

# Monolayer Formation and Sorption of U(VI) on Acetamide Diethylphosphonate-Functionalized Mesoporous Silica

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## SUPPORTING INFORMATION

### Synthesis and Functionalization Details

SBA-15 particles were synthesized following the procedure described by Sayari, Han, and Yang.<sup>1</sup> In a typical synthesis, 2 g P123 were combined with 60 g 2 M HCl and 15 g H<sub>2</sub>O. The mixture was gently rocked for approximately 2 hours, until homogeneous. The mixture was then transferred to a PTFE reaction vessel in a water bath heated to 35 °C, where it was stirred at 350 rpm for approximately 20 hours. Following this equilibration, 4.25 g tetraethyl orthosilicate (TEOS) was added dropwise under 500 rpm stirring. The reaction mixture was stirred at 500 rpm for five minutes, followed by 20 hours under static conditions in the same 35 °C water bath. For this stage, the stir bar was removed and the vessel sealed tightly for the remainder of the synthesis. The PTFE reaction vessel was then transferred to an oven at 100 °C and left under static conditions for 24 hours. The reaction vessel was allowed to cool completely before opening. Particles were collected by vacuum filtration, rinsed thoroughly with water, and dried under atmospheric conditions in an oven at 100 °C. Template removal was achieved via calcination in air using the following procedure: particles were transferred to an alumina crucible and heated in a muffle furnace. The temperature was ramped to 550 °C at a rate of 1 °C min<sup>-1</sup>,

held at 550 °C for 6 hours, and then cooled at a rate of 5 °C min<sup>-1</sup>. Particles were stored in a desiccator under vacuum to minimize adsorption of water from air.

The “AcPhos” ligand (diethyl (2-oxo-2-((3-(triethoxysilyl)propyl)amino)ethyl)phosphonate) was purchased from Technocomm, Ltd. The compound was stored under nitrogen gas in a desiccator to minimize reaction with moisture in the air. The functionalization procedure was adapted from a surface polymerization method<sup>2</sup> designed to encourage cross-linking of ligands at the surface simultaneously with condensation to the silica surface. Synthesis of the four AcPhos-SBA materials is described in the main text.

### **Nitrogen Adsorption Isotherm Measurements**

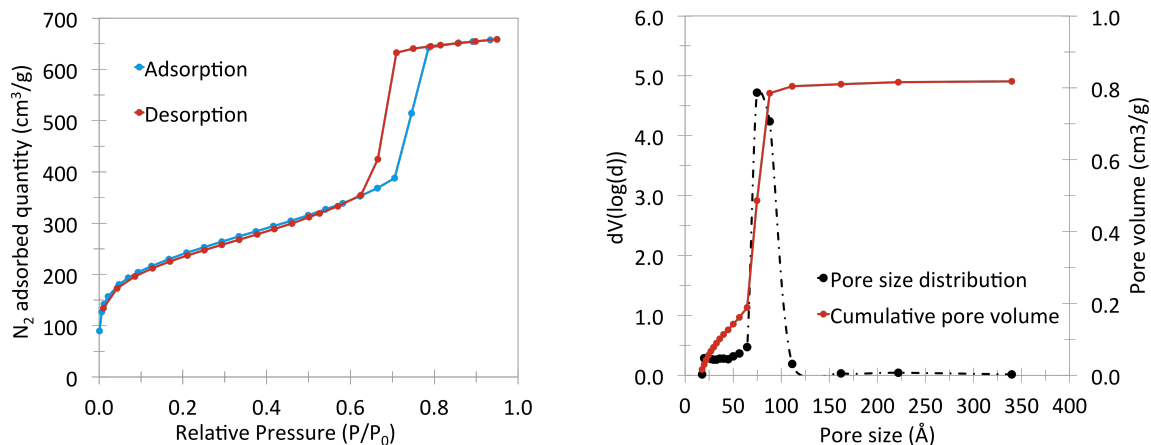
All nitrogen adsorption isotherm measurements were made using a Micromeritics Accelerated Surface Area and Porosity (ASAP) 2420 System instrument. For each measurement, approximately 30 mg of solid sample was transferred to a pre-weighed glass sample tube under an atmosphere of nitrogen and capped with a Transeal. The sample was then transferred to a Micromeritics ASAP 2420 gas adsorption analyzer and heated at a rate of 0.5 K min<sup>-1</sup> from room temperature to a final temperature of 343 K under dynamic vacuum. The sample was considered activated when the outgas rate at 343 K was less than 2 μbar min<sup>-1</sup> (approximately 24 hours). The evacuated tube containing degassed sample was then transferred to a balance and weighed to determine the mass of sample. The tube was transferred to the analysis port of the instrument where the outgas rate was again determined to be less than 2 μbar min<sup>-1</sup> at 343 K. For all isotherms, free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). Nitrogen isotherms at 77 K were measured in liquid nitrogen baths using UHP-grade gas sources. Oil-free vacuum pumps and oil-free pressure regulators

were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements.

