Supporting Information for:

Removal of Lead Ions from Water Using Thiophene-Functionalized Metal-Organic Frameworks

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I. Materials and Methods

I.a Reagents and Instrumentation

Acetic acid, thiophene, tetrahydrothiophene, terephthalic acid, zirconium chloride, and D_6-DMSO were purchased from Sigma-Aldrich and used as received. Lead (II) nitrate and DMF were purchased from Fisher Scientific and used as received. 2,5-Thiophenedicarboxylic acid was purchased from TCI Chemicals and used as received. *N*-Methyl-2-pyrolidone was purchased from Acros Organics and used as received. 200 proof ethyl alcohol was purchased from pharmco Aaper and used as received.

ICP data were collected on a Thermo Scientific ICAP Qc equipped with a Cetac ASX-520 autosampler.

NMR data were collected on a 400 MHz Bruker Avance NMR Spectrometer.

I.b X-ray Powder Diffraction

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 IμS microsource with a laterally graded multilayer (Goebel) mirror for monochromatization (λ = 1.54178 Å, 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 (Chi = 0°) 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.

II. Experimental Procedures

II.a Synthesis of MOFs

Synthesis of DUT-67

To a premixed solution of DMF (25 mL) and NMP (25 mL) was added $ZrCl_4$ (460 mg, 2.00 mmol, 1.57 equiv). The mixture was then sonicated for 10 minutes until the solution was homogeneous. 2,5-Thiophenedicarboxylic acid (220 mg, 1.27 mmol, 1.00 equiv) was added to the resulting solution, which was then sonicated for 10 minutes. Acetic acid (20 mL, 334 mmol) was then added to the resulting solution, which was then sonicated for an additional 10 minutes. The reaction solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 µm) in 5 mL portions into fourteen individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps and heated in an oven at 120 °C for 48 hours. At this time, the vials were removed from the oven and cooled to room temperature. The contents of each vial were combined and the combined crystalline powder product was separated from the reaction liquid by centrifugation (5000 rpm for 5 minutes) and then washed several times with both DMF and EtOH. The powder was then dried at room temperature *in vacuo* for 24 hours. At this time, the powder was activated *in vacuo* at 100 °C for 2 hours. Powder samples were then thoroughly ground before use to assure a homogeneous representation of crystallites. Powder X-ray diffraction data matched that as previously reported.[1]

Synthesis of UiO-66

To a 50 mL Erlenmeyer flask loaded with $ZrCl_4$ (250 mg, 1.07 mmol, 1.00 equiv) and DMF (10 mL) was added conc. HCl (2 mL, 20.40 mmol, 19.03 equiv). The resulting solution was sonicated for 20 minutes. In a second 50 mL Erlenmeyer flask, terephthalic acid (246 mg, 1.48 mmol, 1.38 equiv) was dissolved in DMF (20 mL) and sonicated for 10 minutes. The ligand and metal solutions were then combined and sonicated together for an additional 20 minutes. The resulting solution was then filtered through a GE 25 mm PVDF syringe filter (0.45 µm) into 5.3 mL portions into 6 individual 20 mL scintillation vials. The vials were sealed with Teflon-lined caps and heated in an oven at 80 °C for 24 hours. At this time, the vials were removed from the oven and cooled to room temperature. The contents of each vial were combined and the combined crystalline powder product was separated from the reaction liquid by centrifugation (5000 rpm for 5 minutes) and washed several times with both DMF and EtOH. The powder was then dried at room temperature under high vacuum for 24 hours. At this time, the powder was activated at 100 °C under high vacuum for 2 hours. Powder samples were then thoroughly ground before use to assure a homogeneous representation of crystallites. Powder X-ray diffraction data matched that as previously reported.[2]

Synthesis of TC@UiO-66 and THTC@UiO-66

To a 20 mL scintillation vial containing 10 mL of a 1 M solution of the desired dopant (thiophenecarboxylic acid or tetrahydrothiophenecarboxylic acid) in DMF was added 500 mg of ground, activated UiO-66. The vial was then agitated on an orbital shaker (~100 RPM) for 24 hours, after which the powder was analyzed via powder X-ray diffraction and digested for ^{1}H NMR and ^{13}C NMR spectroscopy.

IIb. Lead Adsorption in Batch

General Conditions for Batch Experiment

To a 4 mL screw thread vial was added 20 mg of the requisite MOF followed by 3 mL of either a 21, 210, or 2100 ppm aqueous solution of $PbNO_3$. MOFs were left to sit in the Pb^{2+} solution for 24 hrs before aliquots of the solution were taken, diluted, and analyzed using inductively coupled plasma mass spectroscopy (ICP-MS).

Conditions for Experiments at different pH.

Aqueous $Pb(NO_3)_2$ solutions were prepared in the usual manner. However, prior to exposure to MOF, the solutions were either basified with 0.1M $NaOH_{(aq)}$ or acidified with 0.1M $HNO_{3(aq)}$. Note upon exposure to 0.1M NaOH, some $Pb(OH)_2$ precipitated from solution. All solutions were tested for Pb^{2+} content via ICP-MS both before and after exposure to MOF. It was found that the starting basified solutions had little to no Pb^{2+}at the time of analysis and thus Pb adsorption data could not be collected.

IIc. Lead Adsorption in Flow

General Conditions for Flow Experiment

Pb^{2+} loading in MOFs was determined by flowing either a 21 or 2100 ppm aqueous solution of $PbNO_3$ through a 1 in. stainless steel column (1/4 OD), packed with 250 mg of the requisite MOF*, using a Waters 515 HPLC pump at a flow rate of 0.5 mL/min. Each column volume was fractionated and aliquots were taken of each column (1 mL), diluted, and analyzed using ICP-MS.

