

Electronic Supporting Information

Solvent-assisted linker exchange enabled preparation of cerium-based metal-organic frameworks constructed from redox active linkers

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Materials

All reagents were purchased and used as received.

Cerium (IV) ammonium nitrate (98.5%, $(\text{NH}_4)\text{Ce}(\text{NO}_3)_6$, Alfa Aesar), Terephthalic acid (98%, H_2BDC , Aldrich), 2-aminoterephthalic acid (99%, H_2BDC -amino, Acros Organics), 2,5-dihydroxyterephthalic acid (95%, H_2BDC -(OH)₂, Fisher), Fumaric acid ($\geq 99\%$, H_2Fum , Sigma Aldrich), 2-hydroxyterephthalic acid (98%, H_2BDC -OH, TCI), Acetylenedicarboxylic acid (95%, H_2ADC , Aldrich), N-ethylmorpholine (0.45 M, 99%, Fisher), Methanol (Fisher), Ethanol (Fisher), N,N-Dimethylformamide (Fisher)

Instrumentation

Nuclear Magnetic Resonance (NMR). ^1H NMR and ^{13}C NMR spectra of samples were obtained using a Bruker Avance III 500 MHz (IMSERC-Northwestern University). Hydrolysis experiments were carried out on a Bruker Avance III 600 MHz (IMSERC-Northwestern University).

Scanning Electron Microscopy (SEM). SEM images were obtained using a FEI Quanta 650 at the EPIC facility (NUANCE Center-Northwestern University). The samples were coated with 9 nm of osmium using an SPF Osmium Coater (NUANCE Center-Northwestern University) prior to imaging.

Thermogravimetric analysis (TGA). Defects were measured by collecting weight loss data on a Mettler Toledo TGA/DSC 1 Star System instrument. Samples were heated in air from 30°C to 600°C at a rate of 10°C/minute. The sample was held at 600°C for 120 minutes and then cooled back down to 30°C at a rate of -20°C/minute.

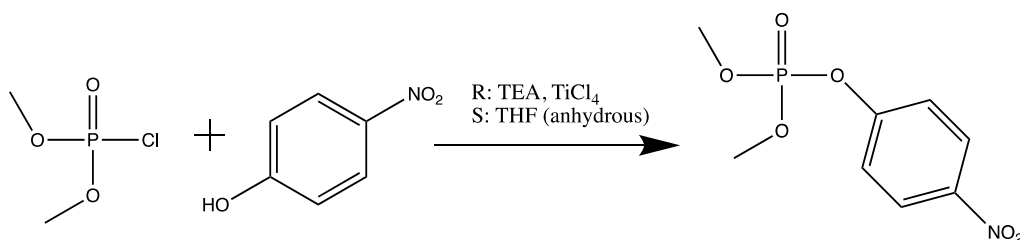
Gas Adsorption. Nitrogen isotherm measurements were obtained on a Micromeritics Tristar II 3020 at 77 K. Samples were activated at temperatures specified in their synthetic procedures on a Micromeritics Smart VacPrep instrument.

Powder X-ray Diffraction (PXRD). PXRD data was obtained using an XRD STADI P with $\text{CuK}\alpha 1$ radiation (IMSERC-Northwestern University).

X-ray Photoelectron Spectroscopy (XPS). XPS data was collected on a Thermo Scientific ESCALAB 250Xi at the KECK facility (NUANCE-Northwestern University). Carbon scans were obtained to account for any charge shift that occurred.

Synthesis of Materials

Ce-UiO-66-BDC. Ce-UiO-66-BDC was synthesized according to published procedures, but with slight alterations.^{1,2} In a 2-dram vial, terephthalic acid (70.8 mg, 0.426 mmol) was dissolved in 2.5 mL of DMF. Following this, 800 μL of a 0.533 M solution of $\text{Ce}(\text{NH}_4)_2(\text{NO}_2)_6$ was added and the mixture was stirred at 800 rpm for 15 minutes at 100 °C on an aluminum heating block. Based on the desired sample amount, the process was repeated in additional vials. The mixture was transferred to collect the sample via centrifugation and washed three times with DMF and then three times with ethanol. For every washing step, the sample was left to soak in the fresh solution for approximately one hour. After the final ethanol wash, the sample was left to soak in ethanol overnight. The solid was collected by centrifugation, dried under vacuum at 85 C for an hour, and then activated at 85 C for 15 hours.



