/oil slick on the surface of the water. Then 0.015 g of MOF were added directly to the spill. Adsorption was recorded and timed. The point of completion was determined when no more “free” contaminant was observed floating on the water surface.

Contaminant	Amount used
Benzene	0.0367 mL
Toluene	0.0315 mL
hexane	0.0315 mL
cyclohexane	0.0375 mL
Motor oil	0.0743 mL

Table S1: amounts of contaminant used in the spill test

² 75% of the maximum adsorbed amount (as determined by the column tests) of contaminant was used.

Spill test experiments with Sudan Blue

To a 740 mL 125 mm x 65 mm crystallizing dish filled halfway with d.i. water was added the contaminant³ (see table S1 for amounts). The contaminant dyed with Sudan Blue (1 mg) was added via syringe in which the tip of the needle was placed just below the water surface and slowly dispensed to limit dispersion of the contaminant and to replicate a solvent/oil slick on the surface of the water. Then 0.015 g of MOF were added directly to the spill. Adsorption was recorded and timed. The point of completion was determined when no more “free” dyed-contaminant was observed floating on the water surface.

Synthesis of liquid marbles

To a small pile of HFBA@UiO-66 an 8 μ L water droplet is set onto the pile of MOF and rolled around until the full droplet is completely coated in powder, thus forming the marble. See figure S18 and supporting video.

Water Contact Angle Measurements:

10 mg of MOF were ground and packed onto the surface of a standard glass microscope slide. An 8 μ L water droplet was placed onto the packed MOF, and a photo was taken of the droplet on the slide. The water contact angle was measured using a standard protractor on the photograph (Figures S15-S17).

³ 75% of the maximum adsorbed amount (as determined by the column tests) of contaminant was used.