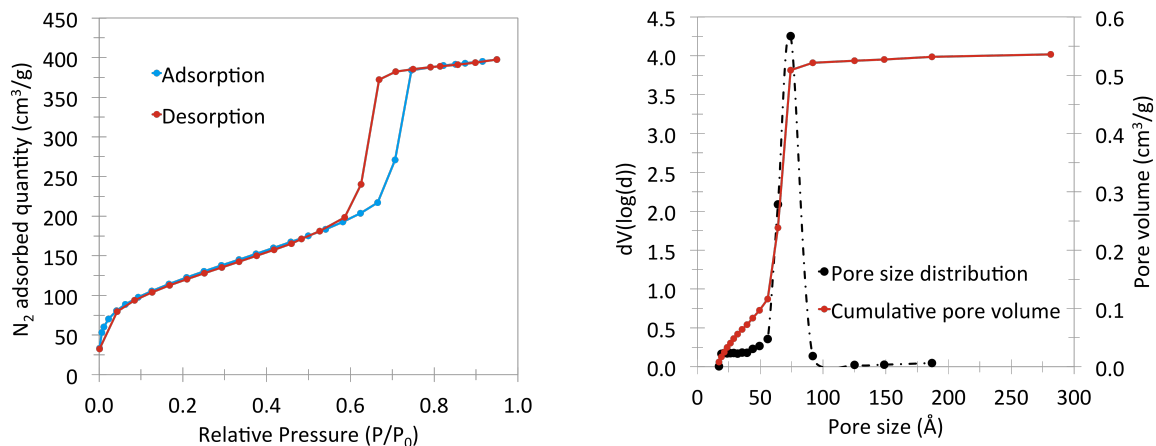
### **<sup>233</sup>U Stock Purification Details**

Prior to purification by ion-exchange, <sup>233</sup>U(VI) was first precipitated as UO<sub>2</sub>(OH)<sub>2</sub> by dropwise addition of 10 M NaOH. The yellow-orange precipitate was collected by centrifugation and dissolved in 1 mL 0.1 M HCl, with a few drops of 1 M HCl added to increase dissolution rate. The stock was then purified using Dowex analytical grade cation exchange resin (AG 50W-X8, 100-200 mesh, hydrogen form). The column was washed with HCl increasing in concentration. <sup>233</sup>U(VI) was eluted with 3 M HCl. Final stock radiopurity was determined to be greater than 99.9% using alpha spectroscopy following electrodeposition of stock aliquots on stainless steel plates. For use in batch experiments, a <sup>233</sup>U(VI) working stock was prepared in 1 M HNO<sub>3</sub> by evaporation and redissolution in 1 M HNO<sub>3</sub>, repeated three times. Stock and sample concentrations were determined using liquid scintillation counting of the <sup>233</sup>U alpha activity.

## Nitrogen Adsorption Isotherms

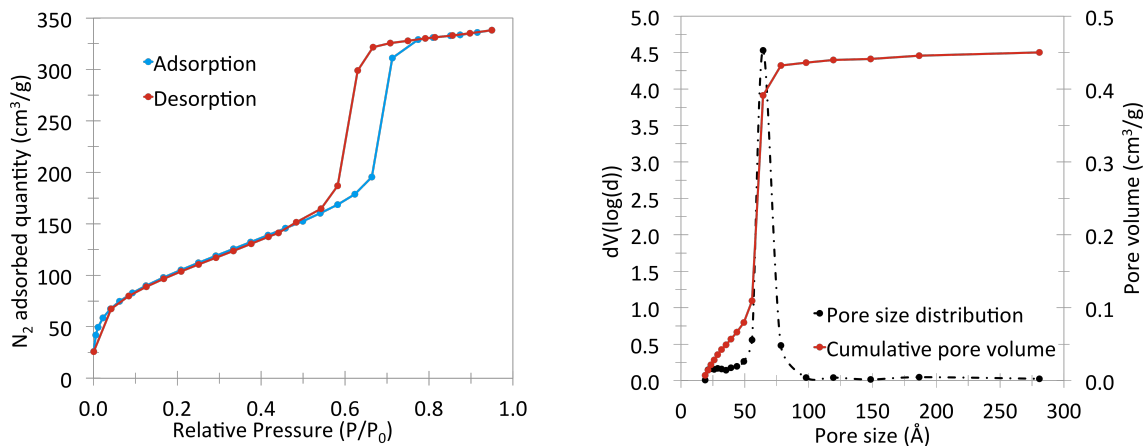


**Figure S1.** Nitrogen adsorption isotherm data for non-functionalized SBA-15 rods used to make the AcPhos-SBA materials. Surface area = 831 m<sup>2</sup> g<sup>-1</sup>, pore volume = 0.818 cm<sup>3</sup> g<sup>-1</sup>, pore diameter = 7.47 nm.