Dimethyl (4-nitrophenyl) phosphate (DMNP). To a magnetically stirring solution of TiCl_4 (50 μL) in 80 mL anhydrous THF in a 250 mL Schlenk flask was added 4-nitrophenol (3.4 g) at room temperature under argon atmosphere. A solution of dimethylchlorophosphate (3.2 g) in 20 mL anhydrous THF was added using a gas tight syringe followed by distilled triethylamine (6.5 mL). The resulting mixture was allowed to stir for 2 hrs. at r.t. The resulting yellow solution was quenched with water and extracted with EtOAc (three times). The combined organics were dried over NaSO_4 , filtered and concentrated under reduced pressure. The resulting slight yellowish oily crude product was purified using silica gel column with eluent of EtOAc:Hexanes (1:1).

Caution: The product is highly toxic.

^1H NMR (500 MHz, CDCl_3 -*d*) δ 8.09 (d, $J = 9.2$ Hz, 2H), 7.25 (d, $J = 9.2$ Hz, 2H), 3.77 (d, $J = 11.5$ Hz, 6H).

^{13}C NMR (126 MHz, CDCl_3 -*d*) δ 155.32, 155.27, 144.65, 125.61, 120.49, 120.45, 77.49, 77.24, 76.98, 55.25, 55.20.

Synthesis of defective UiO-66. UiO-66 was synthesized according to the published procedure, but with slight alterations.³ In a 100 mL Pyrex bottle, ZrCl_4 (140 mg, 0.602 mmol) and 15 mL DMF were added and sonicated until complete dissolution. Terephthalic acid (100 mg, 0.602 mmol) and 15 mL DMF were added to a different vial and sonicated until complete dissolution. The two solutions were mixed and acetic acid (10 mL) was added. The obtained mixture was placed in an oven and heated at 120 $^\circ\text{C}$ for 3 days. After cooling down to room temperature, the resulting solid was centrifuged, and washed with DMF three times followed by three washes of acetone. The solid was dried in vacuum oven at 85 $^\circ\text{C}$ overnight, and then activated at 120 $^\circ\text{C}$ for 12 hours.

Ce-UiO-66-BDC-OH, -(OH)₂ and -NH₂. Calculations for Ce-UiO-66-BDC were performed under the assumption of a defect-free MOF. In a 15 mL centrifuge tube, 32.63 mg of Ce-UiO-66-BDC (0.1 mmol BDC), 72.46 mg of 2-aminoterephthalic acid (0.4 mmol), and 10 mL of methanol were added. The solution was vortexed to ensure that all of the compounds were dispersed in solution. The mixture was sonicated for 5 minutes, checking periodically to ensure no sample had settled to the bottom. If the linker or MOF remained at the bottom of the tube, the sonication was paused, and the sample was vortexed to obtain a homogeneous mixture. The SALE sample was then centrifuged to remove the methanol, and then washed three times with DMF and then three times with ethanol. The sample was soaked in fresh solvent for an hour for each washing step. After the final wash, the sample was soaked in ethanol overnight. The collected sample was then dried under vacuum at 85 $^\circ\text{C}$ for half an hour and activated at 40 $^\circ\text{C}$ for 24 hours. The same conditions were used for all other linkers. The Ce-UiO-66-(OH)₂ could not be activated without causing for the MOF to collapse. The procedure used can be effectively scaled up. This procedure resulted in approximately 80% yield, due to the loss of materials in the washing steps.