III. Supplemental figures

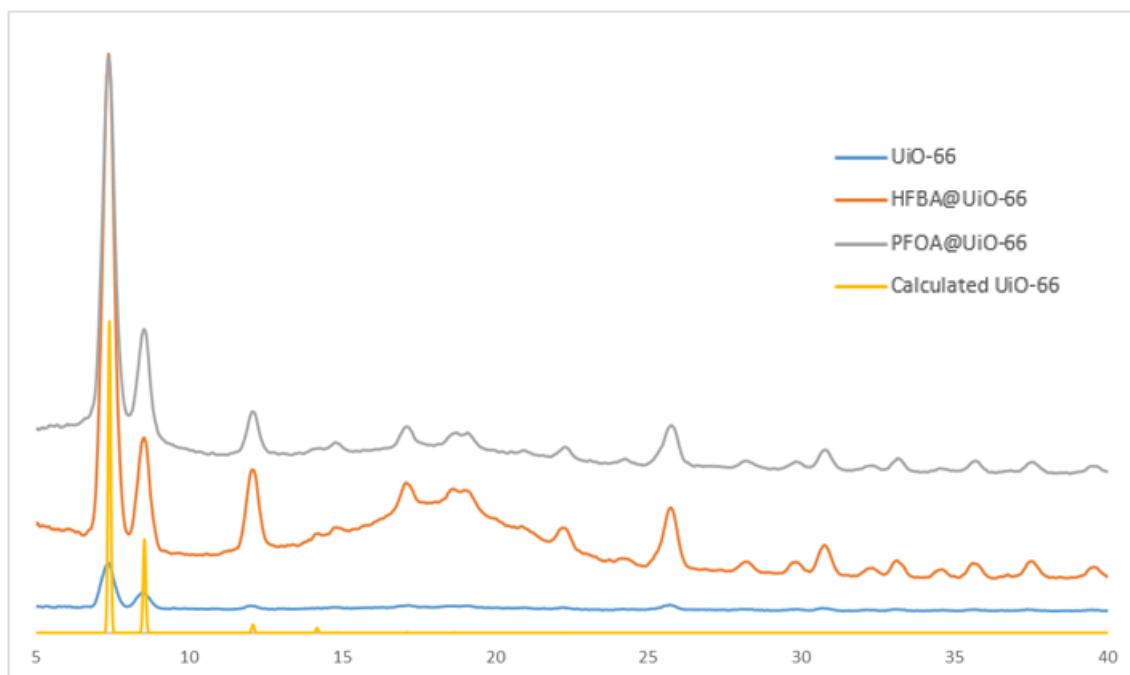


Fig S1. PXRD patterns of UiO-66, HFBA@UiO-66, and PFOA@UiO-66

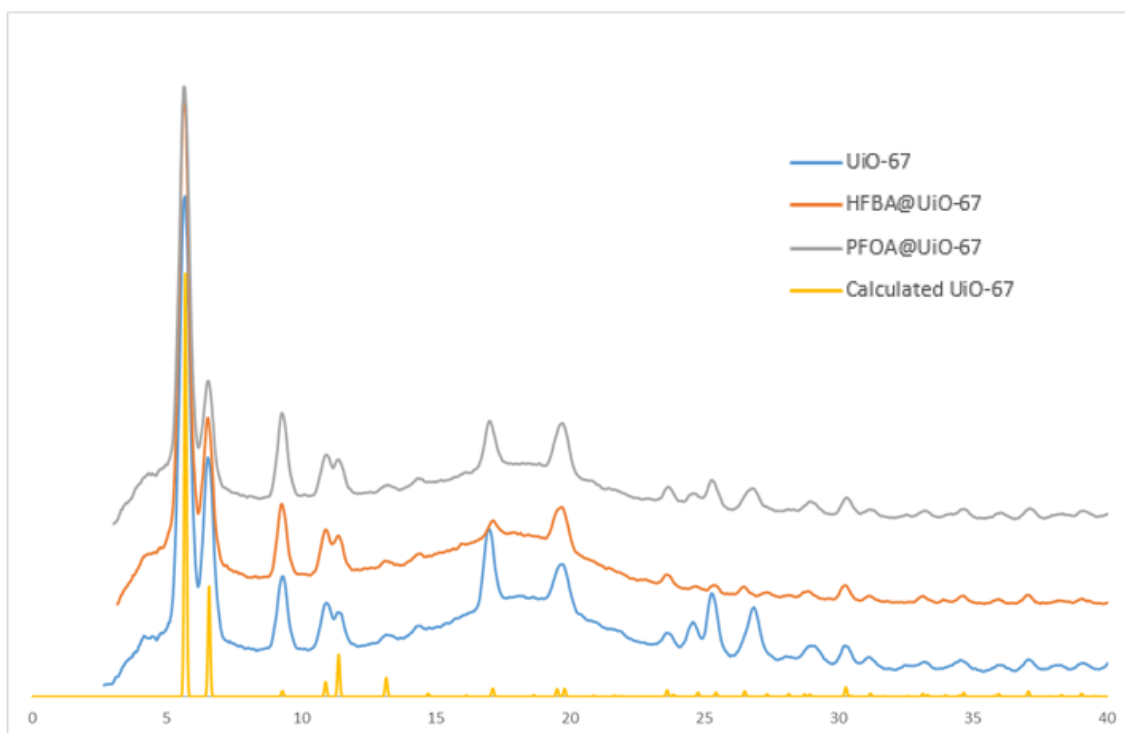


Fig S2. PXRD patterns of UiO-67, HFBA@UiO-67, and PFOA@UiO-67

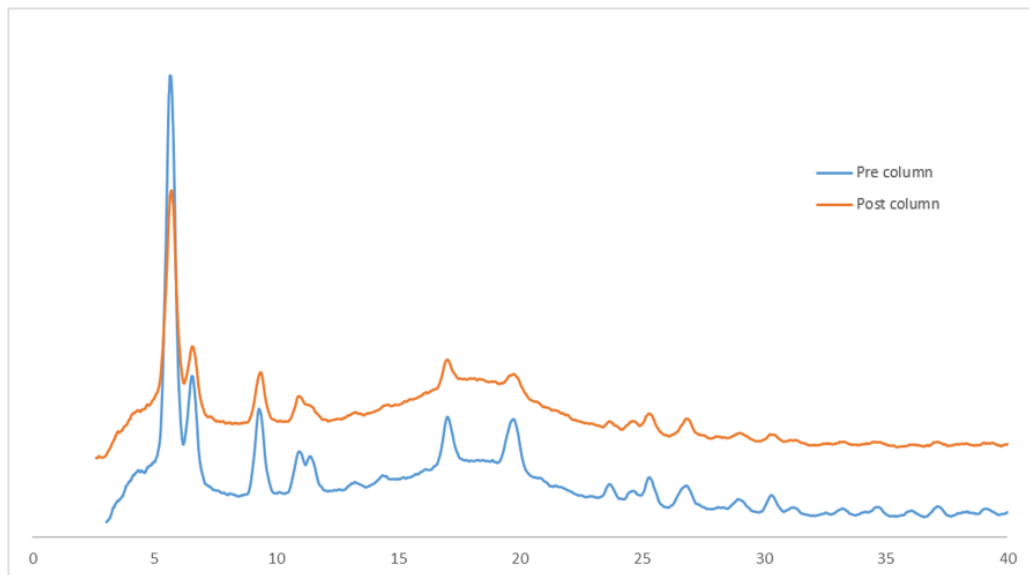


Fig S3. PXRD of PFOA@UiO-67 before the column experiment with benzene and after the column experiment to show retention of UiO-67 structure.

