

Room Temperature Aqueous Synthesis of UiO-66 Derivatives via Postsynthetic Exchange

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SUPPORTING INFORMATION

Materials Synthesis

All solvents and starting materials were purchased from chemical suppliers and used without further purification (Sigma Aldrich, Alfa Aesar, EMD, and TCI).

MOF Syntheses

UiO-66-F₄. This MOF was synthesized using a previously reported method (*CrystEngComm* **2019**, *21*, 2409-2415). In a 100 mL Erlenmeyer flask, zirconium (IV) oxynitrate hydrate ($\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) (1.62 g, 7.02 mmol) was dissolved in 36 mL of DI H₂O via sonication. In a separate 100 mL Erlenmeyer flask, tetrafluoroterephthalic acid (1.08 g, 4.54 mmol) was dissolved in 36 mL of DI H₂O via sonication. The two solutions were mixed together and stirred for 40 h at room temperature. The crystalline powder was collected by centrifugation (8500 rpm for 10 min). The crystalline powder was washed 3×40 mL of DI H₂O and subsequently with 2×40 mL of ethanol and immersed in acetone for 2 d. Fresh acetone was exchanged every 24 h. The powder was isolated and dried in a vacuum oven at room temperature overnight.

UiO-66 PSE Synthesis. Terephthalic acid (1.65 g, 9.93 mmol) was dissolved in 50 mL of 4% KOH solution (0.2 mM). The solution was then neutralized to pH = 7 using 1M HCl. 4 mL (0.8 mmol) of terephthalic acid solution was added to 256 mg (0.8 mmol ligand) of UiO-66-F₄. The mixture was sonicated for 5 min and allowed to sit at room temperature for 2 h. The crystalline powder was collected by centrifugation (8000 rpm for 10 min). The solids were then washed 3×20 mL of H₂O and 3×20 mL of methanol. After washing the solids were immersed in methanol for 3 d, with fresh methanol being exchanged every

24 h.

UiO-66-NH₂ PSE Synthesis. 2-Aminoterephthalic acid (1.80 g, 9.93 mmol) was dissolved in 50 mL of 4% KOH solution (0.2 mM). The solution was then neutralized to pH = 7 using 1M HCl. 4 mL (0.8 mmol) of 2-aminoterephthalic acid solution was added to 256 mg (0.8 mmol ligand) of UiO-66-F₄. The mixture was sonicated for 5 min and allowed to sit at room temperature for 2 h. The crystalline powder was collected by centrifugation (8000 rpm for 10 min). The solids were then washed 3×20 mL of H₂O and 3×20 mL of methanol. After washing the solids were immersed in methanol for 3 d, with fresh methanol being exchanged every 24 h.

UiO-66-Br PSE Synthesis. 2-Bromoterephthalic acid (2.43 g, 9.93 mmol) was dissolved in 50mL of 4% KOH solution (0.2 mmol). The solution was then neutralized to pH = 7 using 1M HCl. 4 mL (0.8 mmol) of 2-bromoterephthalic acid solution was added to 256 mg (0.8 mmol ligand) of UiO-66-F₄. The mixture was sonicated for 5 min and allowed to sit at room temperature for 2 h. The crystalline powder was collected by centrifugation (8000 rpm for 10 min). The solids were then washed 3×20 mL of H₂O and 3×20 mL of methanol. After washing the solids were immersed in methanol for 3 d, with fresh methanol being exchanged every 24 h.

UiO-66-I PSE Synthesis. 2-Iodoterephthalic acid (2.90 g, 9.93 mmol) was dissolved in 50mL of 4% KOH solution (0.2 mM). The solution was then neutralized to pH = 7 using 1M HCl. 4 mL (0.8 mmol) of 2-iodoterephthalic acid solution was added to 256 mg (0.8

mmol ligand) of UiO-66-F₄. The mixture was sonicated for 5 min and allowed to sit at room temperature for 2 h. The crystalline powder was collected by centrifugation (8000 rpm for 10 min). The solids were then washed 3×20 mL of H₂O and 3×20 mL of methanol. After washing the solids were immersed in methanol for 3 d, with fresh methanol being exchanged every 24 h.