Catalysis Studies

Hydrolysis of DMNP. The hydrolysis experiments were performed based on a published procedure,¹ with a few modifications. In a 1.5-dram vial, 1 mL of a 10% D₂O solution (0.9 mL DI water/0.1 mL D₂O) was added. Promptly before starting the experiment, Ce-UiO-66 (1.5 μmol, 2.94 mg) was added and the solution was sonicated for 15 seconds. The buffer N-ethylmorpholine (50 μL, 0.45 M) was added and mixed in. Finally, DMNP (4 μL, 25 μmol) was added and the solution was vigorously shaken for 10 seconds. The mixture was then transferred to an NMR tube and in situ ³¹P NMR spectra was collected every minute for 60 minutes. The conversion was tracked by the integration of the peaks associated with the DMNP versus the dimethyl phosphate product peak.

Scanning Electron Microscopy (SEM)

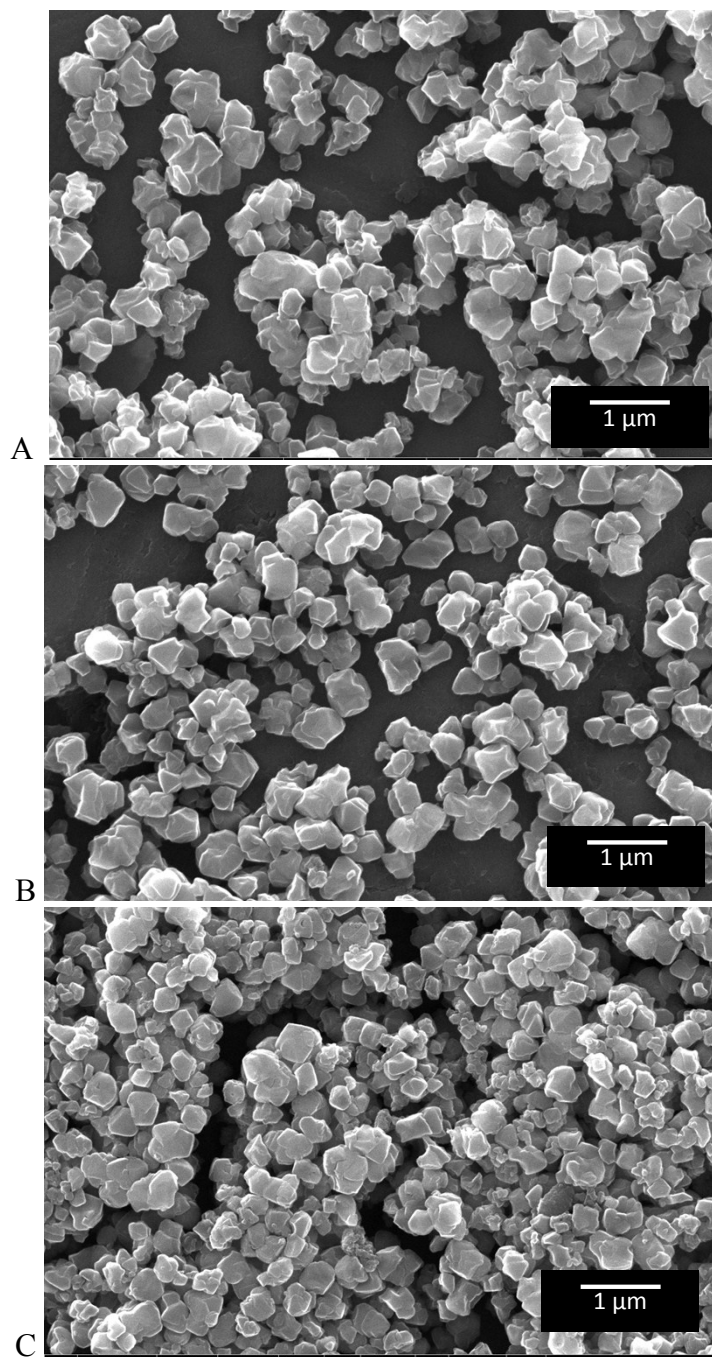


Figure S1. SEM images of A) Ce-UiO-66, B) Ce-UiO-66-NH₂ and C) Ce-UiO-66-(OH)₂

Thermogravimetric Analysis (TGA)

