## **Supporting Information**

Scalable, Room Temperature, and Water-based Synthesis of Functionalized Zirconium-based Metal-Organic Frameworks for Toxic Chemical Removal

Zhijie Chen,<sup>a</sup> Xingjie Wang,<sup>a</sup> Hyunho Noh,<sup>a</sup> Ghada Ayoub,<sup>a</sup> Gregory W. Peterson,<sup>b</sup> Cassandra T. Buru,<sup>a</sup> Timur Islamoglu<sup>a</sup> and Omar K. Farha<sup>\*a</sup>

<sup>a</sup>Department of Chemistry and International Institute of Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States <sup>b</sup>Edgewood Chemical Biological Center, U.S. Army Research, Development, and Engineering Command, 5183 Blackhawk Road, Aberdeen Proving Ground, Maryland 21010, United States

### **Table of Contents**

1. Materials and general procedures	2
2. Synthesis of MOFs	3
3. SEM images	9
4. TGA Plots	10
5. Diffuse Reflectance for Infrared Fourier Transform Spectroscopy (DRIFTS)	11
6. Low-Pressure Gas Adsorption Measurements	12
7. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra	16
8. NMR spectra for the hydrolysis of VX	18
9. References	19

## 1. Materials and general procedures

All reagents were obtained from commercial sources and used without further purification, unless otherwise noted. Zirconium (IV) oxynitrate hydrate (99%) was purchased from Sigma-Aldrich.

**X-ray Diffraction Analyses.** Powder X-ray diffraction (PXRD) of MOFs were measured at room temperature on a STOE-STADIMP powder diffractometer equipped with an asymmetric curved Germanium monochromator (CuK $\alpha$ 1 radiation,  $\lambda = 1.54056$  Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). The line focused Cu X-ray tube was operated at 40 kV and 40 mA. The activated powder was sandwiched between two Kapton foils and measured in transmission geometry in a rotating holder. Intensity data from 1 to 30 degrees two theta were collected over a period of 6 min. The instrument was calibrated against a NIST Silicon standard (640d) prior to the measurement.

 $N_2$  Sorption Measurements.  $N_2$  adsorption and desorption isotherms on activated materials were measured on a Micromeritics Tristar (Micromeritics, Norcross, GA) instrument at 77 K. In general, about 30-50 mg of sample was used in each measurement.

**Diffuse Reflectance for Infrared Fourier Transform Spectroscopy (DRIFTS).** DRIFTS spectra were recorded on a Nicolet 6700 FTIR spectrometer equipped with an MCT detector. The detector was cooled with liquid  $N_2$  and the spectra were collected under Ar atmosphere. KBr was utilized as a background spectrum.

**Thermogravimetric analyses (TGA).** TGA was performed on a TGA/DCS 1 system (Mettler-Toledo AG, Schwerzenbach, Switzerland), which runs on a PC with STARe software. Samples were heated from 30 to 600 °C at a rate of 10 °C/min under air with flow rate 20 mL/min.

**Scanning electron micrographs (SEM)** images were taken using a Hitachi SU8030 at the EPIC facility (NUANCE Center-Northwestern University). Samples were activated and coated with OsO4 to ~9 nm thickness in a Denton Desk III TSC Sputter Coater before imaging.

**Magic angle spinning nuclear magnetic resonance spectroscopy**. VX degradation was measured by magic angle spinning nuclear magnetic resonance spectroscopy using a Varian INOVA 400 MB instrument spinning at 2000 Hz. 5 uL of VX were dosed onto 50 mg of MOFs. The peaks were integrated to determine the degradation as a function of time. Samples were pre-equilibrated at 50% RH prior to analysis.

### 2. Synthesis of MOFs

#### Synthesis of UiO-66-(COOH)<sub>2</sub>

- 1) The 32 mg (~0.126 mmol) of linker (1,2,4,5-benzenetetracarboxylic acid) was solubilized in 1.5 mL of water via heating in 100 °C oven for 5-7 min.
- 2) Separately, 45 mg (~0.195 mmol) of zirconyl nitrate hydrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O) was solubilized in 1.5 mL of water again via sonication.
- 3) After the clear solution of ligand cool down to room temperature, the two solutions were combined, followed by an addition of 500  $\mu$ L (~6.53 mmol) of trifluoroacetic acid (TFA).
- 4) The mixture was stirred for 48 h at room temperature.
- 5) The crystalline powders were collected by centrifugation (7000 rpm for 5 min). Assynthesized sample was washed 3 times with DI water and then sequentially washed with 2 times ethanol, and finally immersed in acetone for 2 days, during which time the acetone was replaced 2 times per day. The product was isolated after air dry; yield: 30 mg.

#### Synthesis of UiO-66-F4

- 1) The 30 mg (~0.126 mmol) of linker (tetrafluoroterephthalic acid) was solubilized in 1 mL of water via sonication at room temperature.
- 2) Separately, 45 mg (~0.195 mmol) of zirconyl nitrate hydrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O) was solubilized in 1 mL of water again via sonication.
- 3) The two solutions were combined, followed by an addition of 250  $\mu L$  (~4.37 mmol) of acetic acid
- 4) The mixture was stirred for 40 h at room temperature.
- 5) The crystalline powders were collected by centrifugation (7000 rpm for 5 min). Assynthesized sample was washed 3 times with DI water and then sequentially washed with 2 times ethanol, and finally immersed in acetone for 2 days, during which time the acetone was replaced 2 times per day. The product was got after air dry; yield: 28 mg.