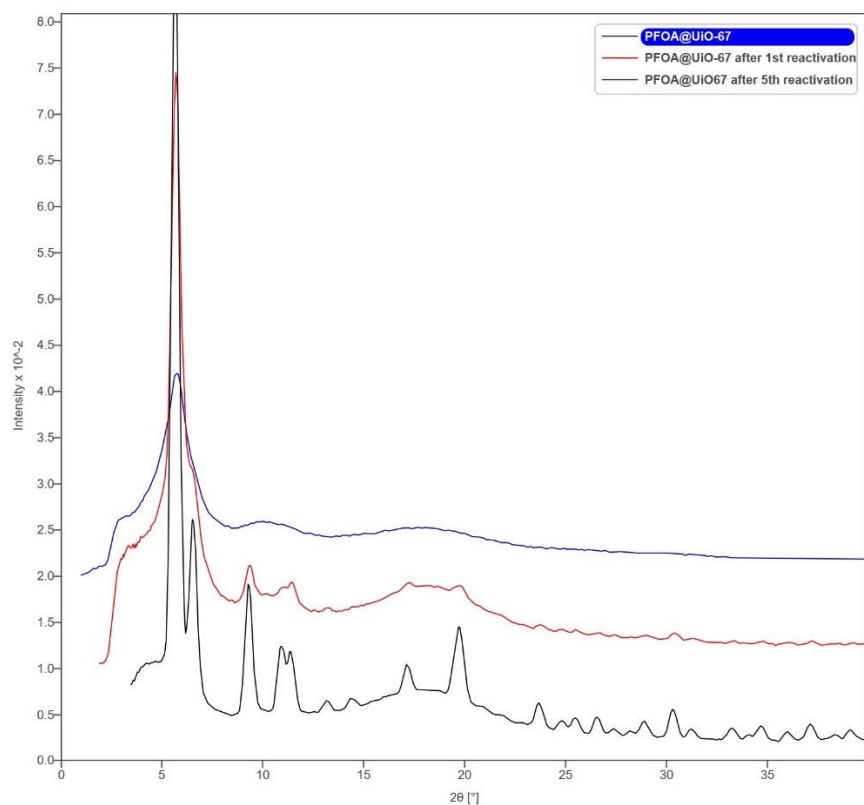


Fig S4. PXRD of PFOA@UiO-67 before the column experiment (black) with benzene, after the first reactivation at 120 °C (red) and after the 5th reactivation at 120 °C (blue).