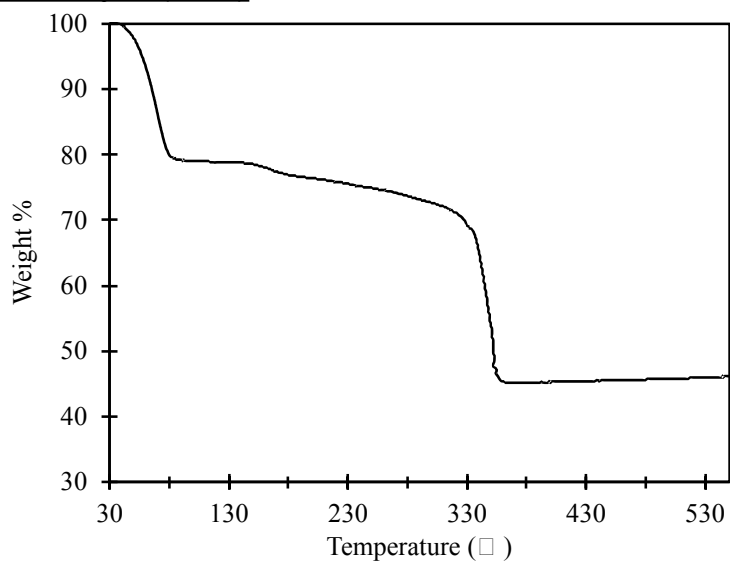


Figure S2. TGA profile of Ce-UiO-66. The weight losses in order of increasing temperature correspond to physisorbed water and ethanol, physisorbed DMF, and finally the loss of the linker.