UiO-66-Naphth PSE Synthesis. Naphthalene terephthalic acid (2.15 g, 9.93 mmol) was dissolved in 50mL of 4% KOH solution (0.2 mM). The solution was then neutralized to pH = 7 using 1M HCl. 4 mL (0.8 mmol) of naphthalene terephthalic acid solution was added to 256 mg (0.8 mmol ligand) of UiO-66-F₄. The mixture was sonicated for 5 min and allowed to sit at room temperature for 2 h. The crystalline powder was collected by centrifugation (8000 rpm for 10 min). The solids were then washed 3×20 mL of H₂O and 3×20 mL of methanol. After washing the solids were immersed in methanol for 3 d, with fresh methanol being exchanged every 24 h.

Table S1. Ligand percentages of MOFs synthesized through postsynthetic exchange (PSE) of UiO-66-F₄.

MOF	% F ₄ -bdc ²⁻ linker after PSE	% R-bdc ²⁻ linker after PSE
UiO-66-F ₄	100%	0%
UiO-66-PSE	7 ± 2%	93 ± 2%
UiO-66-NH ₂ -PSE	4 ± 2%	96 ± 2%
UiO-66-Br-PSE	10 ± 2%	90 ± 2%
UiO-66-I-PSE	19 ± 2%	81 ± 2%
UiO-66-Naphth-PSE	24 ± 2%	76 ± 2%

Characterization Methods

Powder X-ray Diffraction (PXRD). PXRD data was collected at room temperature on a Bruker D8 Advance diffractometer running at 40 kV, 40 mA for Cu K α ($\lambda = 1.5418 \text{ \AA}$), with a scan speed of 0.5 sec/step, a step size of 0.01° in 2θ , and a 2θ range of $3\text{-}50^\circ$ at room temperature.

Scanning Electron Microscopy (SEM). MOFs were placed on conductive carbon tape on an aluminum sample holder and coated using an iridium-sputter coating for 8 s. A FEI Quanta FEG 250 microscope was used for acquiring images using a 5 kV energy source with a spot size of 3 under high vacuum at a working distance of 10 mm.

Nuclear Magnetic Resonance.

NMR experiments were carried out on a JOEL ECA 500 MHz spectrometer equipped with a Jeol 2 channel inverse-detect $^1\text{H}/^{19}\text{F}$ probe. MOFs were digested for NMR analysis by immersion of $\sim 5\text{-}10$ mg MOF in 500 μL DMSO- d_6 with 5 μL HF (48% in water). Samples were kept in this acidic solution at room temperature until the MOF was fully dissolved. In each NMR experiment was included a coaxial tube containing a reference sample of 40 μmol of trifluorotoluene in 100 μL deuterated DMSO. The parameters used for each NMR nuclei are included in Table S2.

Table S2. NMR parameters used to analyze digested MOF samples.

Parameter	¹H experiment	¹⁹F experiment
Gain	36	50
Sweep Center	5 ppm	-100 ppm
Sweep Width	15 ppm	150 ppm
X-pts	32768	262144
Scan Number	128	128
Acquisition time	4.367 s	3.713 s
Acquisition delay	5 s	5 s

N₂ Gas Sorption Analysis: Samples for analysis were evacuated in a vacuum oven overnight at room temperature prior to analysis. ~50 mg of sample was then transferred to pre-weighed sample tubes and degassed at 105 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. After degassing, the sample tubes were re-weighed to obtain a consistent mass for the samples. Sorption data and BET surface area (m²/g) measurements were collected at 77 K with N₂ on a Micromeritics ASAP 2020 Adsorption Analyzer using volumetric technique.

