

## Supporting Information

### **Tuning the Lewis Acidity of Metal-Organic Frameworks for Enhanced Catalysis**

Venkata Swaroopa Datta Devulapalli<sup>a</sup>; MéliSSandre Richard<sup>a</sup>; Tian-Yi Luo<sup>b</sup>; Mattheus L. De Souza<sup>b</sup>, Nathaniel. L Rosi<sup>b</sup>; Eric Borguet <sup>\*a</sup>

<sup>a</sup>Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States of America

<sup>b</sup>Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States of America

\*Eric Borguet (Department of Chemistry, Temple University, 1901 N. 13<sup>th</sup> Street, Philadelphia, PA 19122, [eborguet@temple.edu](mailto:eborguet@temple.edu), phone: 215-204-3164)

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## 1. Synthesis of MOFs

ZrCl<sub>4</sub>, HfCl<sub>4</sub>, 4-Ethylmorpholine were purchased from Sigma. Nanoparticulate Zr(OH)<sub>4</sub> (40 nm, 99.9%) was acquired US Research Nanomaterials Inc. All chemicals were used as received.

Monocrystalline samples of UiO-67-NH<sub>2</sub> and UiO-67 containing discrete crystallites were synthesized based on previously reported procedures<sup>1</sup> by reacting 2-amino-1,1'-biphenyl-4,4'-dicarboxylic acid and 1,1'-biphenyl-4,4'-dicarboxylic acid with zirconium precursors under solvothermal conditions, respectively.

4,4'-Biphenyldicarboxylic acid (98%) was purchased from Acros Organics.

### Synthesis of 2-amino-1,1'-biphenyl-4,4'-dicarboxylic acid

2-Amino-1,1'-biphenyl-4,4'-dicarboxylic acid was synthesized according to literature conditions.<sup>2</sup>

### Synthesis of UiO-67(Zr) Zr<sub>6</sub>(OH)<sub>4</sub>O<sub>4</sub>(C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>)<sub>5.6</sub>(OH)<sub>0.8</sub>(H<sub>2</sub>O)<sub>0.8</sub>

A stock solution of 1,1'-biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-BPDC) (0.04 M) in DMF was first prepared by dissolving BPDC (106.6 mg, 0.44 mmol) in DMF (11 mL) in a loosely capped 20 mL vial. To facilitate the dissolution of H<sub>2</sub>-BPDC, the vial was heated on a ceramic stir plate at ~150°C until clear solution was formed. The solution was cooled to room temperature. To a flame-dried 250 mL round-bottom flask was added ZrCl<sub>4</sub> (93.2 mg, 0.4 mmol), DMF (43 mL) and acetic acid (7 mL). The reaction mixture was sonicated for 1 min before the flask was capped by a septum and heated in oil bath at 120°C for 10 min. 0.04 M BPDC stock solution (10 mL, 0.4 mmol) was then added to the reaction mixture. The mixture was heated in oil bath at 120°C for 5 hours to yield cloudy suspension. After cooling to room temperature, the reaction mixture was centrifuged at 3000 rpm for 15 min to yield white precipitate. The precipitate was washed with fresh DMF (120 mL, 3x). Calc: C, 45.88; H, 2.51; N, 0.00; Found: C, 45.72; H, 2.04; N, 0.00.

### Synthesis of UiO-67-NH<sub>2</sub> Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(C<sub>14</sub>NH<sub>2</sub>O<sub>4</sub>)<sub>5.5</sub>(OH)(H<sub>2</sub>O)