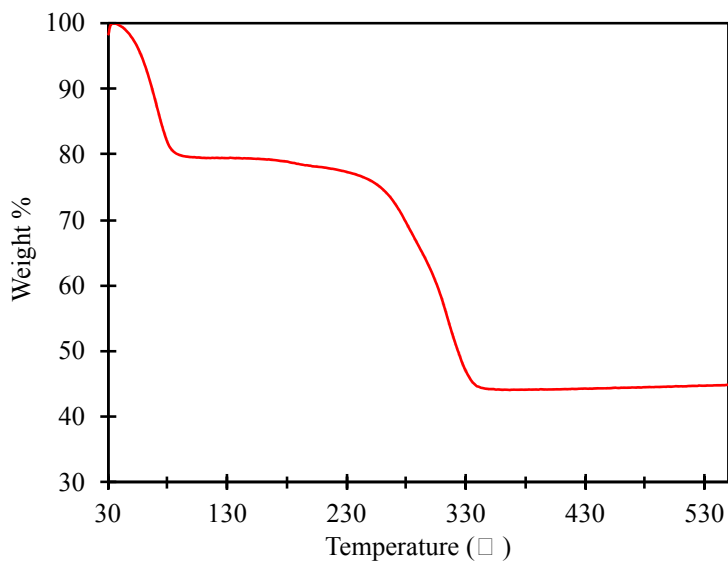


Figure S3. TGA of Ce-UiO-66-NH₂

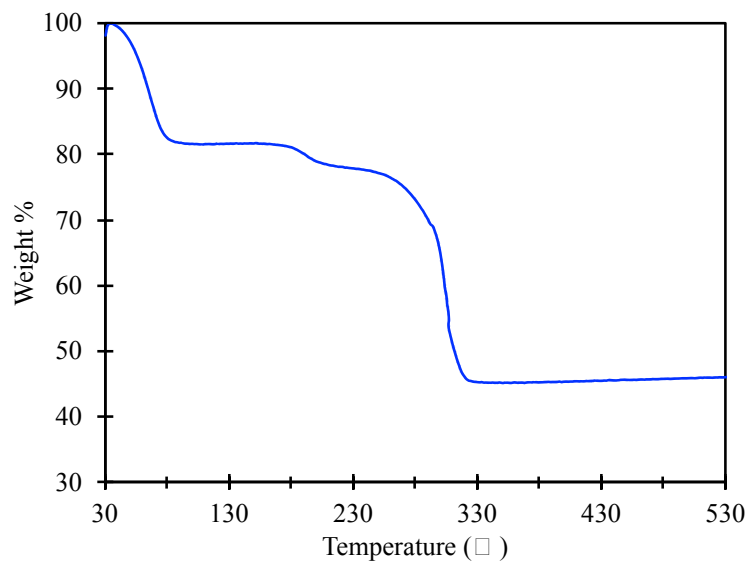


Figure S4. TGA of Ce-UiO-66-OH

NMR Spectra

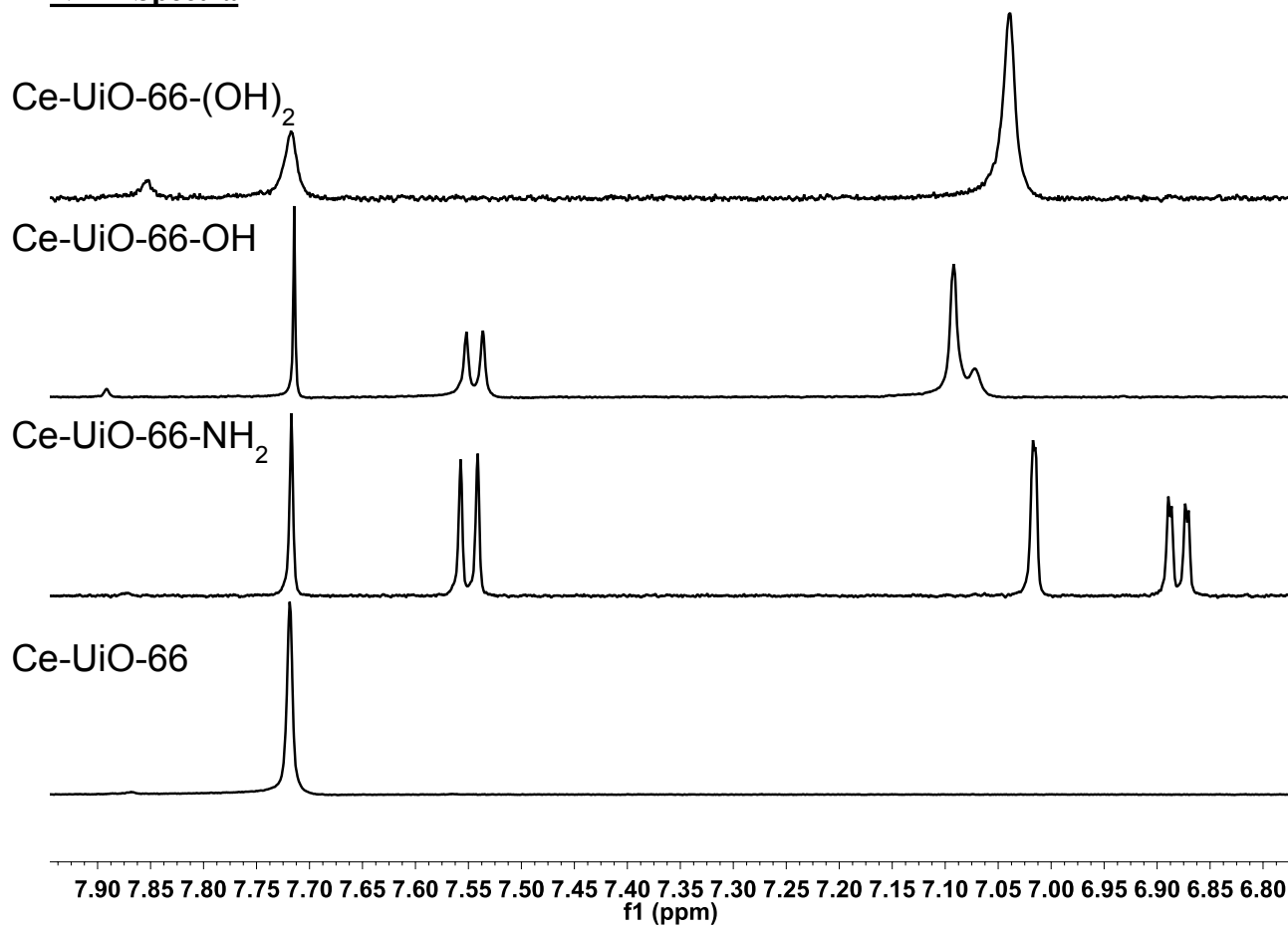


Figure S5. ^1H NMR spectra corresponding from the bottom to the top: as synthesized Ce-UiO-66, Ce-UiO-66-NH₂, Ce-UiO-66-OH, and Ce-UiO-66-(OH)₂