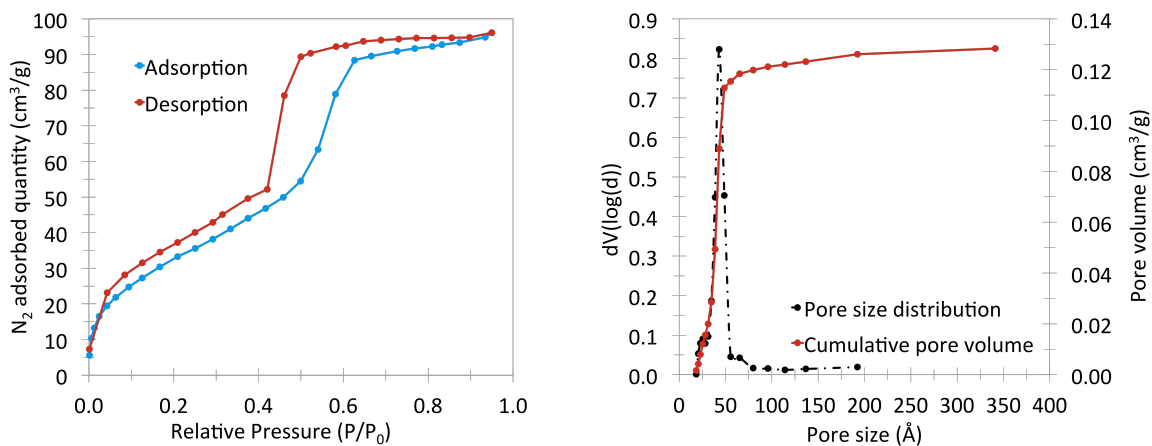


**Figure S2.** Nitrogen adsorption isotherm data AcPhos-SBA (1). Surface area = 442 m<sup>2</sup> g<sup>-1</sup>, pore volume = 0.536 cm<sup>3</sup> g<sup>-1</sup>, pore diameter = 7.42 nm.

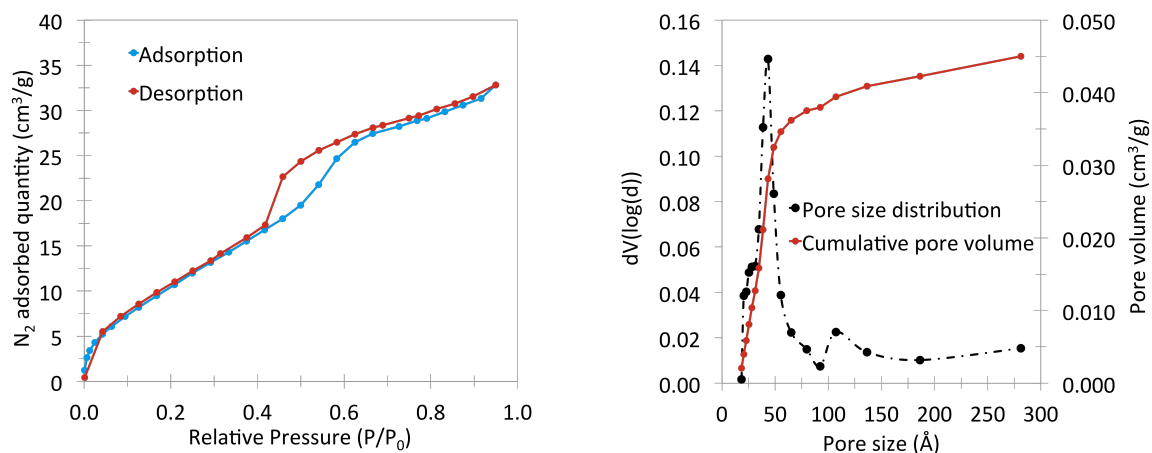




**Figure S3.** Nitrogen adsorption isotherm data AcPhos-SBA (2). Surface area =  $383 \text{ m}^2 \text{ g}^{-1}$ , pore volume =  $0.450 \text{ cm}^3 \text{ g}^{-1}$ , pore diameter = 6.43 nm.