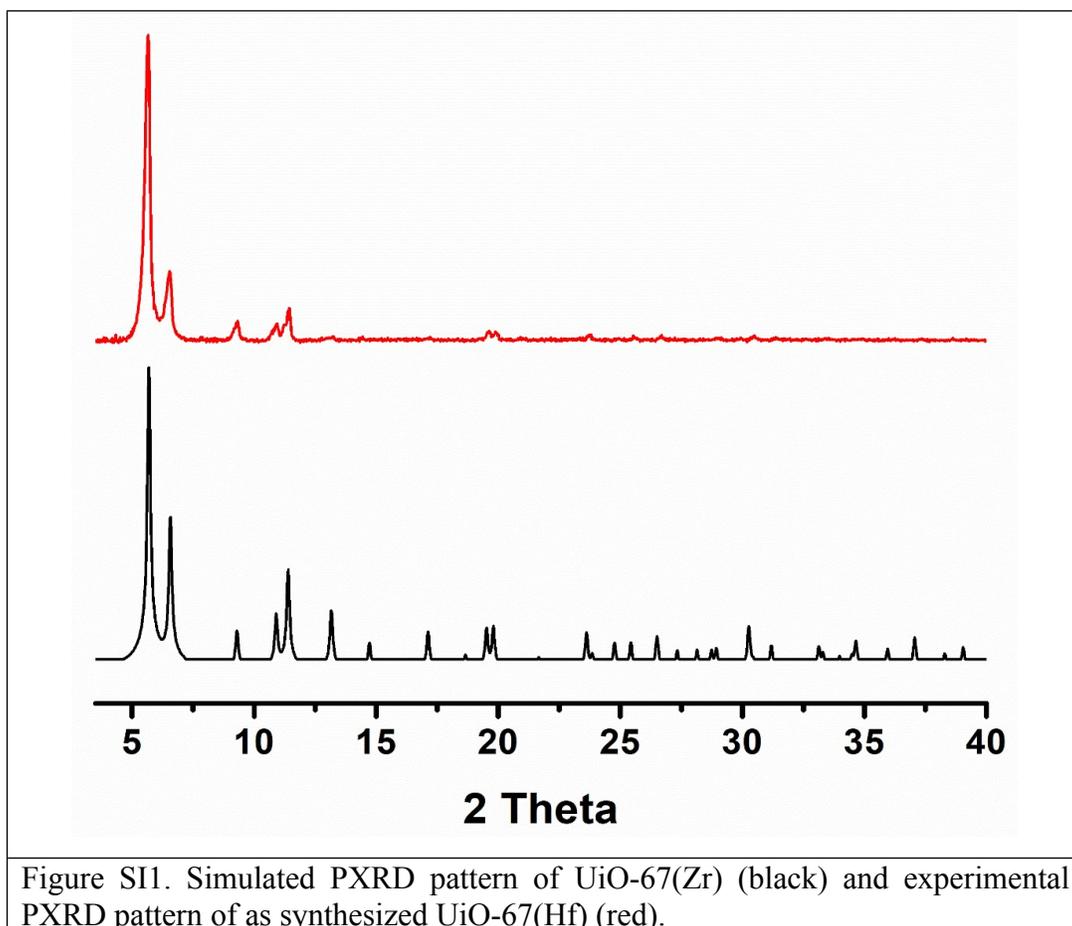
0.4 M solution of Zr(O<sup>n</sup>Pr)<sub>4</sub> in CH<sub>3</sub>COOH was prepared by mixing Zr(O<sup>n</sup>Pr)<sub>4</sub> 70 wt. % in 1-propanol (187.2 mg, 0.04 mmol) with CH<sub>3</sub>COOH (1 mL). To a 40 mL Pyrex vial were added acetic acid (1.2 mL). To a 40 mL Pyrex vial were added in sequence CH<sub>3</sub>COOH (1.2 mL), 0.4 M Zr(*n*-OPr)<sub>4</sub> solution (0.3 mL, 0.12 mmol), DMF (24 mL) and 2-amino-1,1'-biphenyl-4,4'-dicarboxylic acid (H<sub>2</sub>-NH<sub>2</sub>-BPDC) (30.9 mg, 0.12 mmol). After sonication for 1 min, the tightly capped vial was heated at 65°C in an isothermal oven for 16 h to yield a turbid yellow suspension. The mixture was centrifuged at 3000 rpm for 15 min to obtain yellow precipitate. The precipitate was washed with fresh DMF (120 mL, 3x). Calc: C, 43.66; H, 2.69; N, 3.64; Found: C, 43.24; H, 2.32; N, 3.52.

### Synthesis of UiO-67(Hf) $\text{Hf}_6(\text{OH})_4\text{O}_4(\text{C}_{14}\text{H}_8\text{O}_4)_{5.6}(\text{OH})_{0.8}(\text{H}_2\text{O})_{0.8}$

Monocrystalline samples of UiO-67(Hf) containing discrete crystallites were synthesized based on previously reported procedures by reacting 1,1'-biphenyl-4,4'-dicarboxylic acid with hafnium precursors under solvothermal conditions.<sup>3</sup>

## 2. Characterization of MOFs

All characterization data of UiO-67(Zr) and UiO-67-NH<sub>2</sub>(Zr) can be obtained from previous literature.<sup>1</sup>