Catalysis Experiments. In this study, DMNP hydrolysis was measured using a modified version of a previously reported procedure (*Chem. Commun.* **2018**, 54, 5768-5771). All catalytic monitoring was carried out using a BioTek Synergy H4 plate reader using single wavelength absorbance mode. 20 and 40 mM of *N*-ethylmorpholine buffer was prepared from deionized water adjusted to pH = 8.0. A plot of absorbance of *p*-nitrophenol at varying concentrations was measured yielding a calibration curve with a slope of 3.48

Abs/mM (*Chem. Commun.* **2018**, *54*, 5768-5771). MOF samples were prepared by weighing 6 mg of MOF powder and diluting this powder in 10 mL of deionized water. These solutions were rigorously sonicated and vortexed (>3× of each) and diluted in half with 40 mM buffer solution yielding 300 µg/mL MOF in 20 mM buffer solution. Dimethyl *p*-nitrophenylphosphate (DMNP) hydrolysis assays with MOF powders were carried out in Olympus Plastics clear, flat-bottom 96-well plates. Each well was prepared with 100 µL total volume containing: 95 µL MOF suspension in buffer and 5 µL substrate (25 mM DMNP in MeOH; 1.25 mM total concentration; 0.125 µmol). Upon the addition of substrate using a multi-channel pipette, hydrolysis was monitored by the change in absorbance ($\lambda_{\text{max}} = 407 \text{ nm}$) over 15 min at 24 °C with 3 sec shaking of the plate every 10 sec. The absorbance was monitored from the 30 to 360 sec time period, as previously reported in (*Chem. Commun.* **2019**, *55*, 53481-3484).

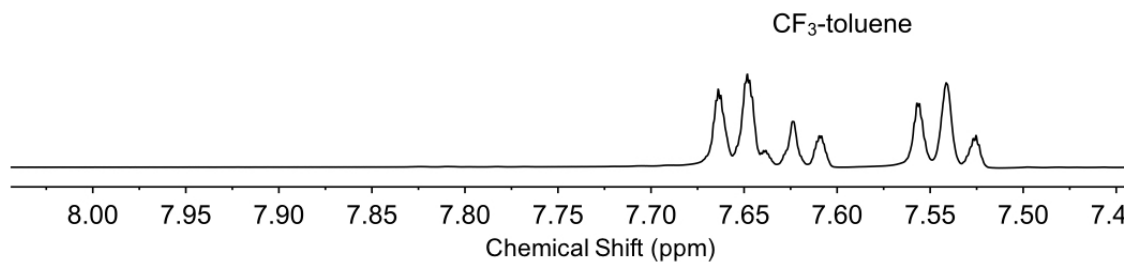
Table S3. Corrected hydrolysis calculation to account for increased mass of MOFs used in this study MOF materials.

MOF	Molar Mass of MOF (g/mol)	Mole ratio to UiO-66 Standard	Experimental Hydrolysis Rate^a (<i>k</i>, mM/sec)	Molar Mass Corrected Hydrolysis Rate (<i>k</i>, mM/sec)
UiO-66-F₄	2070	0.80	24.2	30.3
UiO-66-PSE	1662	1.00	50.6	50.6
UiO-66-NH₂- PSE	1752	0.94	76.9	81.8

^a 6 mg of MOF used in each experiment.

NMR Spectroscopy

a) ^1H NMR



b) ^{19}F NMR

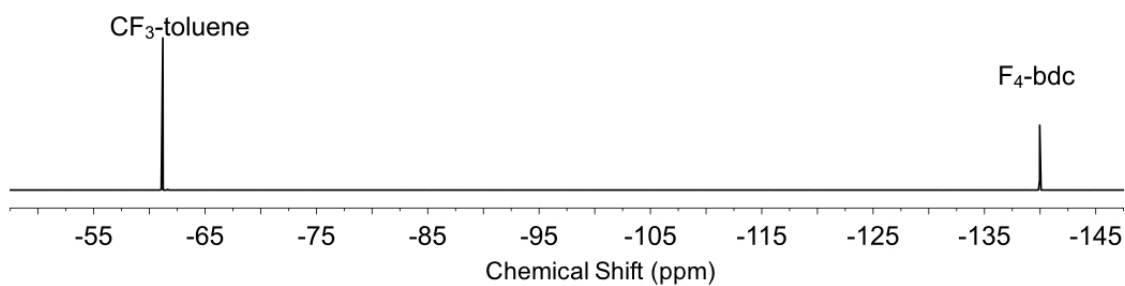
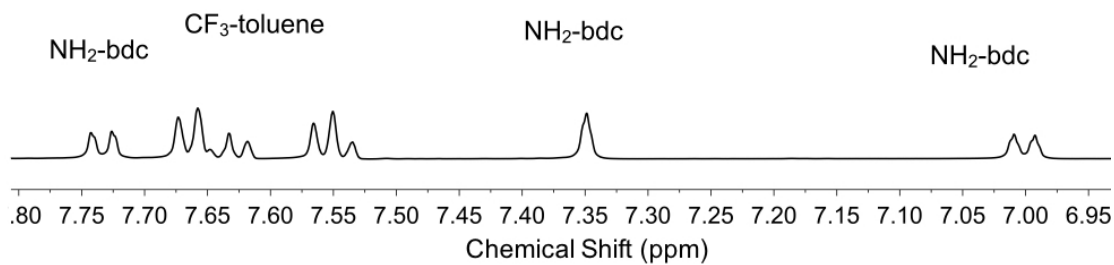