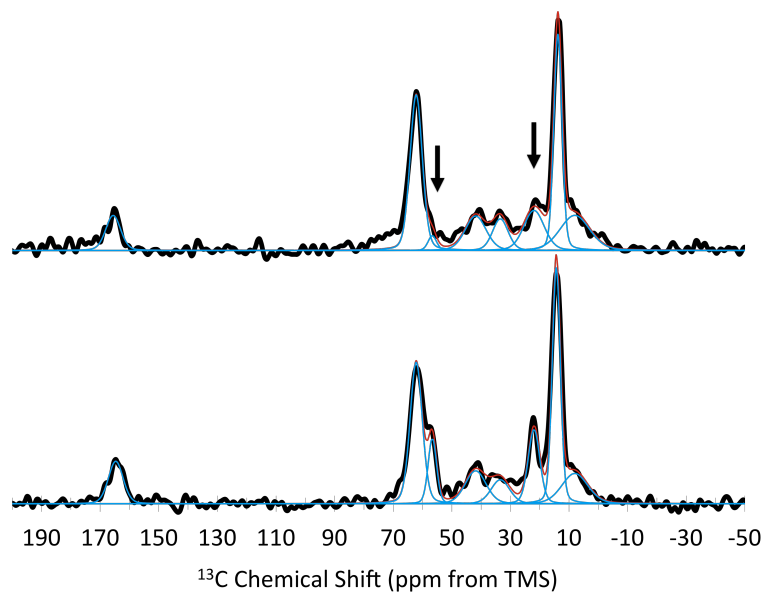


**Figure S4.** Nitrogen adsorption isotherm data AcPhos-SBA (3). Surface area =  $125 \text{ m}^2 \text{ g}^{-1}$ , pore volume =  $0.128 \text{ cm}^3 \text{ g}^{-1}$ , pore diameter = 4.32 nm.

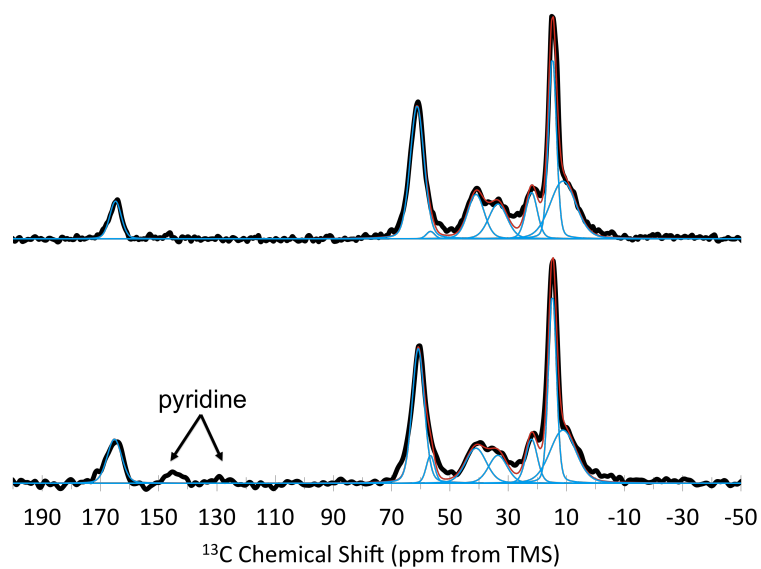


**Figure S5.** Nitrogen adsorption isotherm data AcPhos-SBA (4). Surface area =  $46 \text{ m}^2 \text{ g}^{-1}$ , pore volume =  $0.045 \text{ cm}^3 \text{ g}^{-1}$ , pore diameter =  $4.32 \text{ nm}$ .

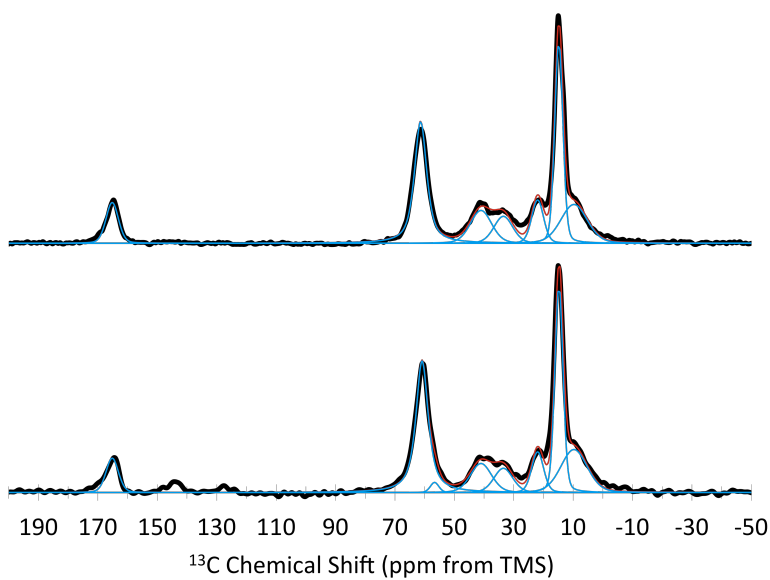
### $^{13}\text{C}\{^1\text{H}\}$ CP/MAS Spectra of Pristine and Acid Washed AcPhos-SBA (2), (3), and (4)