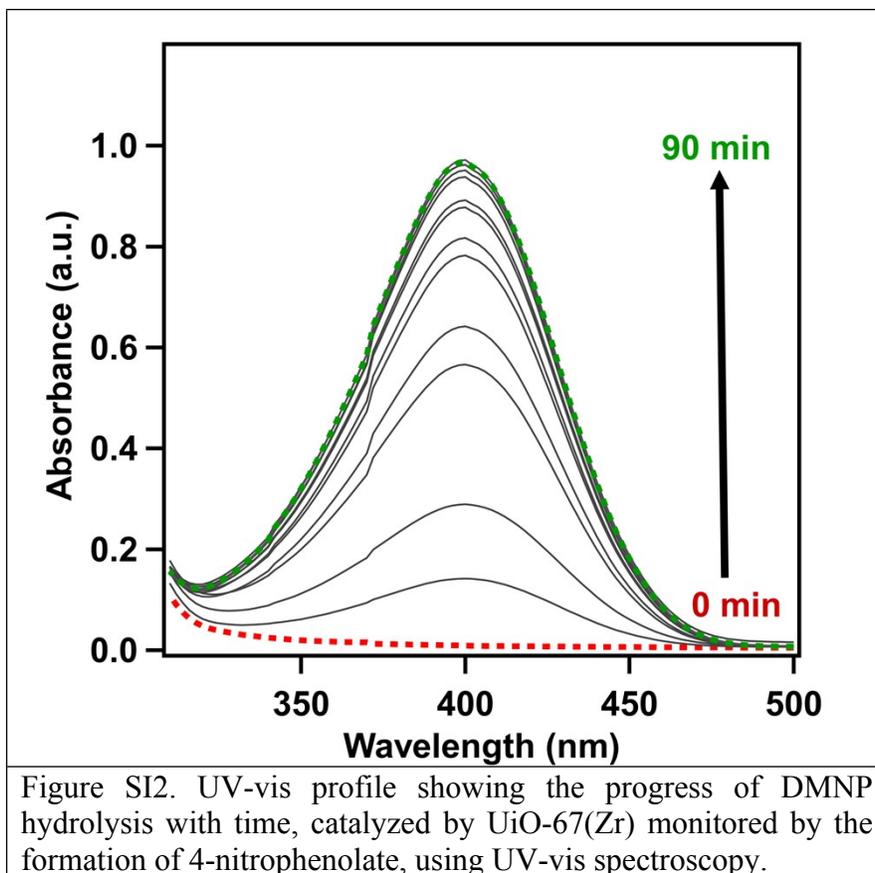


## 3. Procedure for DMNP hydrolysis

Typically, 3 mg of catalyst is added to a 1 mL solution of 0.45 M N-ethyl morpholine (buffer pH = 10) and stirred for 30 min. at ambient temperature. Then 4  $\mu\text{L}$  (21  $\mu\text{mol}$ ) of DMNP is added to the solution.

UV-vis spectra were acquired on a JASCO V630 spectrophotometer (acquisition: 4000 nm/min; interval: 2 nm) at regular intervals of time by diluting 20  $\mu\text{L}$  of the reaction mixture in 10 mL of the buffer solution.

4. Full UV-Vis spectra of DMNP hydrolysis using UiO-67(Zr), ZrCl<sub>4</sub>, Zr(OH)<sub>4</sub>, UiO-67(Hf), HfCl<sub>4</sub>