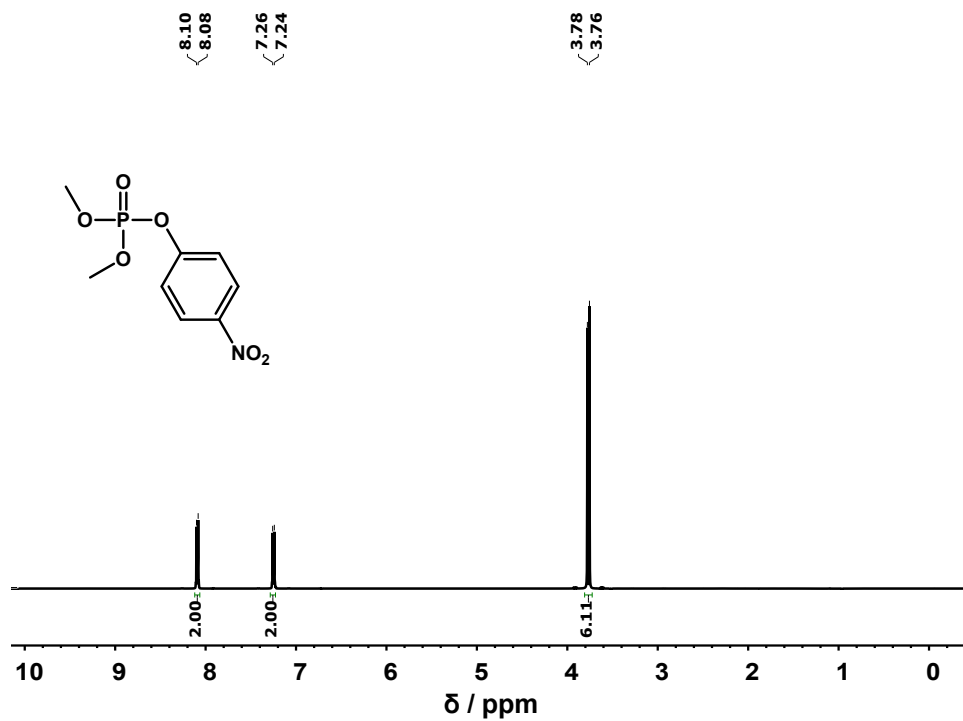


Figure S6. $^1\text{H NMR}$ (126 MHz, CDCl_3-d) spectrum of dimethyl(4-nitrophenyl)phosphate