**Figure S6.**  $^{13}\text{C}\{^1\text{H}\}$  CP/MAS spectra for AcPhos-SBA (2) pristine (bottom) and acid-washed (top). Spectra were normalized to the peak at  $14 \text{ ppm}$ . The black arrows point to the resonances at  $21.7$  and  $56.6 \text{ ppm}$ , which correspond to the carbons on the ethoxy groups of the siloxane.

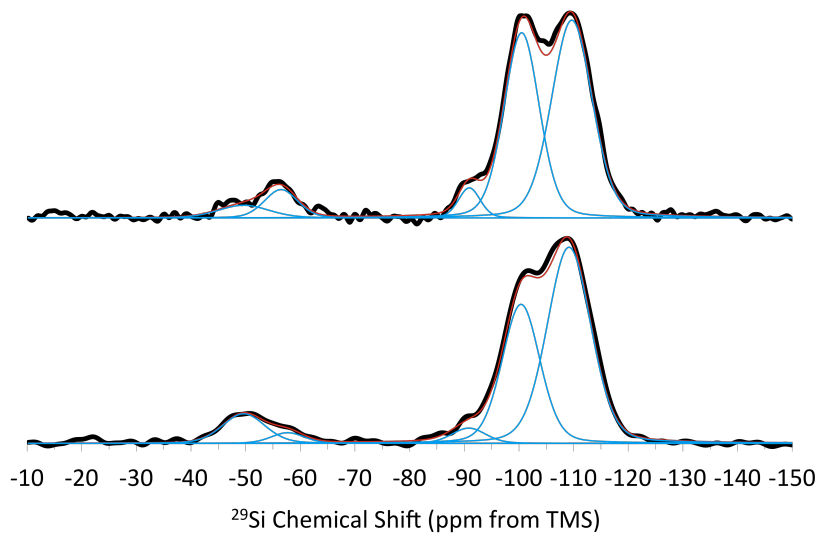


**Figure S7.**  $^{13}\text{C}\{^1\text{H}\}$  CP/MAS spectra for AcPhos-SBA (3) pristine (bottom) and acid-washed (top). Spectra were normalized to the peak at 14 ppm. Experimental data is shown in black. The blue lines show the spectral deconvolution, and the red line is their sum. The resonances at approximately 145 ppm and 128 ppm are from physisorbed pyridine.

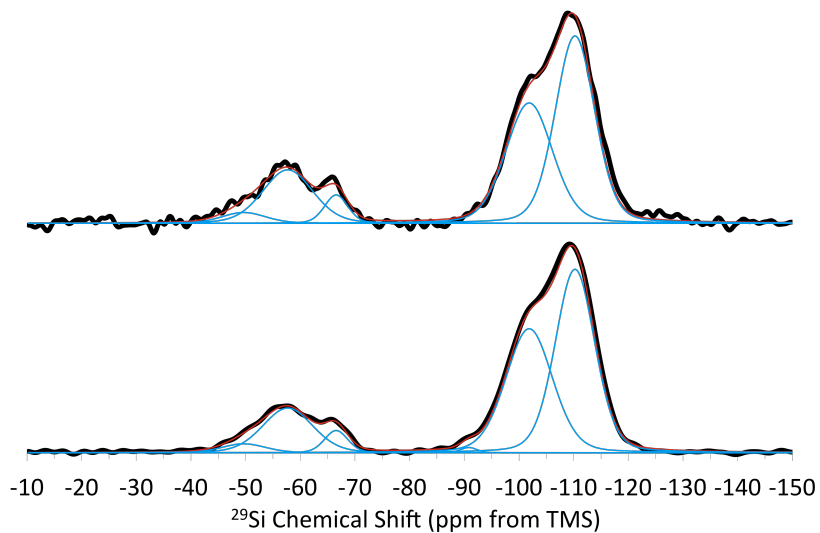


**Figure S8.**  $^{13}\text{C}\{^1\text{H}\}$  CP/MAS spectra for AcPhos-SBA (4) pristine (bottom) and acid-washed (top). Spectra were normalized to the peak at 14 ppm. Experimental data is shown in black. The blue lines show the spectral deconvolution, and the red line is their sum. The resonances at approximately 145 ppm and 128 ppm are from physisorbed pyridine.