Figure S1. a) ^1H NMR spectra of digested UiO-66-F₄. b) ^{19}F NMR spectra of digested UiO-66-F₄.

a) ^1H NMR



b) ^{19}F NMR

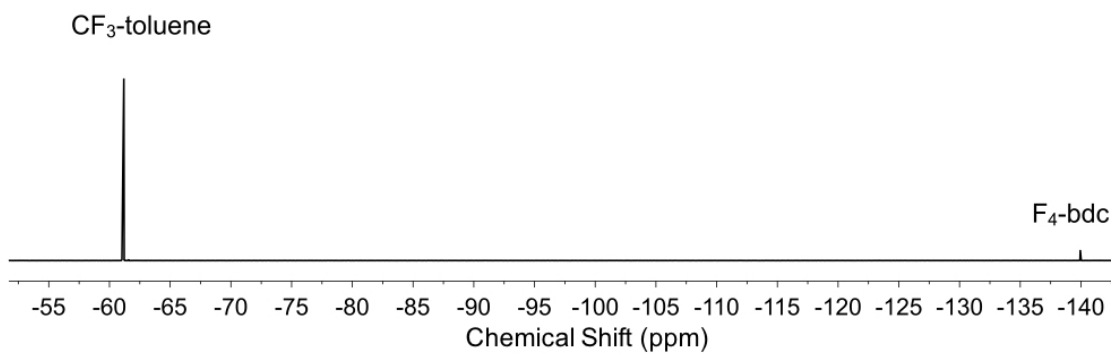
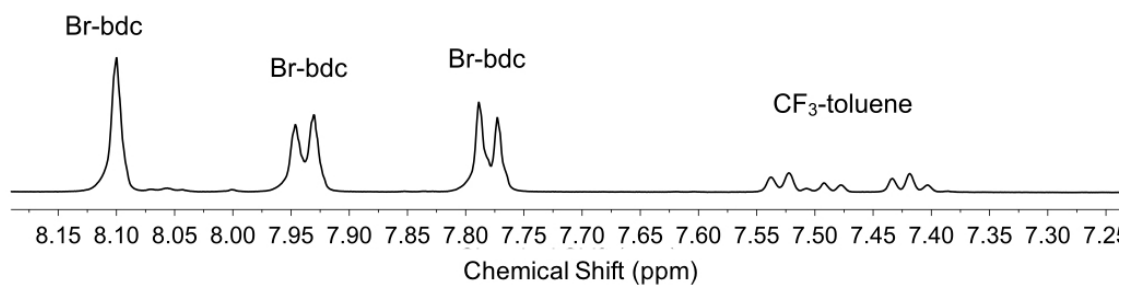


Figure S2. a) ^1H NMR spectra of digested UiO-66- NH_2 -PSE. b) ^{19}F NMR spectra of digested UiO-66- NH_2 -PSE.