Sample: UiO-66
Size: 2.7640 mg
Method: 50-600

TGA

File: C:\TA\Data\TGA\Dante\l
Operator: Dante

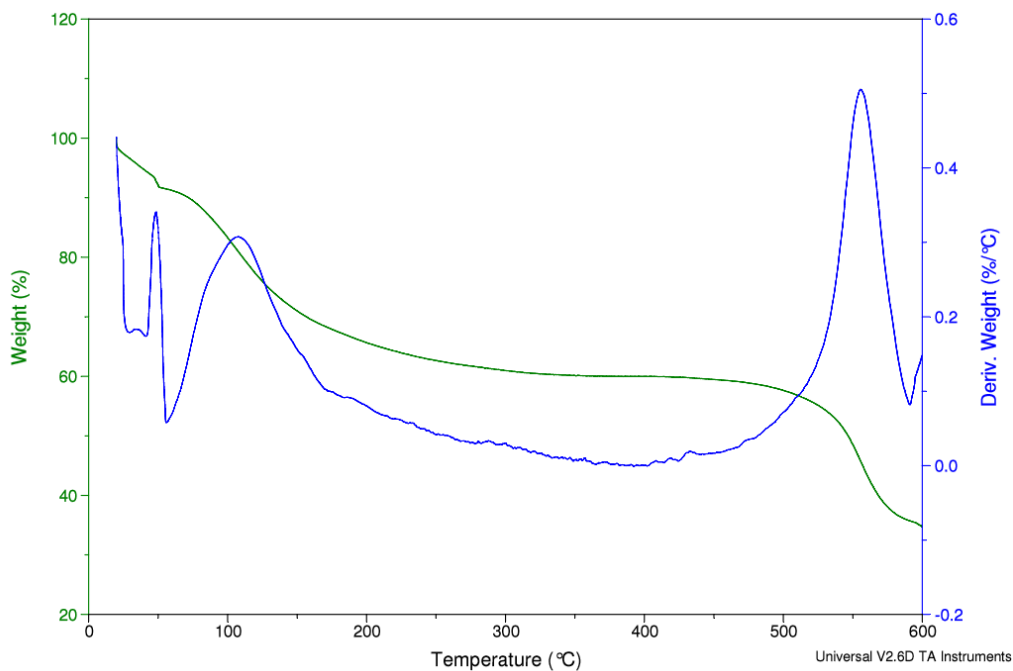


Fig S5. TGA of UiO-66

Sample: UiO-67
Size: 4.4240 mg
Method: 50-600

TGA

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Operator: Dante

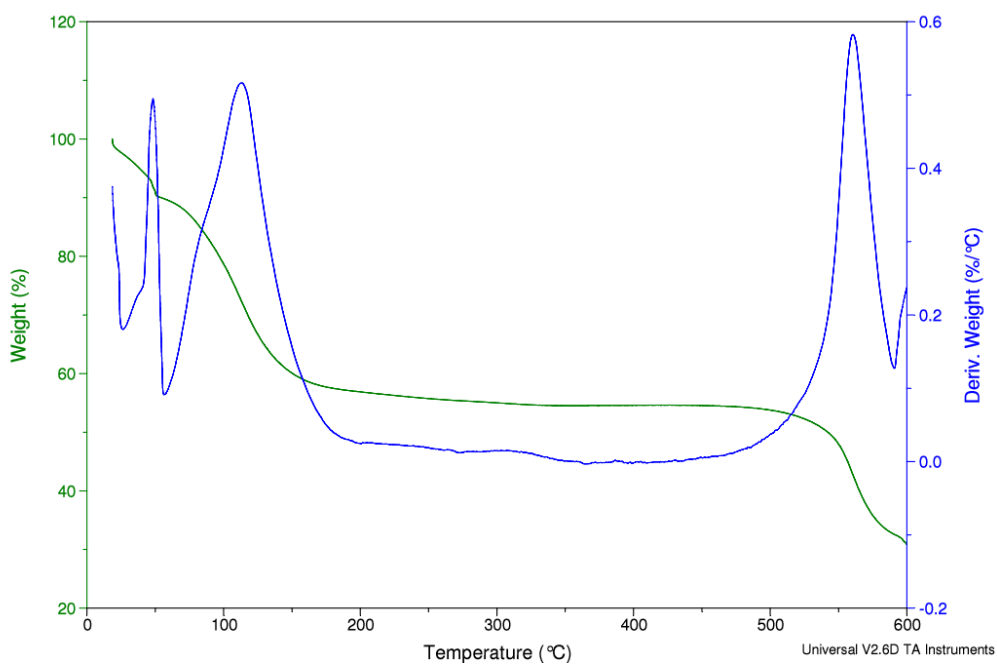


Fig S6. TGA of UiO-67

Sample: DD-2-46
Size: 5.2980 mg
Method: 50-600
Comment: PFOA@UiO-66 140 mg

TGA

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Operator: Dante

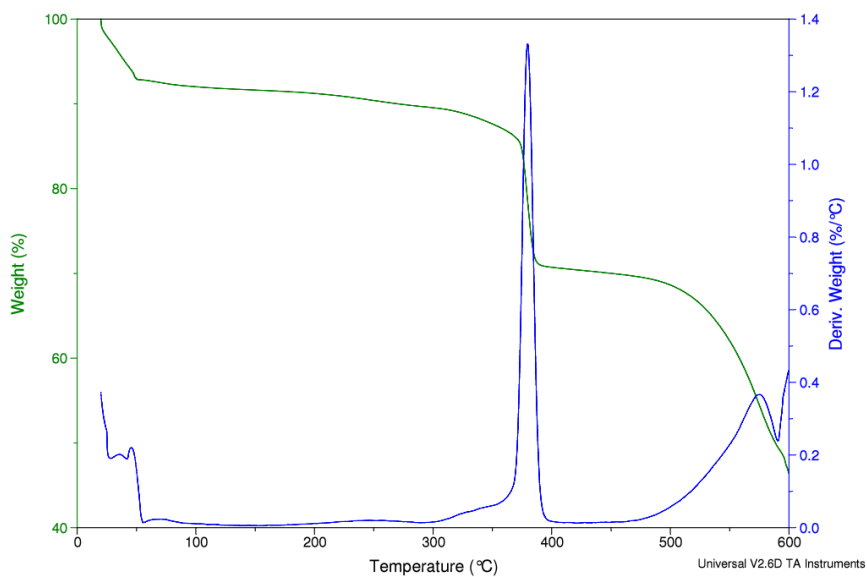


Fig S7. TGA of PFOA@UiO-66

Sample: DD-1-88
Size: 8.0440 mg
Method: 50-600

TGA