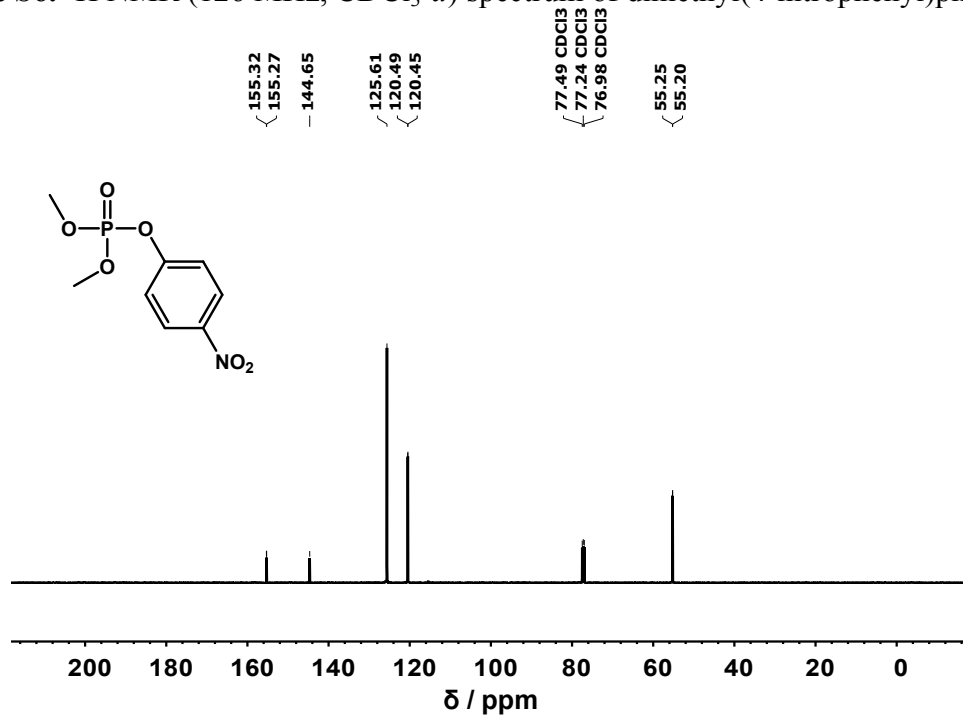


Figure S7. $^{13}\text{C NMR}$ (126 MHz, CDCl_3-d) spectrum of dimethyl(4-nitrophenyl)phosphate