a) ^1H NMR



b) ^{19}F NMR

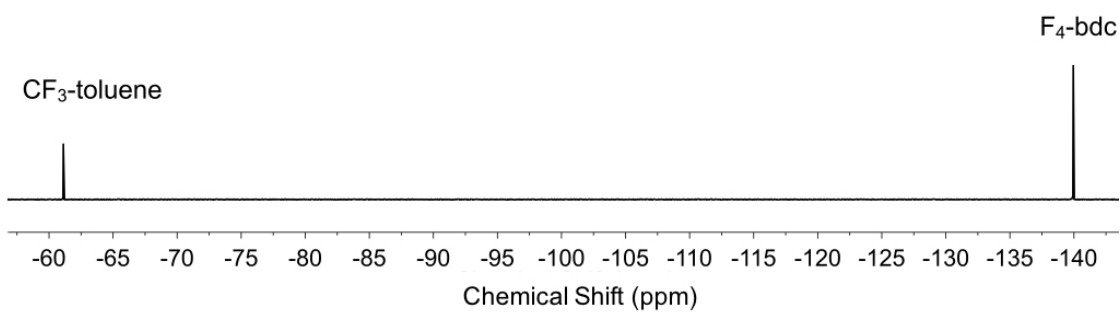
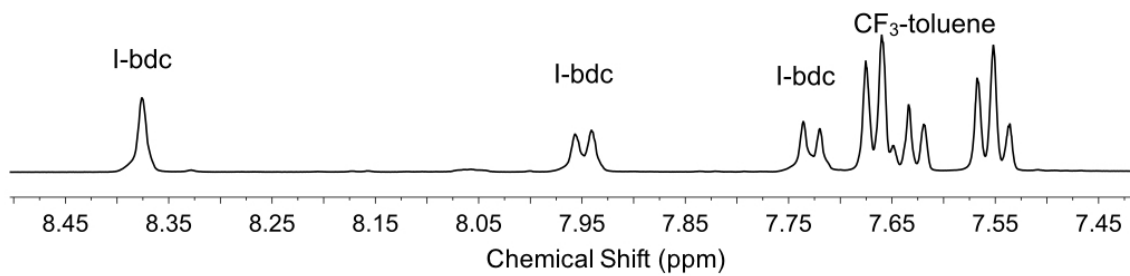


Figure S3. a) ^1H NMR spectra of digested UiO-66-Br-PSE. b) ^{19}F NMR spectra of digested UiO-66-Br-PSE.

a) ^1H NMR



b) ^{19}F NMR

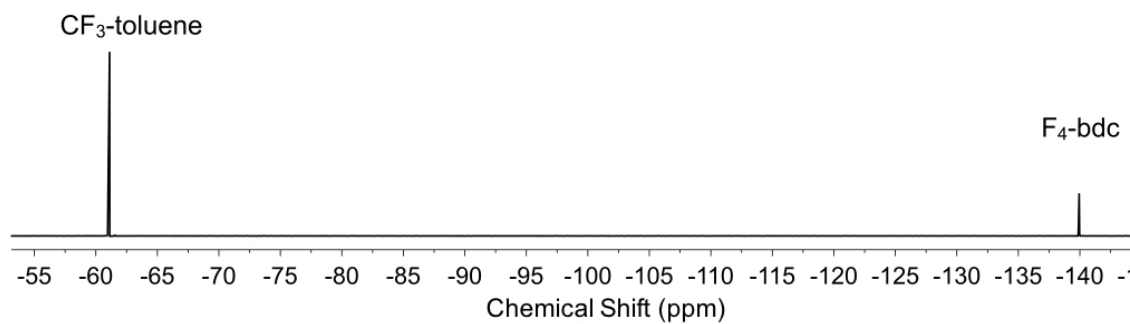
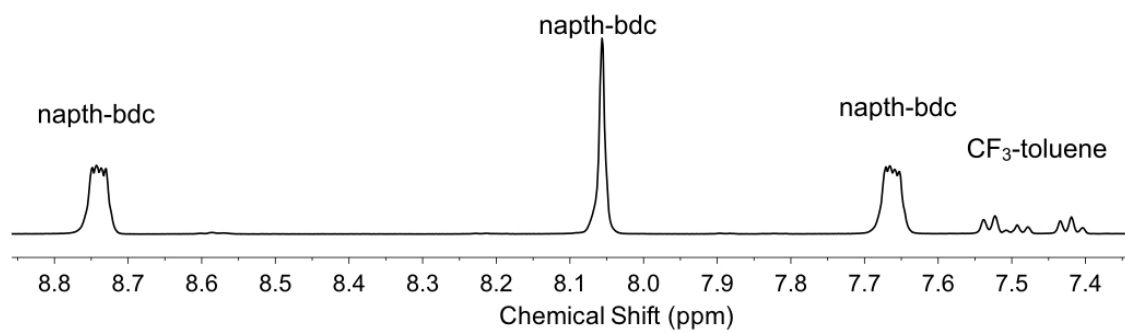