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Operator: Dante

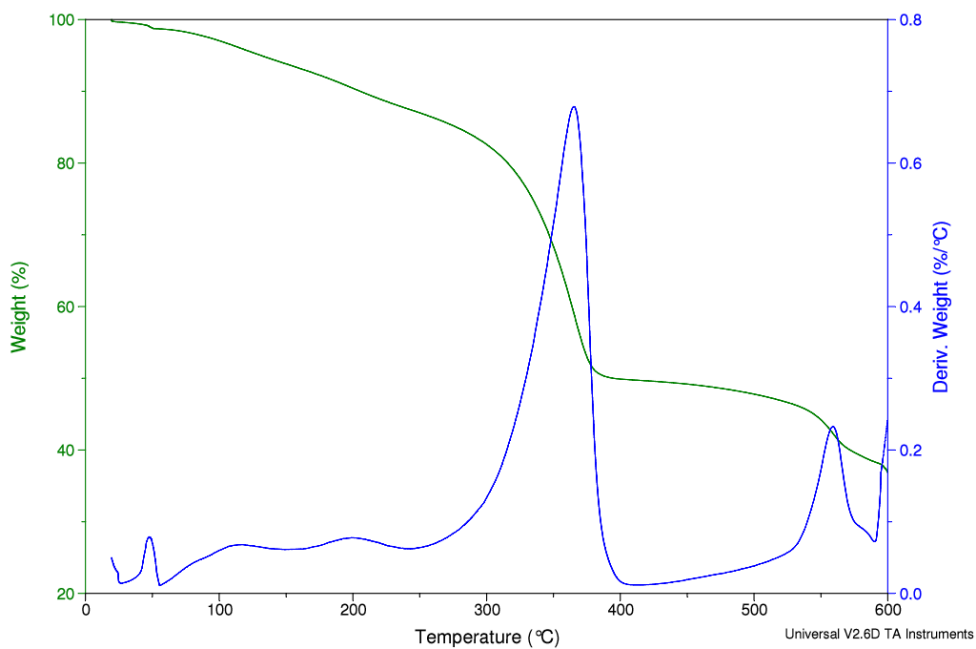


Fig S8. TGA of PFOA@UiO-67

Sample: DD-2-30
Size: 8.6300 mg
Method: Ramp
Comment: HFBA@66 140 mg

TGA

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Operator: Dante
Run Date: 02-Jul-2019 12:47
Instrument: TGA Q50 V20.10 Build 36

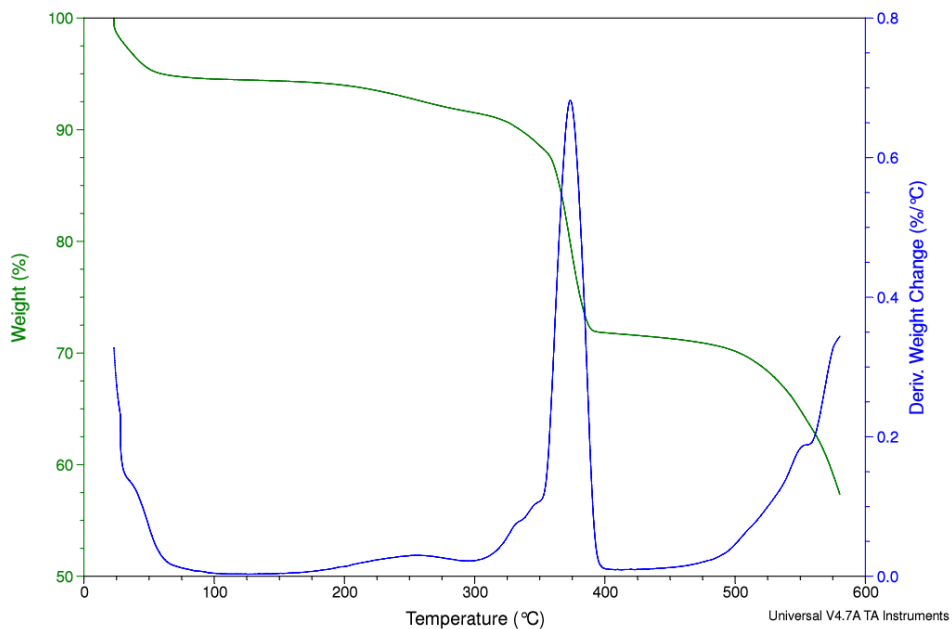


Fig S9. TGA of HFBA@UiO-66

Sample: HFBA@UiO-67-2
Size: 4.9190 mg
Method: Ramp
Comment: HFBA@67

TGA

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Operator: Dante
Run Date: 17-Jul-2019 10:51
Instrument: TGA Q50 V20.10 Build 36