*MOFs were first primed with DI water at a flow rate of 0.5 mL/min for 30 minutes.

Solvent Screening for MOF Regeneration

To a 4 mL vial with a Teflon cap was added 20 mg of DUT-67 post flow experiment of 2100 ppm $Pb(NO_3)_{2(aq)}$ and 3 mL of selected solvent (acetone, isopropyl alcohol, ethyl acetate, or ethanol). 5 minutes following solvent addition, an aliquot of solvent was sampled for subsequent analysis of leached Pb^{2+} via ICP-MS. Instantly after sampling, the solvent was decanted, and the MOF

was submersed in 3 mL of fresh solvent once more. This was carried out for each Pb@MOF and each solvent a total of 5 times. The results are summarized in Figure S1.

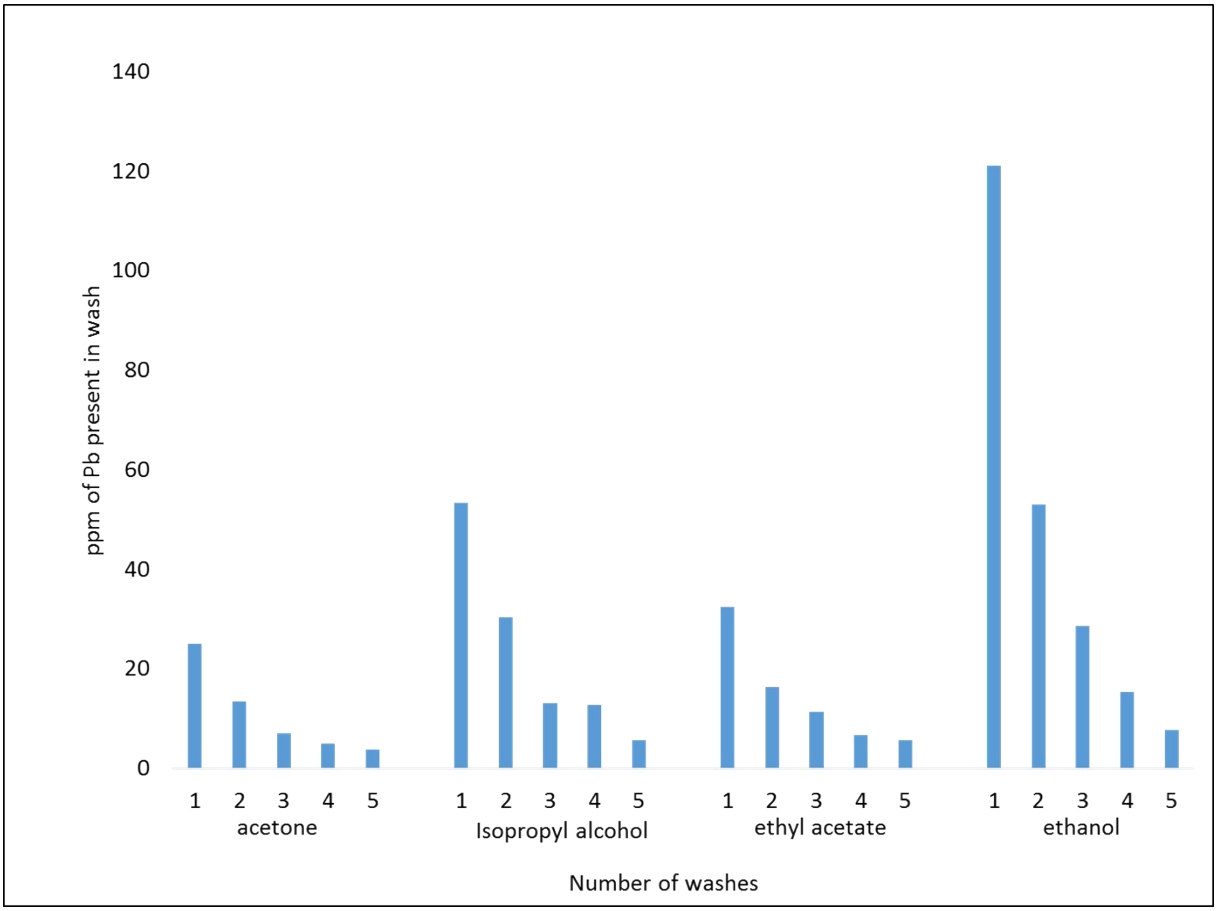

Figure S1: Pb content data for solvent screening for MOF regeneration. Note the numbers on the x-axis correspond to the wash number. For example 1 is the 1st wash and 2 is the 2nd wash, etc. as outlined in the procedure above.

Regeneration of DUT-67 in Flow at 21 ppm Pb^{2+}

After exposing DUT-67 to Pb^{2+} adsorption under flow conditions with 21ppm $Pb(NO_3)_{2(aq)}$, DUT-67 was tested for four additional cycles by first eluting 200 proof ethyl alcohol at a flow rate of 0.5 mL/min for 1 hour and then subsequently flowing fresh DI water through the MOF at a flow rate of 0.5 mL/min for 30 minutes. The washed MOF-containing column was then re-exposed to 21 ppm solutions of $Pb(NO_3)_2$ under flow conditions (as described in IIc.)