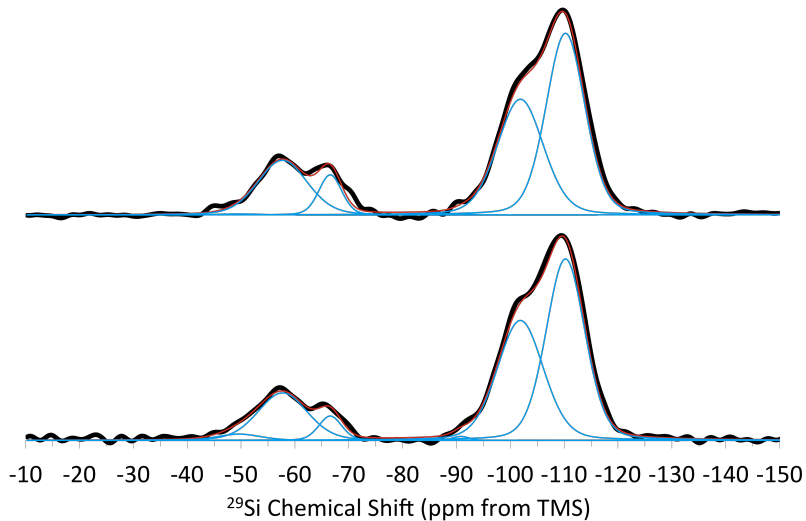
## $^{29}\text{Si}\{^1\text{H}\}$ CP/MAS Spectra of Pristine and Acid Washed AcPhos-SBA (2), (3), and (4)



**Figure S9.**  $^{29}\text{Si}\{^1\text{H}\}$  CP/MAS spectra for AcPhos-SBA (2) pristine (bottom) and acid-washed (top). Spectra were normalized to the peak at -109 ppm. Experimental data is shown in black. The blue lines show the spectral deconvolution, and the red line is their sum.

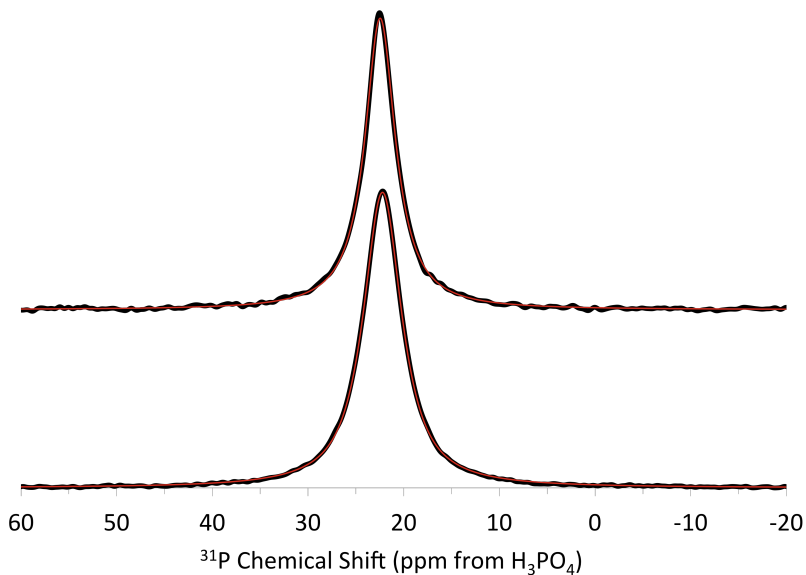


**Figure S10.**  $^{29}\text{Si}\{^1\text{H}\}$  CP/MAS spectra for AcPhos-SBA (3) pristine (bottom) and acid-washed (top). Spectra were normalized to the peak at -109 ppm. Experimental data is shown in black. The blue lines show the spectral deconvolution, and the red line is their sum.