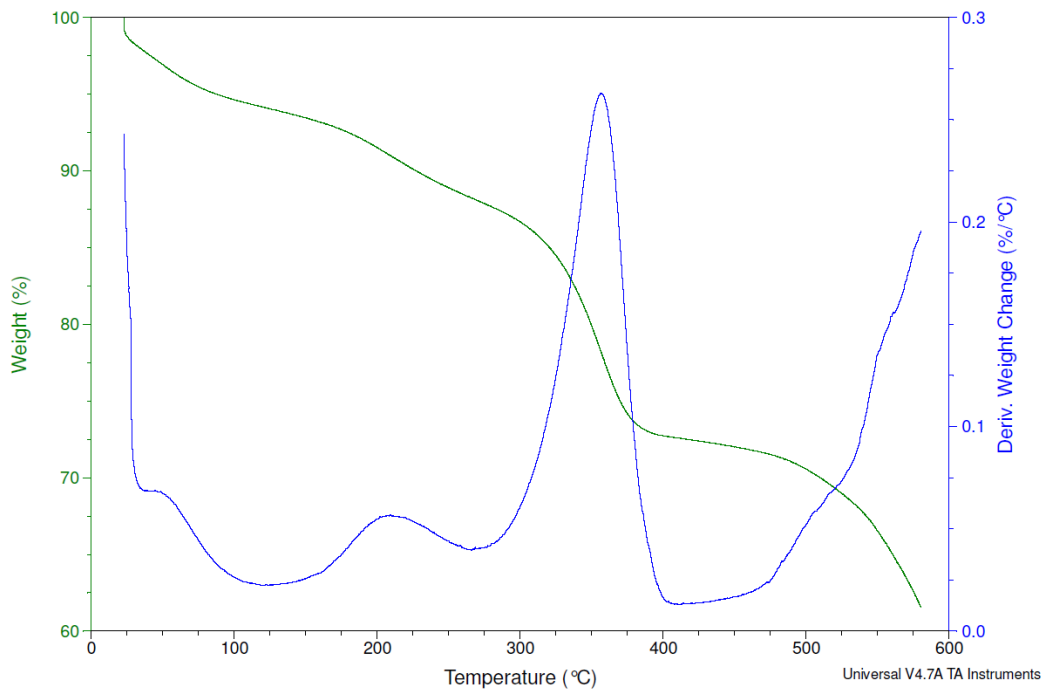


Fig S10. TGA of HFBA@UiO-67



Fig S11. UiO-66 sunken to the bottom of a vial of water



Fig S12. UiO-67 sunken to the bottom of a vial of water

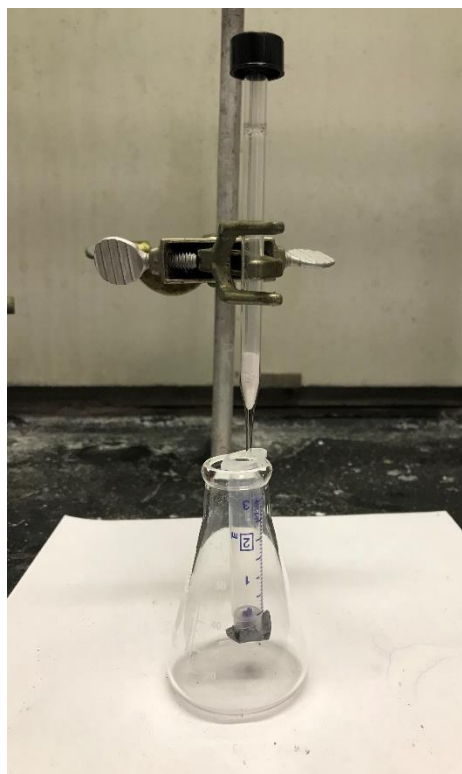


Fig S13. Column test set-up

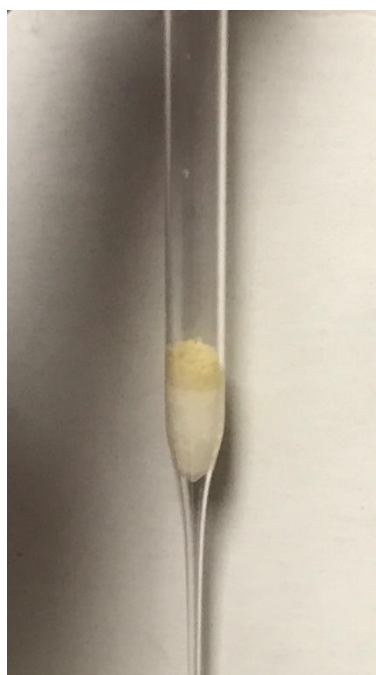


Fig S14. PFOA@UiO-67 post oil column trial. Note yellow color of deposited oil.