MOF digestion for NMR and ICP-MS Analysis

To 0.66 mL of DMSO-d_6 was added approximately 5 mg of the requisite MOF. To this heterogeneous mixture was added 0.33 mL of HF (48% aqueous solution) before being sonicated as needed until the solution was homogeneous. To this solution was added ethyl acetate (5 µL, 0.0512 mmol) as an internal standard. The resulting solution was analyzed via NMR without further preparation. After collection, the solution was diluted with deionized water for analysis via ICP-MS.

Note regarding MOF digestion: Under the acidic conditions of the NMR solution, it was observed via H^1NMR that some of the ethyl acetate had been hydrolyzed to ethanol and acetic acid.

III. Integral Calculation for Flow Experiments

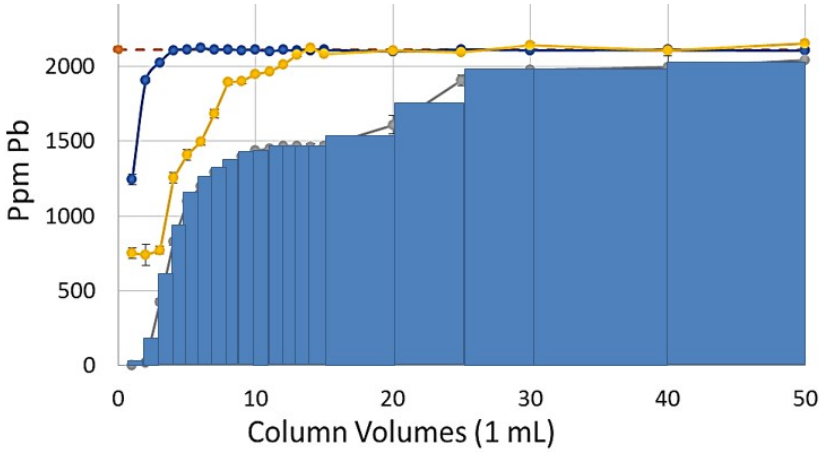

Figure S2. Midpoint Rectangles Drawn under DUT-67's Breakthrough Curve for Visual Aid

To approximate the amount of lead adsorbed under flow conditions, the Midpoint Rectangle Rule was utilized:

$$M_n = \frac{b-a}{n}\left[h_1\left(\frac{x_0+x_1}{2}\right)+h_2\left(\frac{x_1+x_2}{2}\right)+h_3\left(\frac{x_2+x_3}{2}\right)+\ldots+h_n\left(\frac{x_{n-1}+x_n}{2}\right)\right]$$

The area under a breakthrough curve (i.e. mg Pb^{2+} leaving the MOF in the eluent = M_n) between a and b can be approximated by summing midpoint rectangles. Where n is the number of rectangles, $\frac{b-a}{n}$ is the width of each rectangle (in L), and h is the heights of the rectangles (in ppm Pb^{2+} = mg Pb^{2+}/L). M_n is then subtracted from the total amount of lead in the experiment (2100 mg Pb^{2+}/L * 0.05 L = 105 mg Pb^{2+}) to yield the area above each breakthrough curve (the amount of lead captured within each MOF).

IV. Supplemental Figures

IIIa. PXRD Data

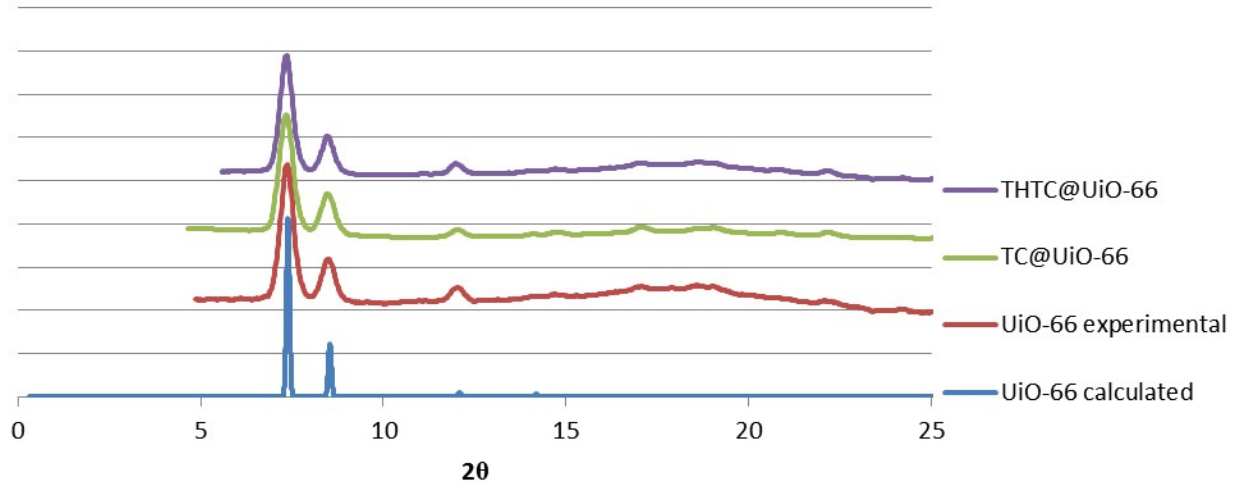

Figure S3. UiO-66 Before and After Exposure to TC and THTC.