Figure S4. a) ^1H NMR spectra of digested UiO-66-I-PSE. b) ^{19}F NMR spectra of digested UiO-66-I-PSE.

a) ^1H NMR



b) ^{19}F NMR

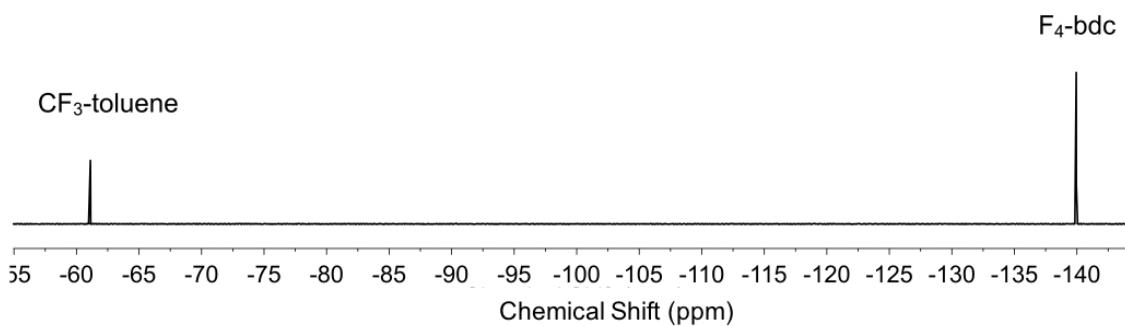


Figure S5. a) ^1H NMR spectra of digested UiO-66-Naph-PSE. b) ^{19}F NMR spectra of digested UiO-66-Naph-PSE.

Scanning Electron Microscopy (SEM)

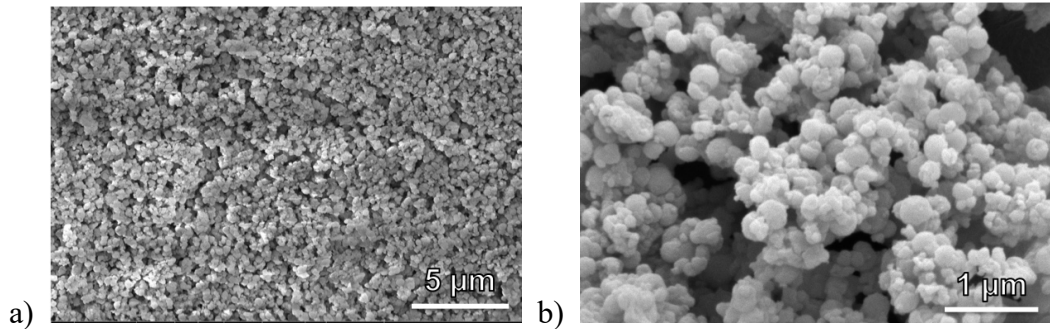


Figure S6. SEM images of UiO-66-F₄.

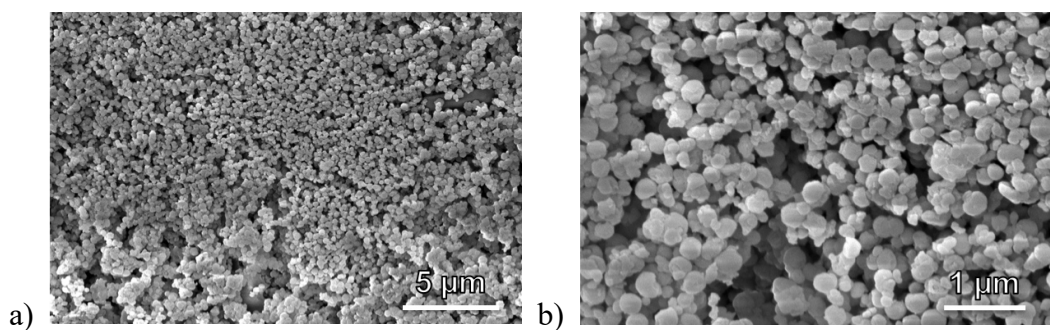


Figure S7. SEM images of UiO-66-PSE.

