Probing the interaction of U(VI) with phosphonate-functionalized mesoporous silica using solid-state NMR spectroscopy

Eva C. Uribe,[a] Harris E. Mason,[b] Jennifer A. Shusterman,[a] Anthony Bruchet,[a] and Heino Nitsche[a]

[a]*Department of Chemistry, University of California, Berkeley, Berkeley, California 94720, USA, Email:* eva.uribe@berkeley.edu

[b]*Glenn T. Seaborg Institute, Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, L-231, PO Box 808, Livermore, California, 94550, USA*

‡Deceased.

SUPPORTING INFORMATION

Detailed procedure for hydrothermal synthesis of silica particles

Pluronic® P-123 (polyethylene glycol-polypropylene glycol-polyethylene glycol), 1,3,5-trimethyl benzene (TMB), tetraethyl orthosilicate (TEOS), and hexadecyl trimethylammonium bromide (CTAB) were purchased from Sigma Aldrich. Anhydrous toluene (99.8%) was purchased from Alpha Aesar. The ligand diethylphosphatoethyl triethoxysilane (DPTS) (95%) was purchased from Gelest. All other reagents, including hydrochloric acid, nitric acid, sodium nitrate, sodium hydroxide, and depleted uranium nitrate hexahydrate (ACS reagent), were purchased from Sigma Aldrich.

Silica particles were synthesized by adapting the procedure for synthesis of spherical particles developed by Katiyar et al.[1] In a typical synthesis, 2.25 g of P-123 was combined with 45 mL 1.5 M HCl. In a separate vial were combined 0.45 g CTAB, 18.75 mL water, and 0.780 mL TMB. Solutions were mixed for several hours to ensure homogeneity, then combined together with 15 mL ethanol (added dropwise) into a polytetrafluoroethylene (PTFE) bottle at 35°C and stirred for 3 hours. To this mixture, 7.5 mL TEOS was added dropwise. The PTFE bottle was then sealed and left stirring at

35 °C for an additional 45 minutes, followed by ageing in a thermostatic water bath at 80 °C for 5 hours. Finally, the sealed PTFE bottle was transferred to an oven at 120°C for approximately 15 hours. The silica particles were collected via vacuum filtration and rinsed thoroughly with water. Calcination was carried out in a Thermolyne muffle furnace under ambient conditions by heating to 550°C at a rate of 1 °C min^{-1}, holding for 6 hours at 550 °C, and cooling back to room temperature at a rate of 5 °C min^{-1}. Calcined particles (SBA) were stored in an evacuated desiccator.

Detailed procedure for nitrogen adsorption measurements

In a typical 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 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 (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 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). N2 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.

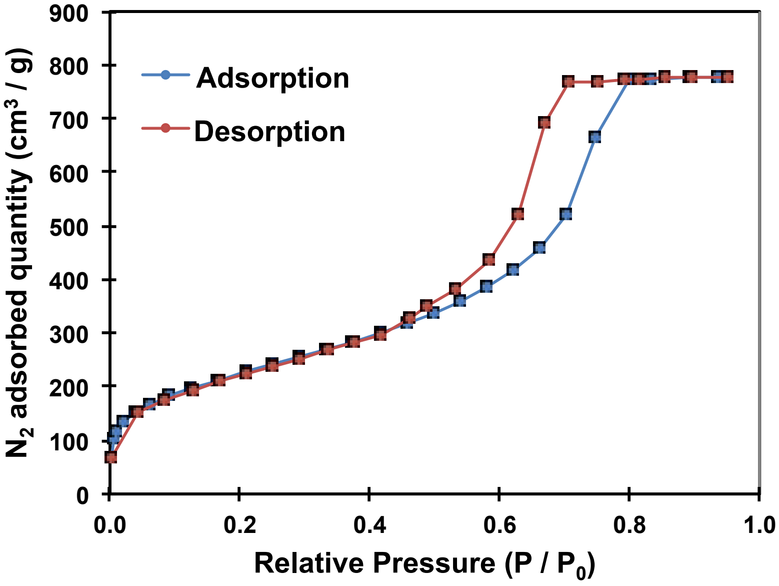

Figure S1. N_2 adsorption isotherm for non-functionalized SBA, demonstrating a type IV isotherm with an H1 hysteresis loop typical for ordered, cylindrical pore structures.