Hydrolysis Kinetics

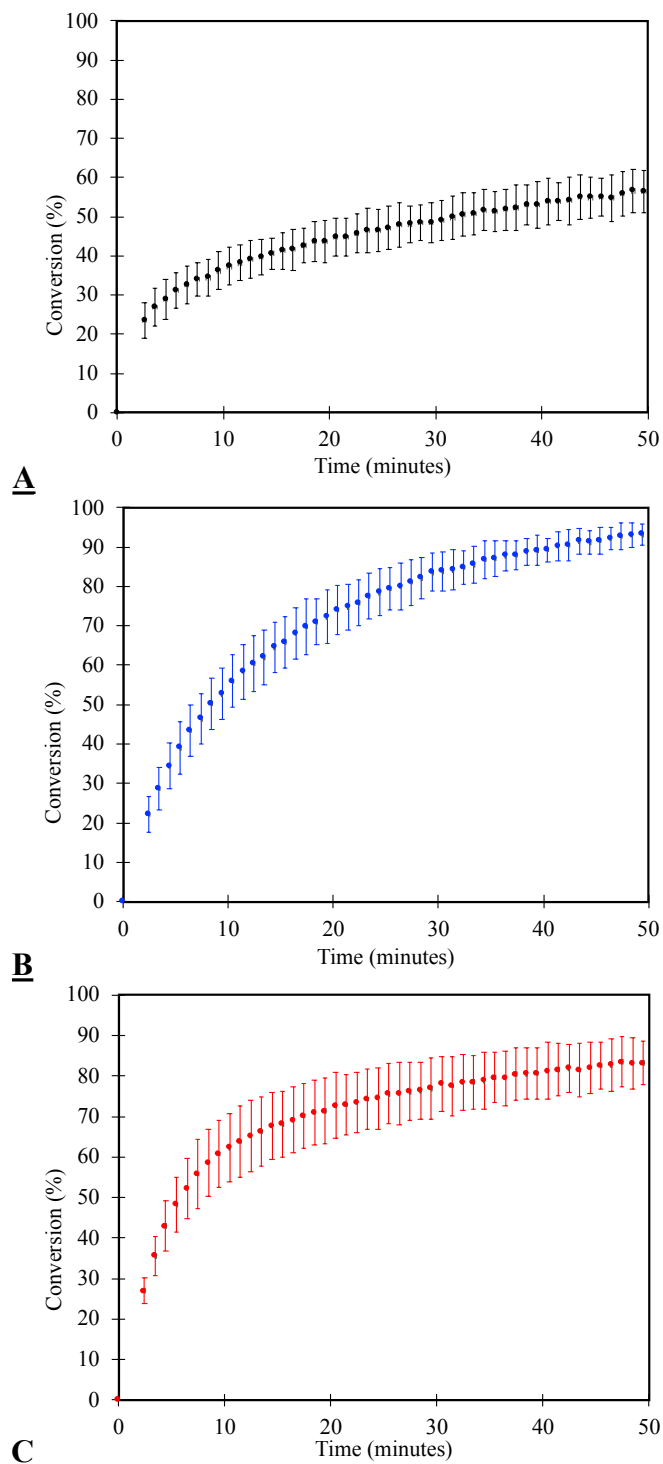


Figure S8. Average conversion versus time for the hydrolysis of DMNP for A) Ce-UiO-66, B) Ce-UiO-66-NH₂, and C) Ce-UiO-66-OH.

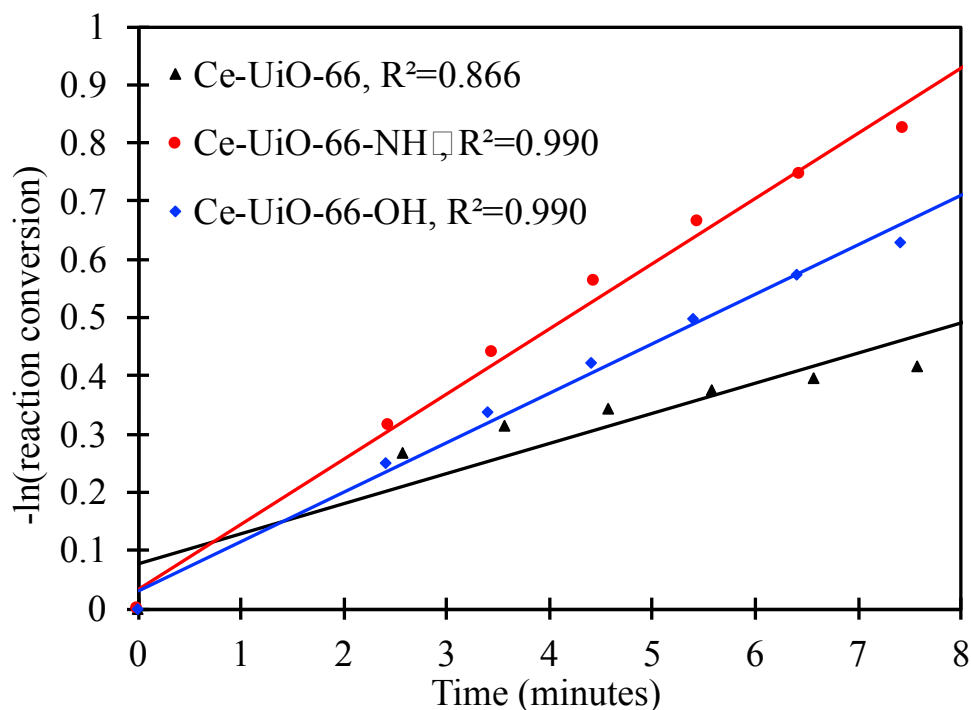


Figure S9. Initial rate kinetic plots for the hydrolysis of DMNP

Table S1. Linear regression analysis of kinetic plots from Figure S8

Sample	Linear regression from initial rates graph
Ce-UiO-66	$(0.052 \pm 0.009)x + (0.078 \pm 0.045)$
Ce-UiO-66-NH ₂	$(0.112 \pm 0.005)x + (0.034 \pm 0.0244)$
Ce-UiO-66-OH	$(0.085 \pm 0.003)x + (0.031 \pm 0.019)$

References

- 1 T. Islamoglu, A. Atilgan, S.-Y. Moon, G. W. Peterson, J. B. DeCoste, M. Hall, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 2672–2675.
- 2 M. Lammert, M. T. Wharmby, S. Smolders, B. Bueken, A. Lieb, K. A. Lomachenko, D. De Vos and N. Stock, *Chem. Commun.*, 2015, **51**, 12578–12581.
3. Y. Zhao, Q. Zhang, Y. Li, R. Zhang, and G. Lu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 15079-15085.