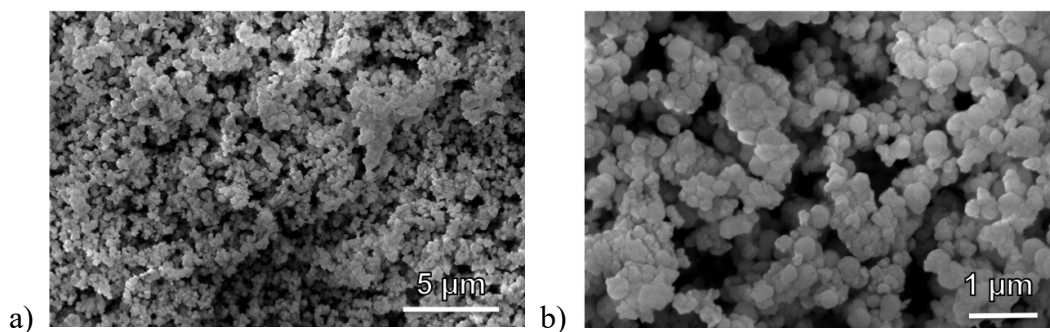


Figure S8. SEM images of UiO-66-NH₂.

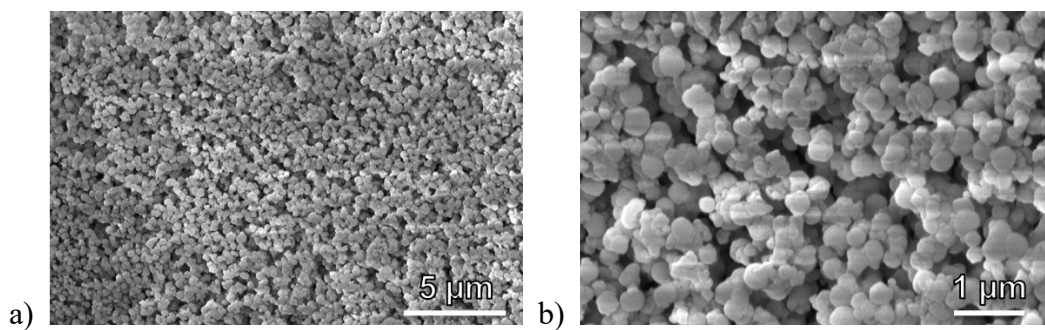


Figure S9. SEM images of UiO-66-Br-PSE.

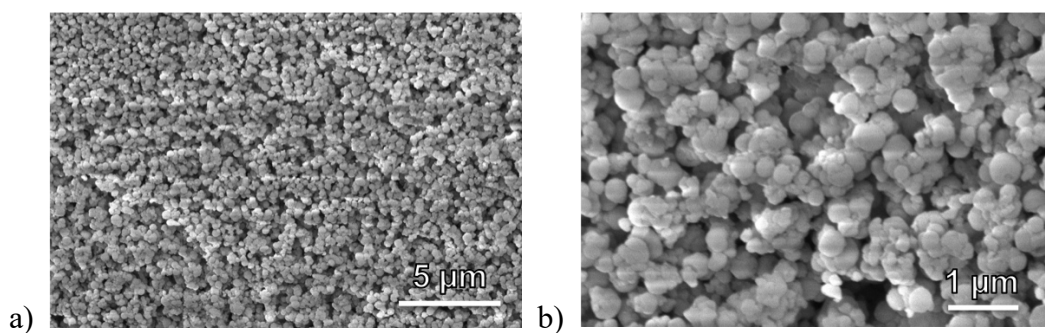


Figure S10. SEM images of UiO-66-I-PSE.