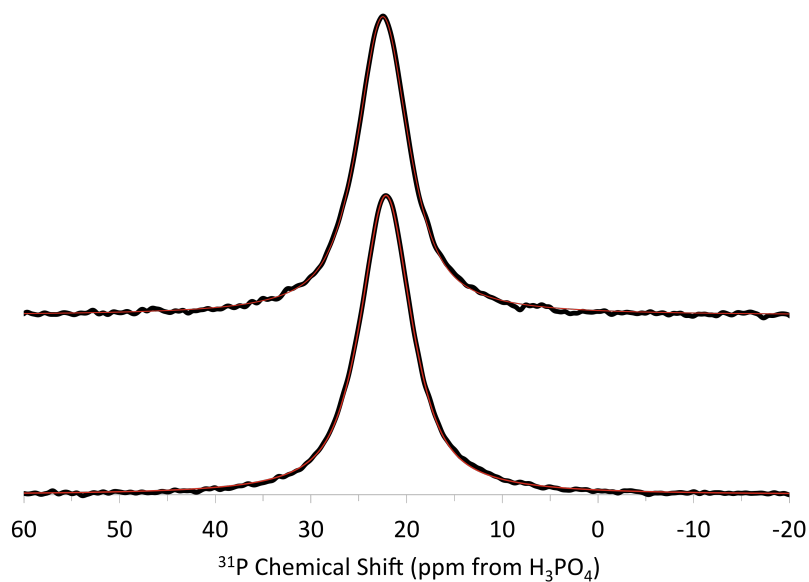


**Figure S11.**  $^{29}\text{Si}\{^1\text{H}\}$  CP/MAS spectra for AcPhos-SBA (4) pristine (bottom) and acid-washed (top). Spectra were normalized to the peak at -109 ppm. Experimental data is shown in black. The blue lines show the spectral deconvolution, and the red line is their sum.

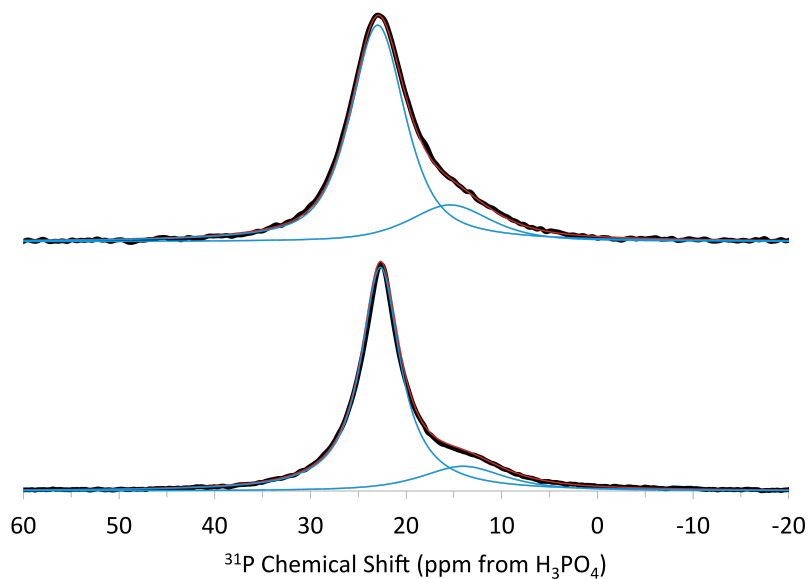
### $^{31}\text{P}$ SP/MAS Spectra of Pristine and Acid Washed AcPhos-SBA (1), (2), and (3)



**Figure S12.**  $^{31}\text{P}$  single-pulse MAS spectra for AcPhos-SBA (1) pristine (bottom) and acid-washed (top). Spectra were normalized to the single peak at 22.2 ppm. Experimental data is shown in black, and the red line is the spectral fit. No  $^1\text{H}$  decoupling was used in the collection of these spectra.

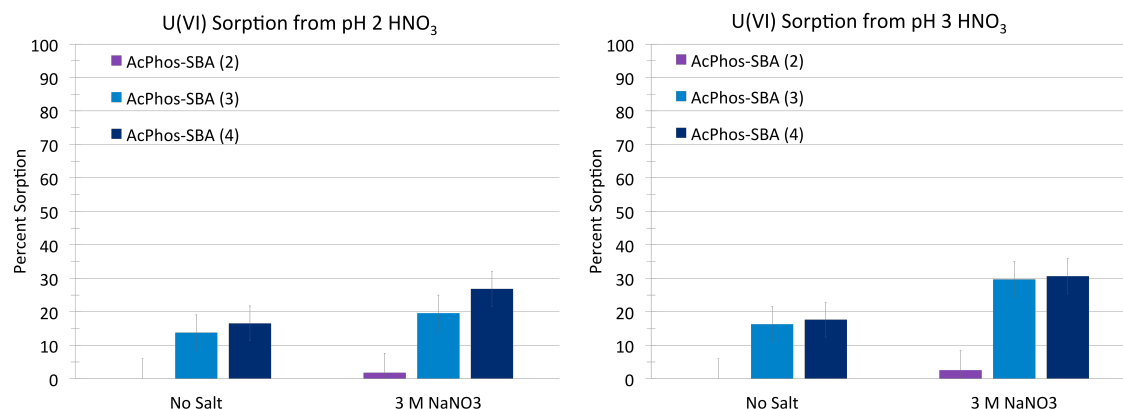


**Figure S13.**  $^{31}\text{P}$  single-pulse MAS spectra for AcPhos-SBA (2) pristine (bottom) and acid-washed (top). Spectra were normalized to the single peak at 22.2 ppm. Experimental data is shown in black, and the red line is the spectral fit. No  $^1\text{H}$  decoupling was used in the collection of these spectra.