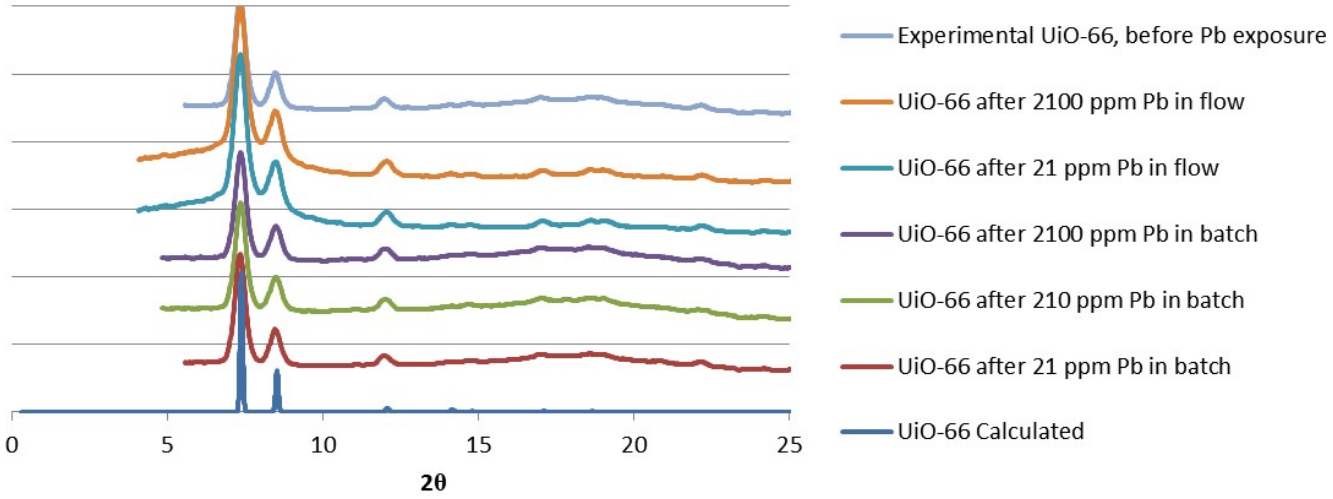

Figure S4. UiO-66 after Batch and Flow Experiments.

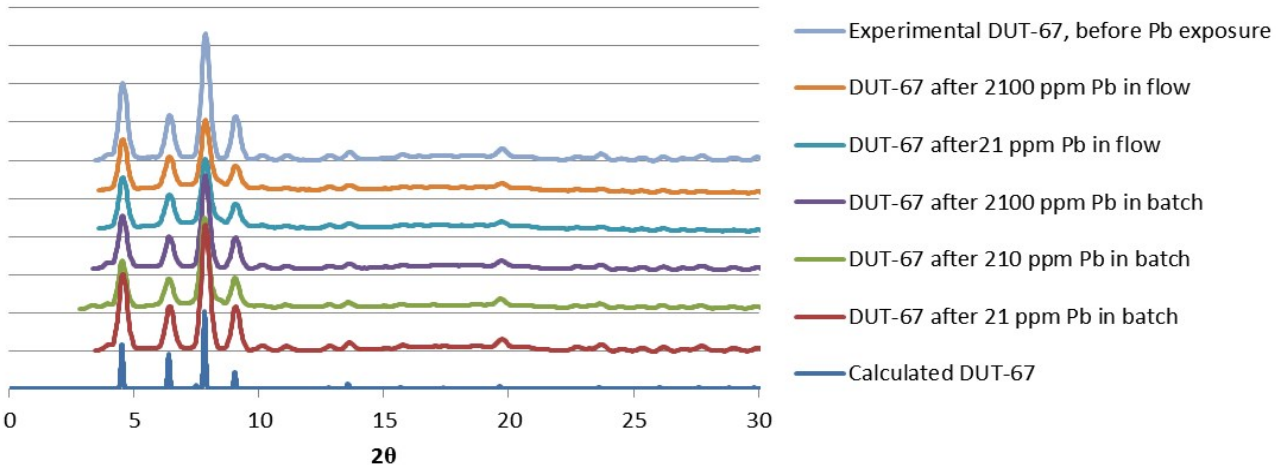

Figure S5. DUT-67 after Batch and Flow Experiments.

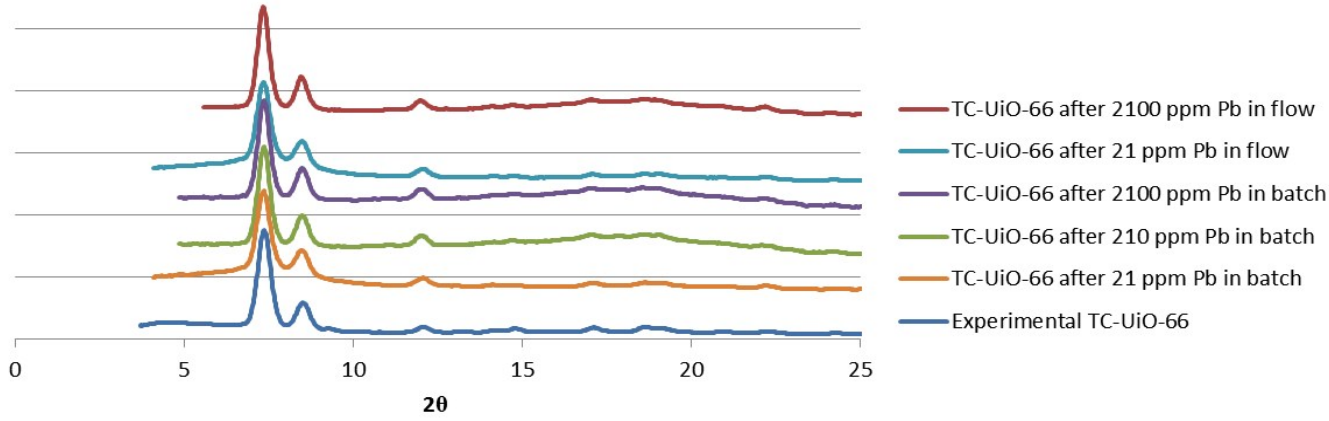

Figure S6. TC@UiO-66 after Batch and Flow Experiments.