MOFs	Metal Source	Modulator	Water/Modulator (v/v)	Temperature	BET surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>a</sup>	Ref.
UiO-66-(COOH) <sub>2</sub>	ZrCl <sub>4</sub>	-	-	reflux	415	1
UiO-66-(COOH) <sub>2</sub>	Zr(NO <sub>3</sub> ) <sub>4</sub>	AA <sup>b</sup>	3/2	reflux	494	2
UiO-66-(COOH) <sub>2</sub>	$Zr(SO_4)_2$	$H_2SO_4$	40/1	90 °C	250	3
UiO-66-(COOH) <sub>2</sub>	Zr(acac) <sub>4</sub>	AA <sup>b</sup>	3/2 or 1/1 or 3/1	90 °C	538	4
UiO-66-(COOH) <sub>2</sub>	$ZrO(NO_3)_2$	TFA <sup>c</sup>	6/1	RT	890	this work
UiO-66-F4	$ZrO(NO_3)_2$	AA <sup>b</sup>	8/1	RT	690	this work

Table S1. Summary of the water-based syntheses of UiO-66 analogues.

<sup>a</sup> Calculated from experimental N<sub>2</sub> adsorption isotherms at 77 K. <sup>b</sup> AA = acetic acid. <sup>c</sup> TFA = trifluoroacetic acid

### Scale-up syntheses of UiO-66-(COOH)2

The scale-up syntheses of UiO-66-(COOH)<sub>2</sub> were illustrated in the below figure. This reaction is very easy to be scaled up, and four reactions based on the amount of linker (i.e. 320 mg, 1.6 g, 3.2 g, 16 g) were performed depending on the size of the reactor.

Typically, the synthesis of UiO-66-(COOH)<sub>2</sub>-16 g is shown below (2 L bottle).

- 1) The 16 g (~62.96 mmol) of linker (1,2,4,5-benzenetetracarboxylic acid) was solubilized in 750 mL of water via heating in 100 °C oven for 5-7 min.
- 2) Separately 22.5 g (~97.3 mmol) of zirconyl nitrate hydrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O) was solubilized in 750 mL of water again under stirring.
- 3) After the clear solution of ligand cool down to room temperature, two solutions were combined, followed by an addition of 250 mL (~3.26 mol) of TFA.
- 4) The mixture was stirred for 48 h at room temperature.
- 5) The white crystalline powders were collected with multiple times by centrifugation (7000 rpm for 5 min). As-synthesized sample was washed 3 times with DI water and then sequentially washed with 2 times ethanol, and finally immersed in acetone for 2 days, during which time the acetone was replaced 2 times per day. The product was got after air dry; yield:  $\sim 20$  g.





UiO-66-(COOH)<sub>2</sub> 1.6g ligand 250ml bottle UiO-66-(COOH)<sub>2</sub> 16g ligand 2000ml bottle

Fig. S1. Scale-up syntheses of UiO-66-(COOH)<sub>2</sub>.

#### The synthesis of UiO-66-(COOH)2 at different temperatures

The synthesis of UiO-66-(COOH)<sub>2</sub> at different temperature were carried out by heating on the aluminum blocks. The reactions are performed on the same scale based on the 320 mg linker, and Findenser<sup>TM</sup> Super Air Condenser was used to do the experiments under reflux (100 °C).

For the synthesis of UiO-66-(COOH)<sub>2</sub>-under reflux, the synthesis of UiO-66-(COOH)<sub>2</sub>-320mg is shown below (100 ml reactor).

- 1) The 320 mg (~1.26 mmol) of linker (1,2,4,5-benzenetetracarboxylic acid) was solubilized in 15 mL of water via heating in 100 °C oven for 5-7 min.
- 2) Separately, 450 mg (~1.95 mmol) of zirconyl nitrate hydrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·xH<sub>2</sub>O) was solubilized in 15 mL of water again via sonication.
- 3) After the clear solution of ligand cool down to room temperature, two solutions were combined, followed by an addition of 5ml (~65.3 mmol) of TFA.
- 4) The mixture was refluxed for 48 h at 100 °C.
- 5) The white crystalline powders were collected with multiple times by centrifugation (7000 rpm for 5 min). As-synthesized sample was washed 3 times with DI water and then sequentially washed with 2 times ethanol, and finally immersed in acetone for 2 days, during which time the acetone was replaced 2 times per day. The product was got after air dry; yield: 450 mg.

### The synthesis of UiO-66-(COOH)<sub>2</sub> with different amounts of modulators.

The synthesis of UiO-66-(COOH)<sub>2</sub> with different amounts of modulators were carried out at the same scale based on the 320 mg linker at room temperature. Instead of using 5 mL TFA, 5 mL acetic acid, 30 mL acetic acid, and 1 mL TFA were used to perform experiments.