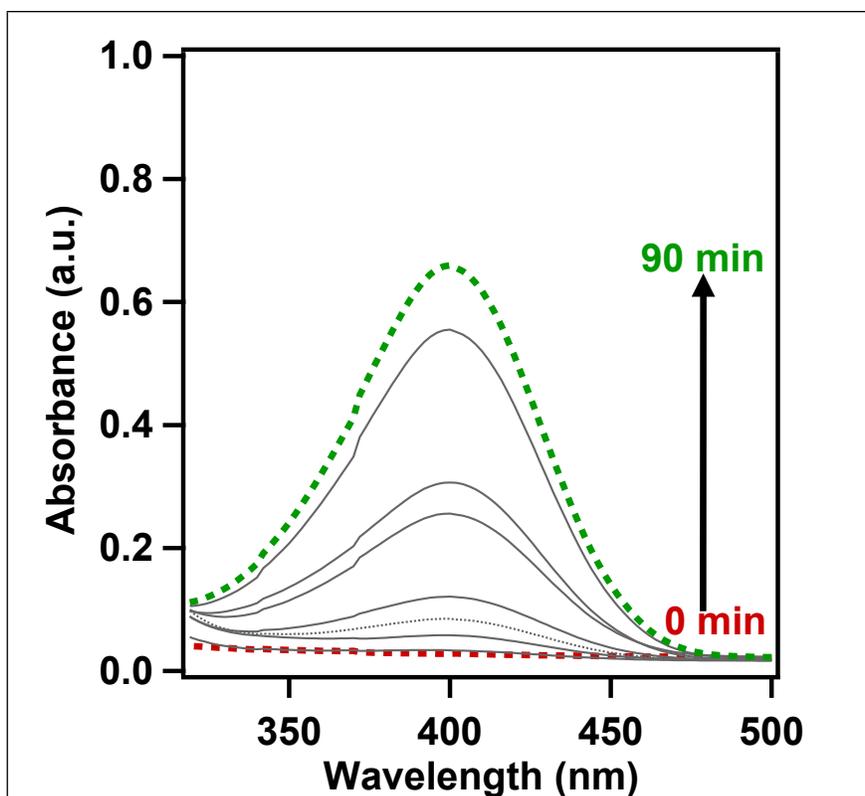


Figure SI3. UV-vis profile showing the progress of DMNP hydrolysis with time, catalyzed by  $ZrCl_4$  monitored by the formation of 4-nitrophenolate, using UV-vis spectroscopy.

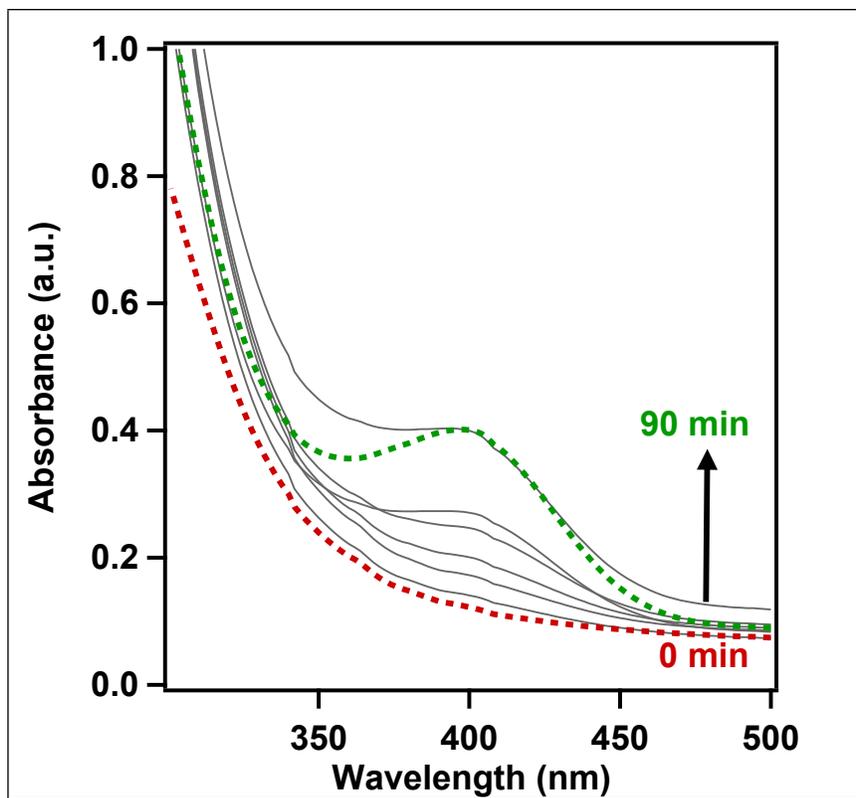


Figure SI4. UV-vis profile showing the progress of DMNP hydrolysis with time, catalyzed by  $\text{Zr}(\text{OH})_4$  monitored by the formation of 4-nitrophenolate, using UV-vis spectroscopy. The shape of the non-zero background suggests scattering by particles of dimension on the order of the wavelength of the light.