**Figure S14.**  $^{31}\text{P}$  single-pulse MAS spectra for AcPhos-SBA (3) pristine (bottom) and acid-washed (top). Spectra were normalized to the single peak at 22.7 ppm. Experimental data is shown in black. Blue lines show the peak deconvolution, and the red line is their sum. No  $^1\text{H}$  decoupling was used in the collection of these spectra.

## U(VI) Sorption Dependence on Ionic Strength



**Figure S15.** Comparison of U(VI) sorption by AcPhos-SBA from solutions with no salt added and 3 M NaNO<sub>3</sub> solutions at pH 2 (left) and pH 3 (right). [U(VI)]<sub>initial</sub> = 5 × 10<sup>-4</sup> M, including [<sup>233</sup>U(VI)] = 2 × 10<sup>-5</sup> M. Data points shown represent percent sorption after 1 hour of mixing time.

## U(VI) Isotherms: Fits to the Langmuir and Freundlich Model

The Langmuir isotherm describes monolayer sorption to uniform binding sites, all with equal binding energy. Its linearized form is:

$$\frac{C_e}{q_e} = \frac{1}{K_{eq}q_m} + \frac{C_e}{q_m}$$

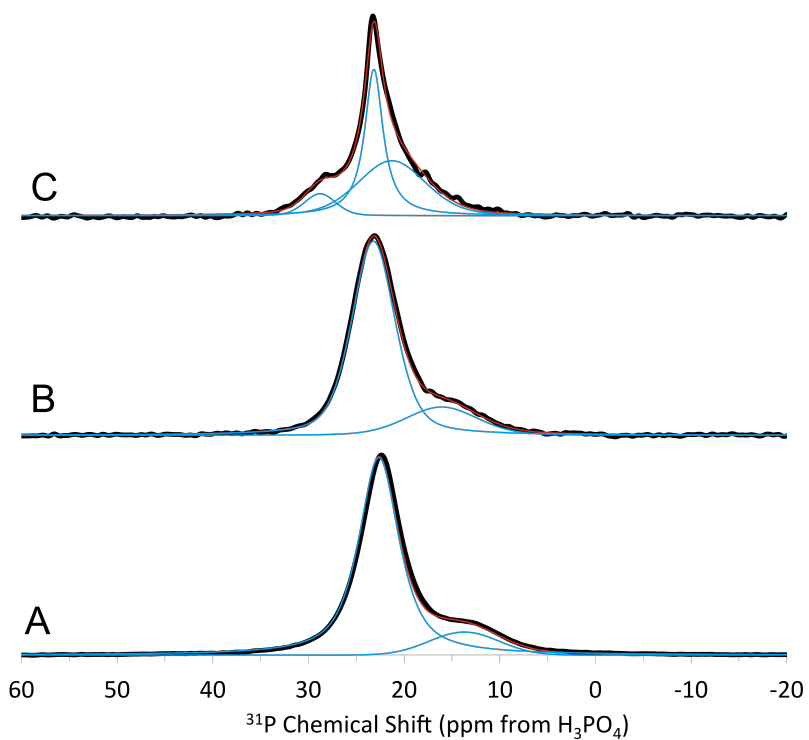
where  $C_e$  is the equilibrium concentration of U(VI) ( $\mu\text{mol mL}^{-1}$ ),  $q_e$  is the amount of U(VI) sorbed at equilibrium ( $\mu\text{mol g}^{-1}$ ),  $K_{eq}$  is the Langmuir adsorption constant (equivalent to the equilibrium constant, in  $\text{mL } \mu\text{mol}^{-1}$ ), and  $q_m$  is the monolayer sorption capacity ( $\mu\text{mol g}^{-1}$ ).

In contrast, the Freundlich isotherm describes sorption to heterogeneous binding sites with a distribution of binding energies. Its linearized form is:

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln(C_e)$$

where  $K_F$  is the Freundlich adsorption constant related to the sorption capacity ( $\mu\text{mol}^{(1-1/n)} \text{mL}^{1/n} \text{g}^{-1}$ ), and  $n$  is the Freundlich constant related to the energy of adsorption.

### $^{31}\text{P}$ SP/MAS Spectra of U(VI)-AcPhos-SBA (4) with $^1\text{H}$ Decoupling



**Figure S16.**  $^1\text{H}$  decoupled single-pulse  $^{31}\text{P}$  NMR spectra for AcPhos-SBA (4) pristine (A), acid-washed (B), and U(VI)-contacted (C).

#### References

- 1 A. Sayari, B. H. Han and Y. Yang, *J. Am. Chem. Soc.*, 2004, **126**, 14348–14349.
- 2 L. C. Sander and S. A. Wise, *Anal. Chem.*, 1995, **67**, 3284–3292.