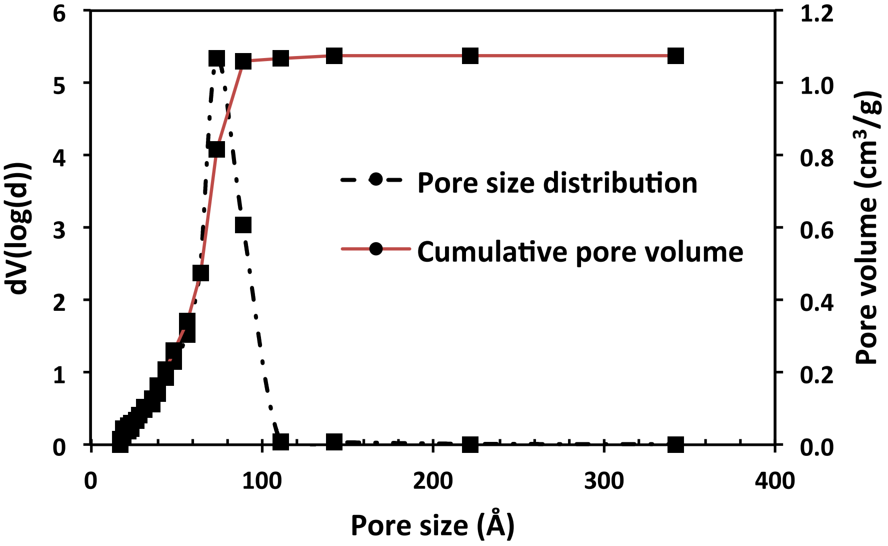

Figure S2. Pore size distribution and cumulative pore volume for non-functionalized SBA.

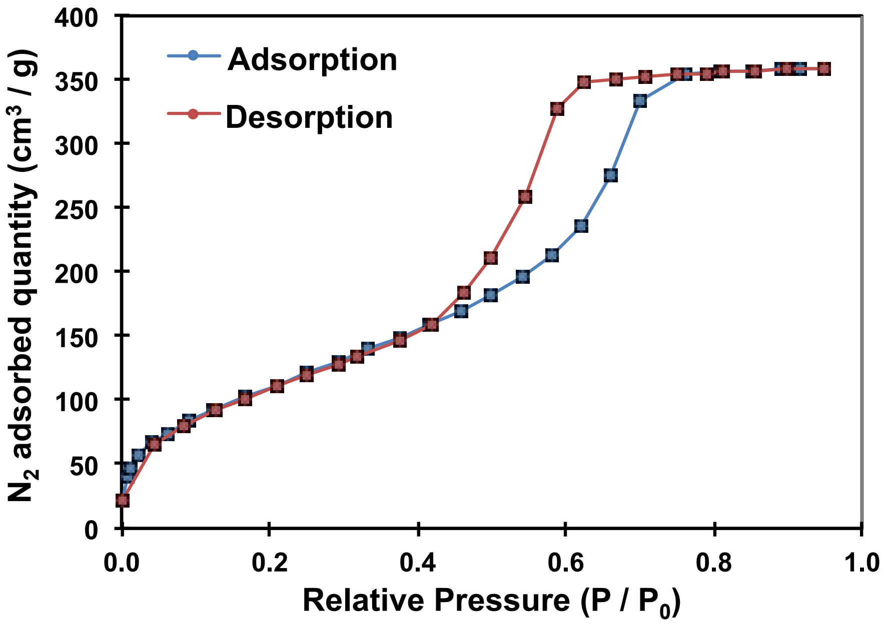

Figure S3. N_2 adsorption isotherm for DPTS-functionalized SBA, which also demonstrates a type IV isotherm with an H1 hysteresis loop.