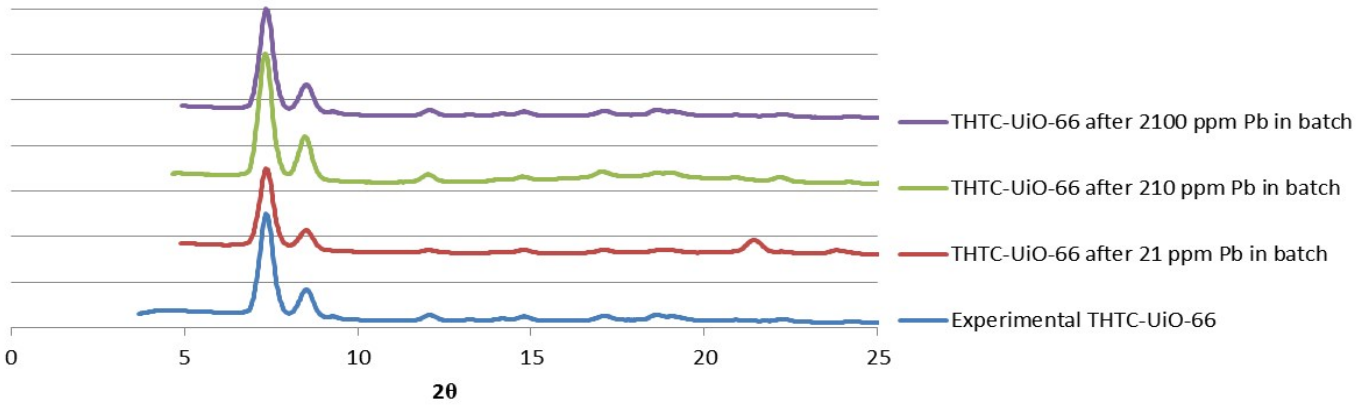

Figure S7. THTC@UiO-66 after Batch Experiments.

IIIb. NMR Data

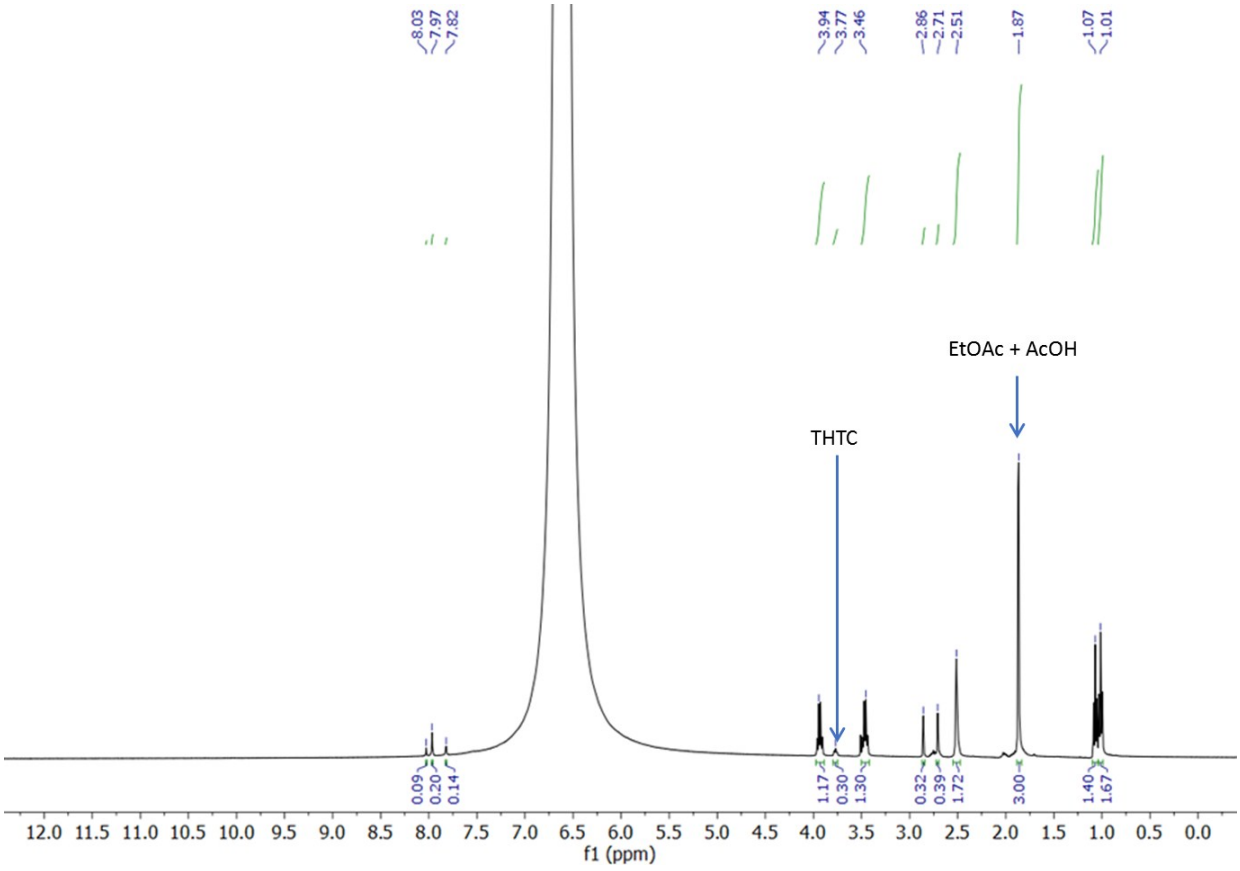

Figure S8. THTC@UiO-66 Proton NMR

Comment regarding NMR Calculations:

A known molar amount of ethyl acetate was added (0.0512 mmol).