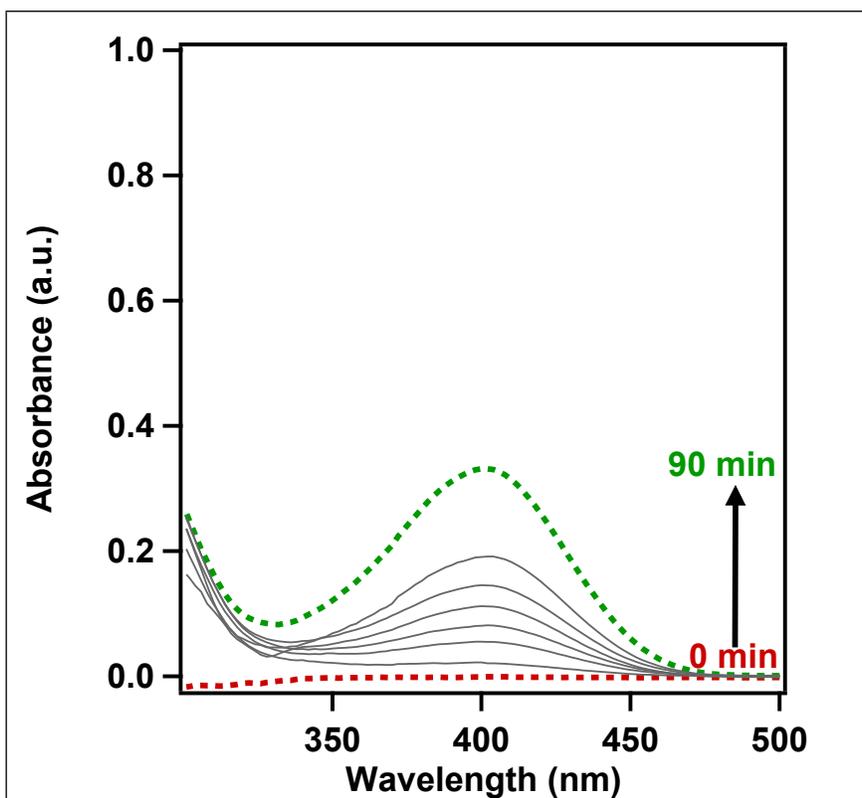
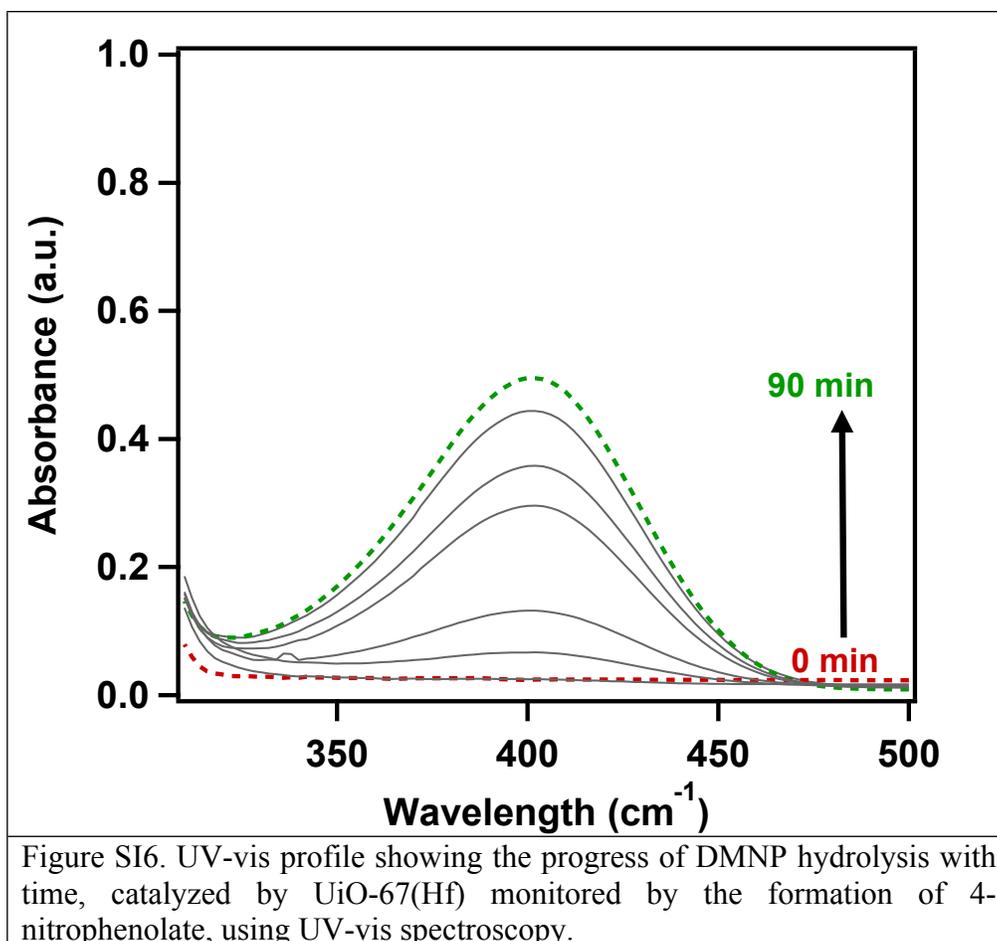
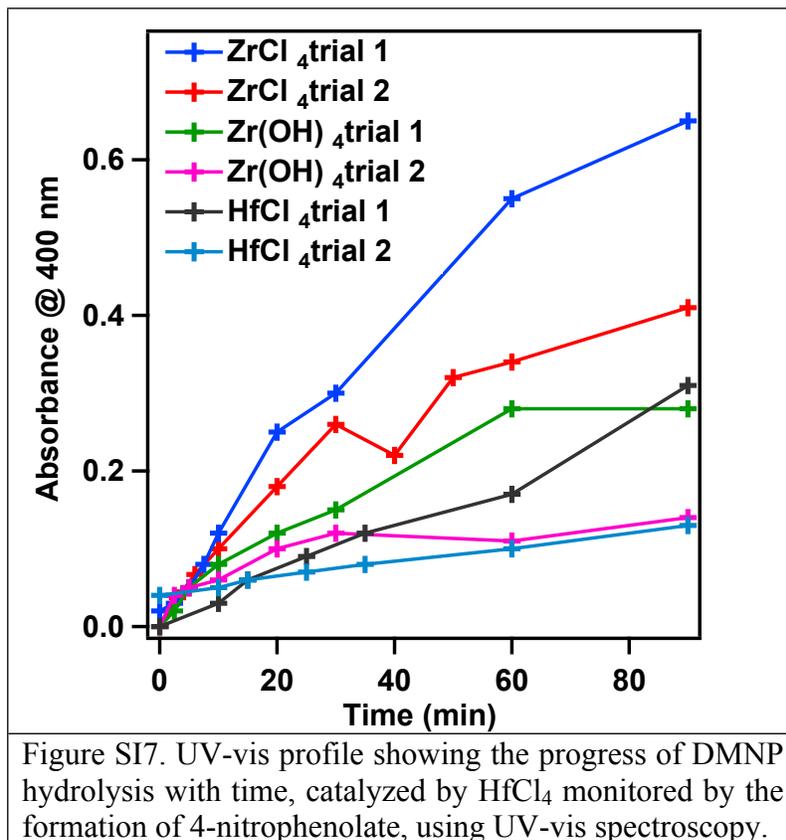