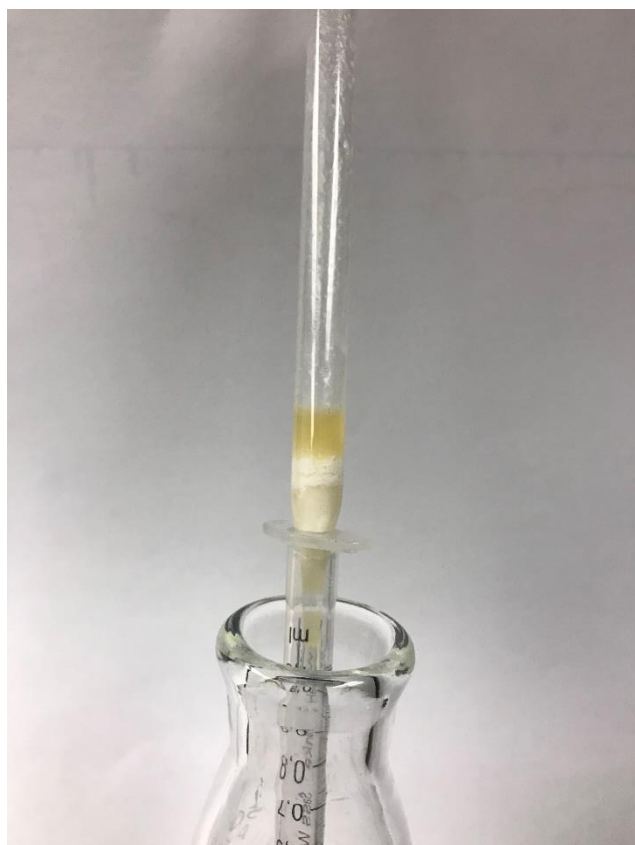


Fig S15. UiO-67 with oil flowing through column with no color change in MOF

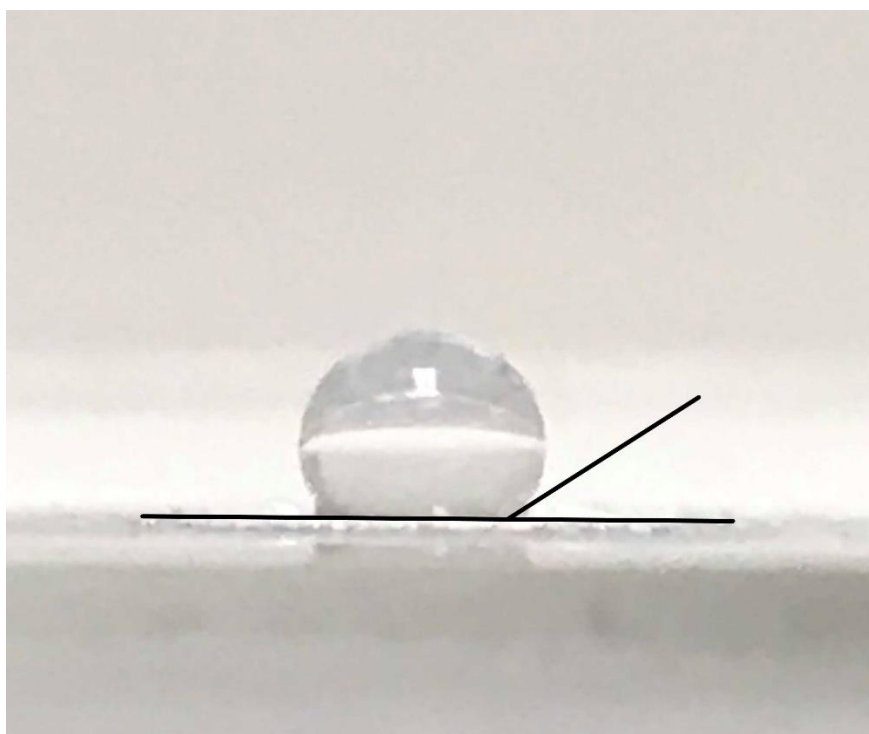


Fig S16. Water contact angle of PFOA@UiO-67 of approximately 147 degrees.

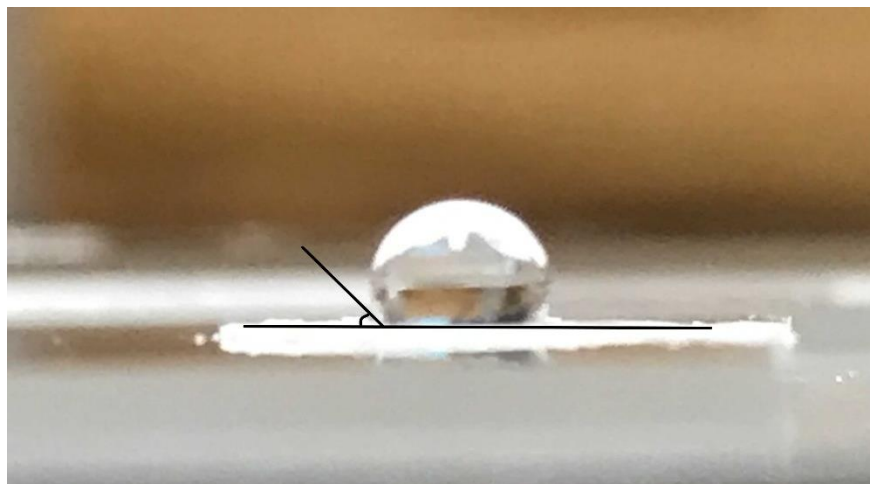


Fig S17. Water contact angle of HFBA@UiO-66 of approximately 135 degrees.