Weight of digested sample was 0.0054 g MOF.

To calculate the amount of heterocycle (THTC or TC) / g MOF, the following formula was used:

$$\frac{(\,heterocyle\ integral\ value\ from\ NMR) * (mmol\ EtOAc)}{(\,g\ MOF\ sample)} = \frac{mmol\ heterocycle}{g\ MOF}$$

Sample Calculation for **Figure S6**:

$$\frac{(0.30\,) * (0.0512)}{0.0054\ g\ MOF} = \frac{3.1\ mmol\ THTC}{g\ MOF}$$

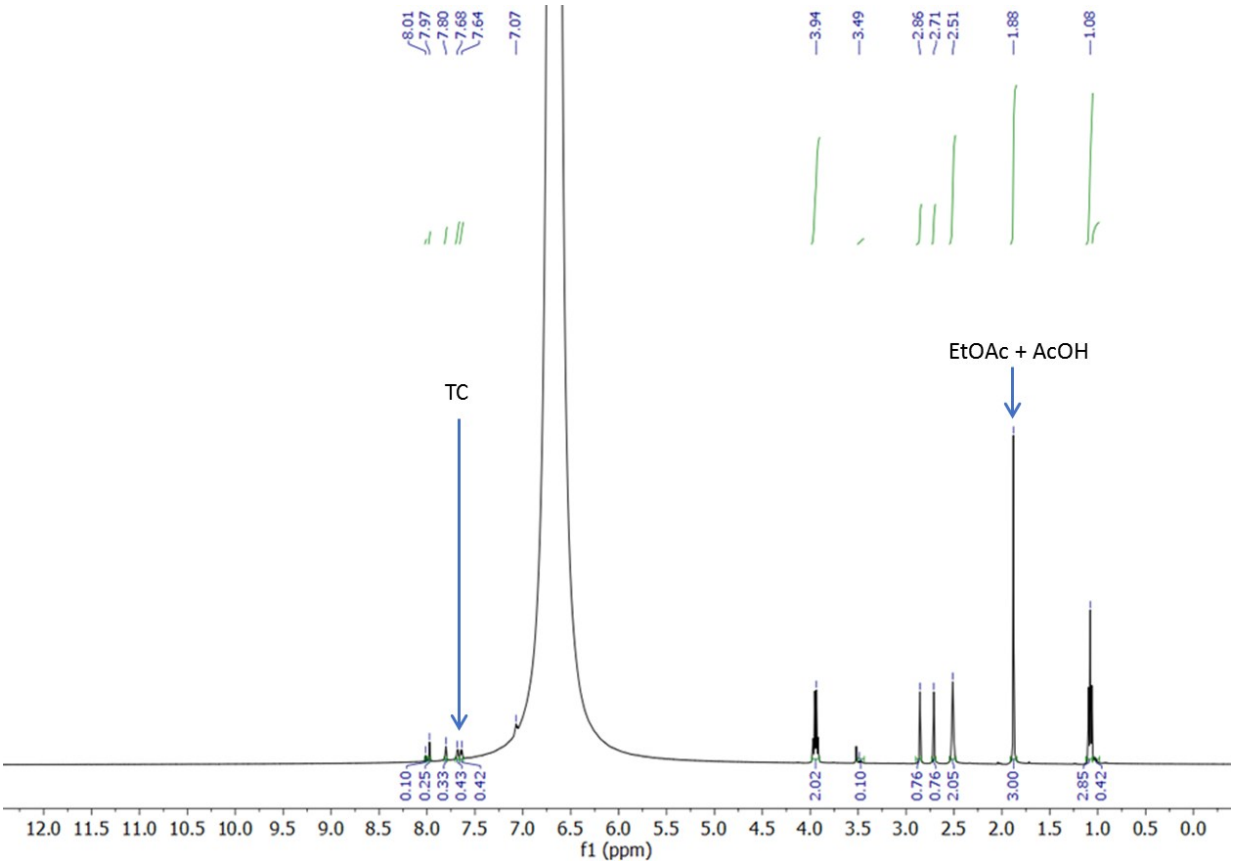

Figure S9. TC@UiO-66 Proton NMR

Sample Calculation for **Figure S7**:

$$\frac{(0.43\ ) * (0.0512)}{0.0052\ g\ MOF} = \frac{5.2\ mmol\ THTC}{g\ MOF}$$

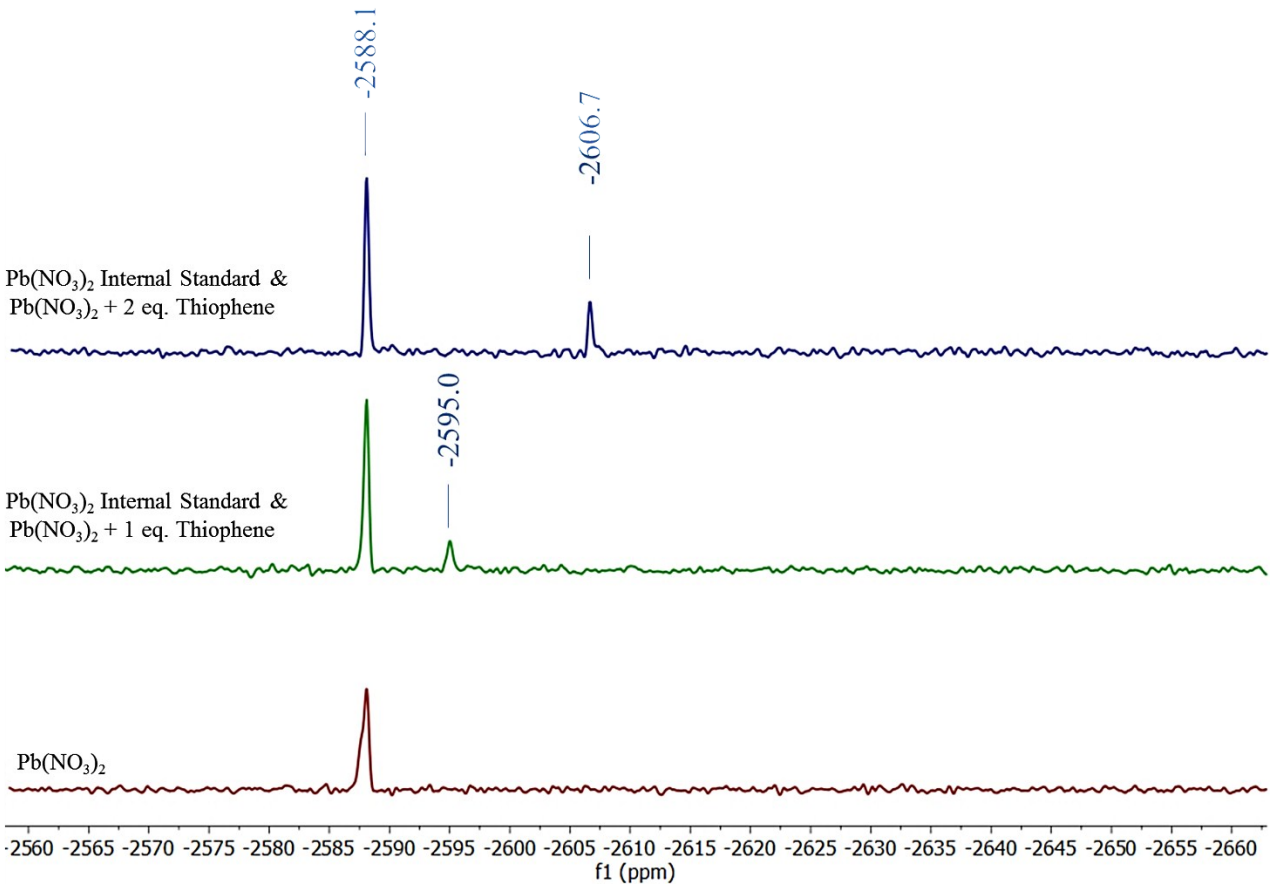

Figure S10. Increasing Equivalents of Thiophene to Lead(II) Nitrate

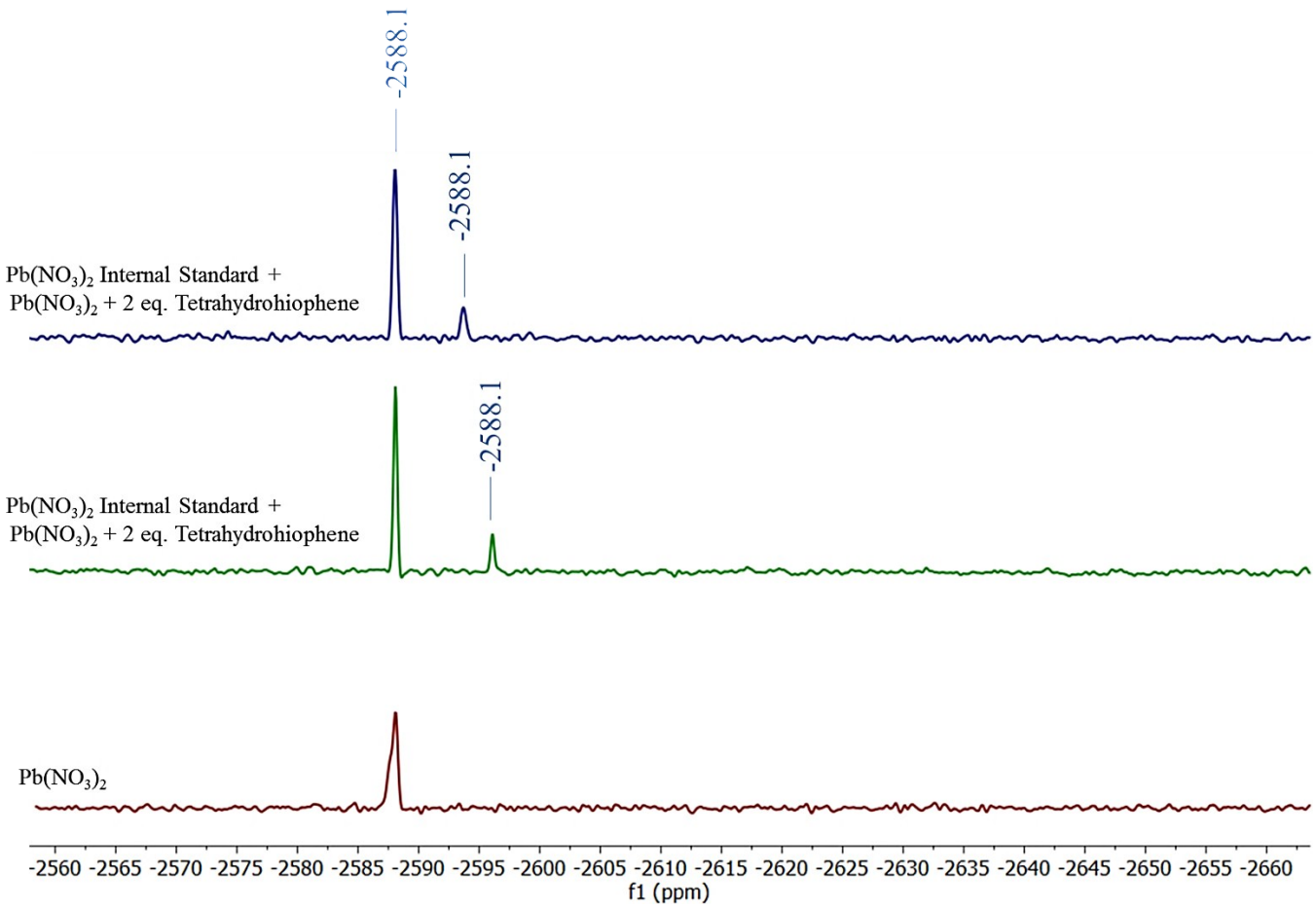

Figure S11. Increasing Equivalents of Tetrahydrothiophene to Lead(II) Nitrate

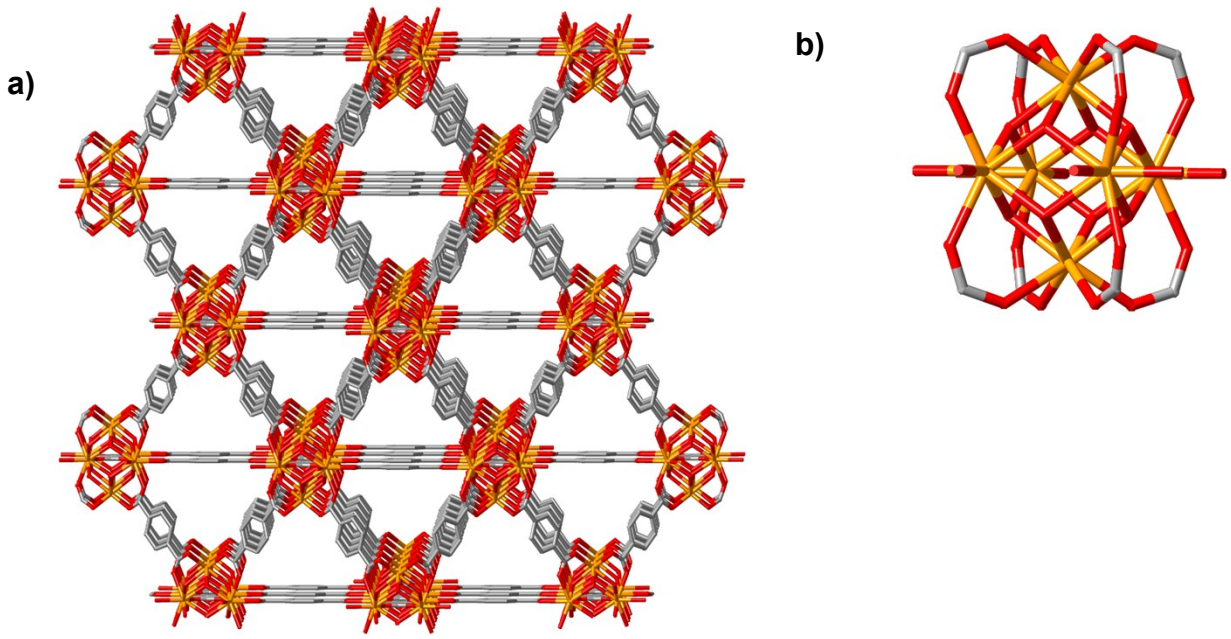

Figure S12: a) structure of UiO-66; b) structure of node of UiO-66. Gray = C, Orange = Zr, Red = O.

	2100 ppm $Pb(NO_3)_{2\,(aq)}$		21 ppm $Pb(NO_3)_{2\,(aq)}$	
	mg Pb adsorbed/ g MOF	**mmol Pb/ mmol thiophene**	**mg Pb adsorbed/ g MOF**	**mmol Pb/ mmol thiophene**
DUT-67	98.5	0.17	0.96	0.0017
TC@UiO-66	8.66	0.00806		
UiO-66	26.8			

Table S1: Table of flow adsorption data. All values are an average of at least 3 experiments.

(1) Kaskel, S.; Bon, V.; Senkovska, I.; Baburin, I. A.; *Cryst. Growth. Des*. **2013**, 13(3): 1231-1237
(2) Lillerud, K. P., Cavka, J. H., Jakobsen, S., Olsbye, U., Guillou, N., Lamberti, C., Bordiga, S.; *J. Am. Chem. Soc.* **2008**. 130, 13850-13851