Figure SI5. UV-vis profile showing the progress of DMNP hydrolysis with time, catalyzed by  $\text{HfCl}_4$  monitored by the formation of 4-nitrophenolate, using UV-vis spectroscopy.



## 5. Comparison of $ZrCl_4$ , $HfCl_4$ and $Zr(OH)_4$ in DMNP hydrolysis



## 6. Spectra correction procedure:

As initial UV-vis spectra of some materials displayed a non-zero background due to scattering, spectra were corrected by subtracting the absorbance at 400 nm (4-nitrophenolate formation) from the absorbance value at 500 nm.

**Table S11. Kinetics of DMNP Hydrolysis using UiO-67 MOFs and their precursors**

Catalyst	t1/2 (min)	%Conversion of DMNP after 60 min
UiO-67(Zr)	10	>90
UiO-67-NH <sub>2</sub> (Zr)	10	~85
UiO-67(Hf)	>90	35
ZrCl <sub>4</sub>	50	65
HfCl <sub>4</sub>	>90	20
Zr(OH) <sub>4</sub>	>90	25

## References

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2. Liu, C.; Luo, T. Y.; Feura, E. S.; Zhang, C.; Rosi, N. L., Orthogonal Ternary Functionalization of a Mesoporous Metal - Organic Framework via Sequential Postsynthetic Ligand Exchange. *Journal of the American Chemical Society* **2015**, *137* (33), 10508-10511.
3. Luo, T. Y.; Liu, C.; Gan, X. Y.; Muldoon, P. F.; Diemler, N. A.; Millstone, J. E.; Rosi, N. L., Multivariate Stratified Metal-Organic Frameworks: Diversification Using Domain Building Blocks. *Journal of the American Chemical Society* **2019**, *141* (5), 2161-2168.