Fig. S2. PXRD patterns of UiO-66-(COOH)<sub>2</sub> from the scale-up syntheses. The scales are based on the linker used for the synthesis.



Fig. S3. PXRD patterns of UiO-66-(COOH) $_2$  from the syntheses based on the different conditions



Fig. S4. PXRD pattern of UiO-66-(COOH)<sub>2</sub> ( $2\theta$  from 1 to  $80^{\circ}$ ).

## 3. SEM images



Fig. S5. SEM images of UiO-66-(COOH)<sub>2</sub> and UiO-66-F<sub>4</sub>.

### 4. TGA Plots



Fig. S6. TGA plots under air flow of UiO-66-(COOH)<sub>2</sub>, UiO-66-NO<sub>2</sub>, and UiO-66-F<sub>4</sub> based on the normalization of  $ZrO_2$  to 100%.

# 5. Diffuse Reflectance for Infrared Fourier Transform Spectroscopy (DRIFTS).



Fig. S7. DRIFTS plots of UiO-66-(COOH)<sub>2</sub> and 1,2,4,5-benzenetetracarboxylic acid (H<sub>2</sub>BTEC).

### 6. Low-Pressure Gas Adsorption Measurements

Activation of UiO-66-NO<sub>2</sub> was performed under vacuum for 12 h on SVP at 120 °C (2 °C/min); Activation of UiO-66-F<sub>4</sub> and UiO-66-(COOH)<sub>2</sub> was performed under vacuum for 14 h on SVP at 30 °C. The pore size distributions of all MOFs in this work are calculated based on the non-local density functional theory (NLDFT) model.



**Fig. S8.** N<sub>2</sub> sorption isotherms at 77 K of UiO-66-(COOH)<sub>2</sub> synthesized at RT (about 298 K) with different scales. The scales are based on the linker used for the synthesis.



**Fig. S9.** N<sub>2</sub> sorption isotherms at 77K of UiO-66-(COOH)<sub>2</sub> synthesized at RT(about 298K), 40 °C, 80 °C, and 100 °C (reflux), respectively.



**Fig. S10.** The non-local density functional theory (NLDFT) pore size distribution of UiO-66-(COOH)<sub>2</sub> synthesized at RT (about 298 K), 40 °C, 80 °C, and 100 °C (reflux), respectively.

Materials	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>a</sup>
UiO-66-(COOH)2-RT	890	0.37
UiO-66-(COOH)2-40 °C	870	0.37
UiO-66-(COOH)2-80 °C	890	0.36
UiO-66-(COOH)2-100 °C	820	0.33

**Table S2.** Summary of  $N_2$  Sorption Data of UiO-66 from water-based synthesis at different temperature.

<sup>a</sup> calculated by single point method at  $P/P_0=0.80$ .

Table S3. Summary of N<sub>2</sub> Sorption Data of UiO-66 from water-based synthesis.

Materials	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> ·g <sup>-1</sup> ) <sup>a</sup>
UiO-66-(COOH) <sub>2</sub>	890	0.37
UiO-66-F <sub>4</sub>	690	0.33

<sup>a</sup> calculated by single point method at  $P/P_0=0.80$ .

## 7. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra



Fig. S11. ATR-FTIR spectrum of UiO-66-(COOH)<sub>2</sub> after breakthrough experiments.



Fig. S12. ATR-FTIR spectrum with zoom-in view of UiO-66-(COOH)<sub>2</sub> after breakthrough experiments.



**Fig. S13.** ATR-FTIR spectrum of UiO-66-(COOH)<sub>2</sub>\_Low Defect (UiO-66-(COOH)<sub>2</sub>-100 °C) after breakthrough experiments.



**Fig. S14.** ATR-FTIR spectrum with zoom-in view of UiO-66-(COOH)<sub>2</sub>\_Low Defect after breakthrough experiments.



# 8. NMR spectra for the hydrolysis of VX

**Fig. S15.** <sup>31</sup>P MAS NMR spectra indicating the progress of hydrolysis of VX to EMPA for UiO-66-F<sub>4</sub> in presence of 50% relative humidity (50% RH).

### 9. References

- 1. Q. Yang, S. Vaesen, F. Ragon, A. D. Wiersum, D. Wu, A. Lago, T. Devic, C. Martineau, F. Taulelle, P. L. Llewellyn, H. Jobic, C. Zhong, C. Serre, G. De Weireld and G. Maurin, *Angew. Chem. Int. Ed.*, 2013, **52**, 10316-10320.
- 2. Z. Hu, Y. Peng, Z. Kang, Y. Qian and D. Zhao, *Inorg. Chem.*, 2015, 54, 4862-4868.
- 3. H. Reinsch, B. Bueken, F. Vermoortele, I. Stassen, A. Lieb, K.-P. Lillerud and D. De Vos, *CrystEngComm*, 2015, **17**, 4070-4074.
- 4. C. Avci-Camur, J. Perez-Carvajal, I. Imaz and D. Maspoch, ACS Sustain Chem Eng., 2018, 6, 14554-14560.