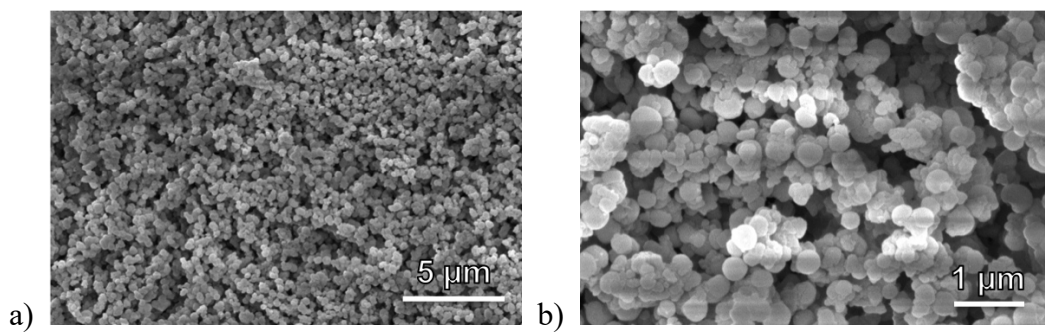


Figure S11. SEM images of UiO-66-Naph-PSE.

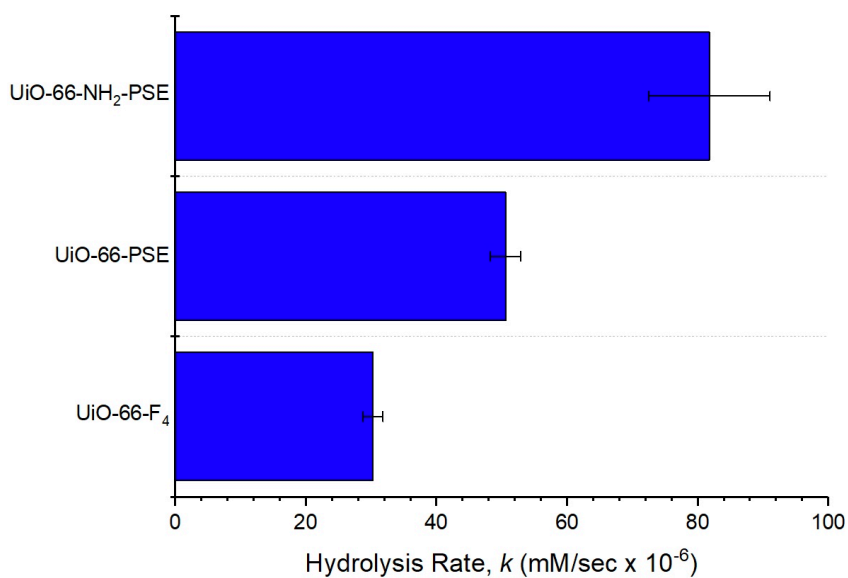
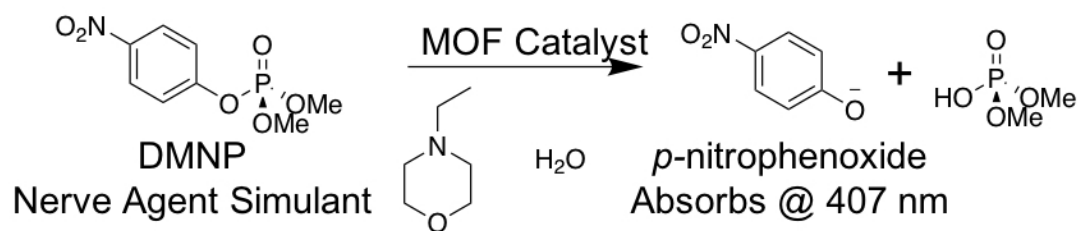


Figure S12. *Top:* DMNP degradation reaction. *Bottom:* Rate of catalytic degradation of DMNP by MOFs measured by UV-visible adsorption (407 nm) at pH = 8 (corrected for differences in the molar mass of each MOF).