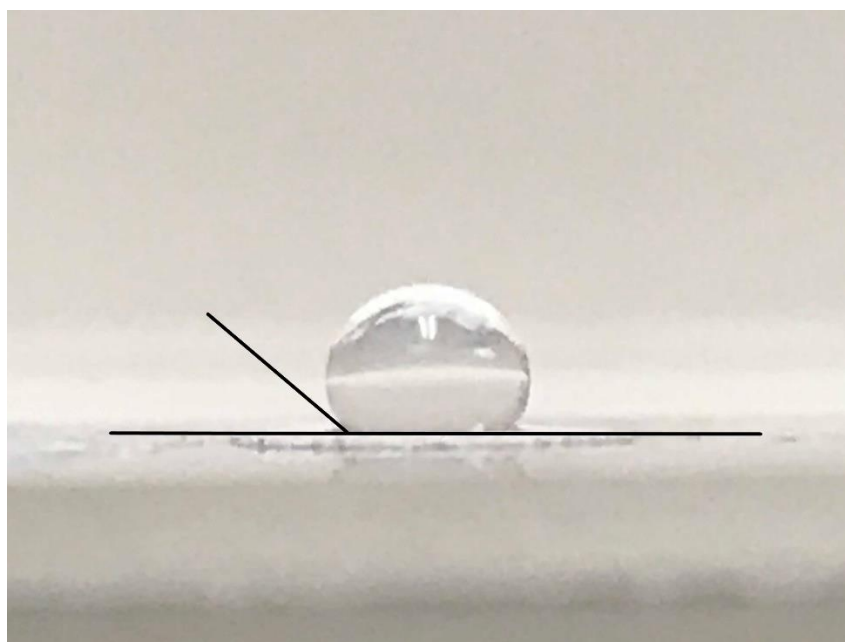


Fig S18. Water contact angle of HFBA@UiO-67 of approximately 141 degrees.

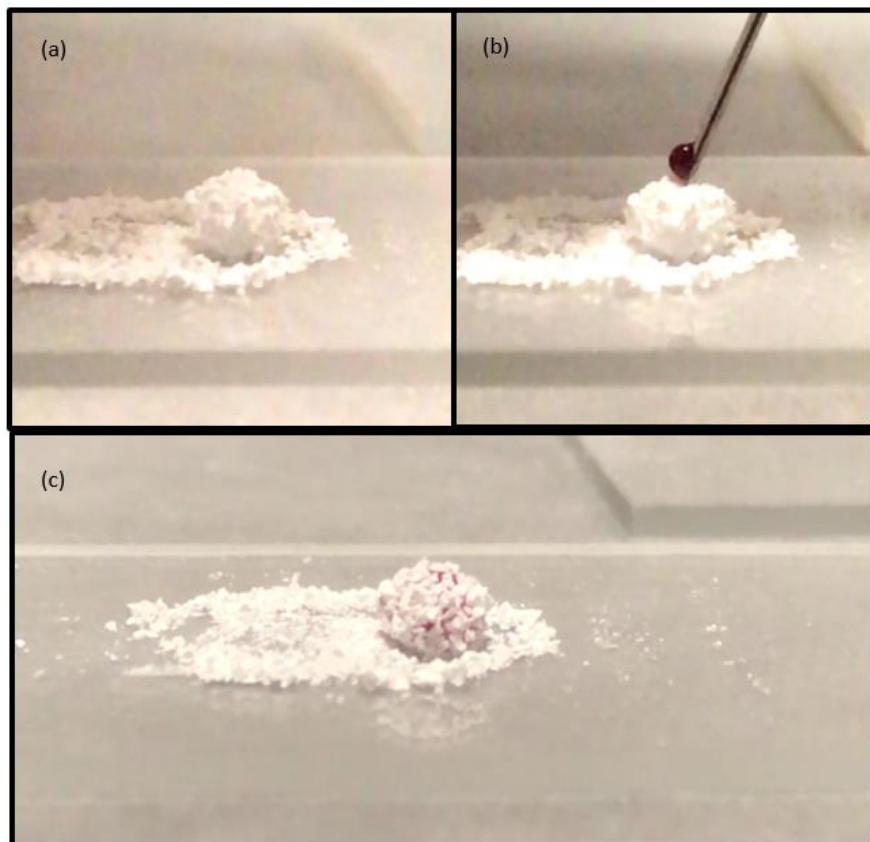


Fig S19. Formation of HFBA@UiO-66 marble (a), pre-injection of Rhodamine B into marble (b), and post-injection with Rhodamine B with retention of marble and coating.

IV. List of Videos of spill tests

- 1) PFOA@UiO-67 adsorbing dyed benzene
- 2) PFOA@UiO-67 adsorbing dyed toluene
- 3) PFOA@UiO-67 adsorbing dyed hexane
- 4) PFOA@UiO-67 adsorbing Subaru® brand motor oil
- 5) Formation of liquid marble
- 6) Collision of two liquid marbles