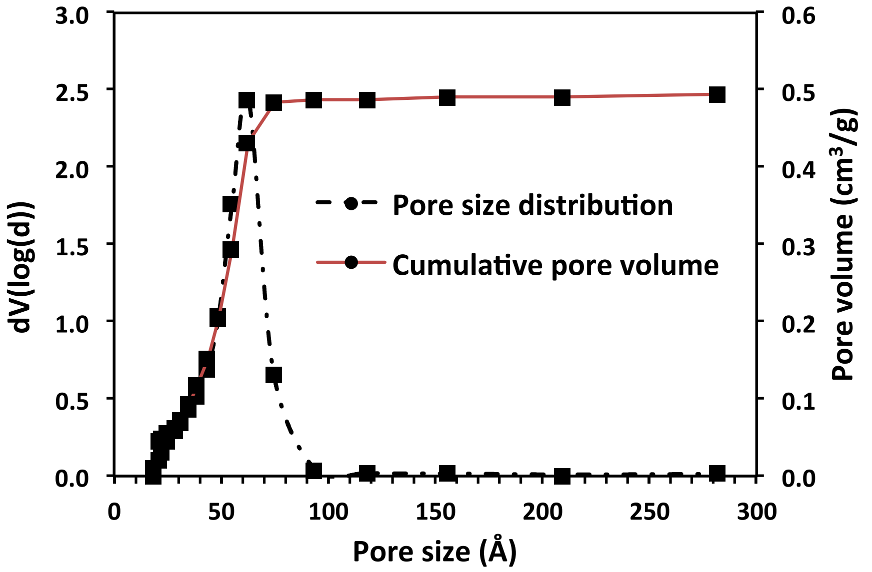

Figure S4. Pore size distribution and cumulative pore volume for DPTS-functionalized SBA.

^{233}U Stock Purification Details

Prior to loading onto a Dowex cation exchange column, the ^{233}U(VI) was first precipitated from solution via dropwise addition of 10 M NaOH. The precipitate was collected by centrifugation, and redissolved in 0.5 mL 0.1 M HCl, then loaded onto the cation exchange column. ^{233}U(VI) was eluted with 3 M HCl. Stock radiopurity (>99.9% based on activity) was verified using alpha spectroscopy following electrodeposition of aliquots of the final stock onto stainless steel plates. For batch experiments, a 1 mM ^{233}U(VI) stock was prepared in 1 M HNO_3 by evaporation and redissolution in 1 M HNO_3, repeated at least three times. Final working stock ^{233}U concentration was assayed using liquid scintillation counting of the ^{233}U alpha activity.

Surface ligand quantification using 31P single pulse NMR and triphenylphosphine standard

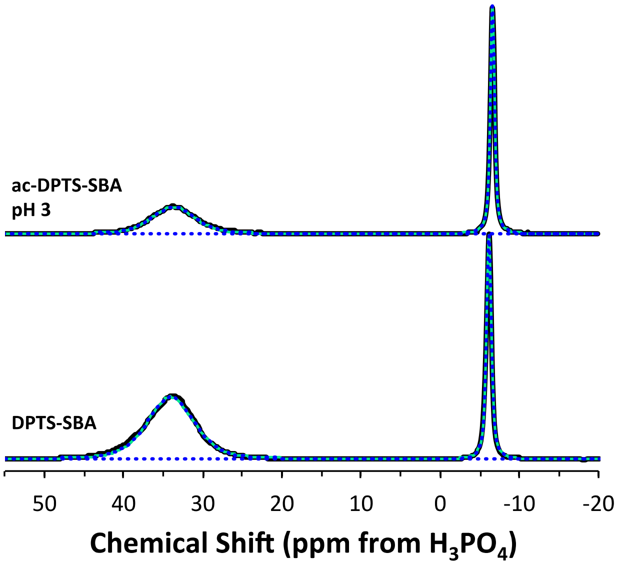

Figure S5. Single pulse ^{31}P spectrum of DPTS-SBA (δ = 34ppm) with a triphenylphosphine internal standard (δ = -6ppm). Spectrum was collected with a delay time of 60 s. Using the mass of triphenylphosphine loaded into the rotor and the relative integrated peak areas above, the number of moles of ligand per gram of DPTS-SBA15 was calculated to be 0.00243 ± 0.00002 mol/g.

U(VI) Isotherm Fit Information

U(VI) isotherm data at pH 4 data were fitted to both Langmuir (Equation S1) and Freundlich (Equation S2) sorption models:

$$\frac{C_e}{q_e} = \frac{1}{K_{eq} q_m} + \frac{C_e}{q_m} \qquad \text{S1}$$

$$\ln\left(q_e\right) = ln\left(K_F\right) + \frac{1}{n} ln\left(C_e\right) \qquad \text{S2}$$

where C_e is the equilibrium $[M^{+n}]$ in solution (µmol/mL), q_e is the amount of metal sorbed on the solid at equilibrium (µmol/g), K_{eq} is the Langmuir adsorption constant (mL/µmol), K_F is the Freundlich adsorption constant ($\mu mol^{(1-1/n)}\ mL^{1/n}\ g^{-1}$) related to the energy of adsorption, q_m is the monolayer sorption capacity (µmol/g), and n is the Freundlich constant related to the energy of adsorption. Fit parameters for each model are given in Table S1.

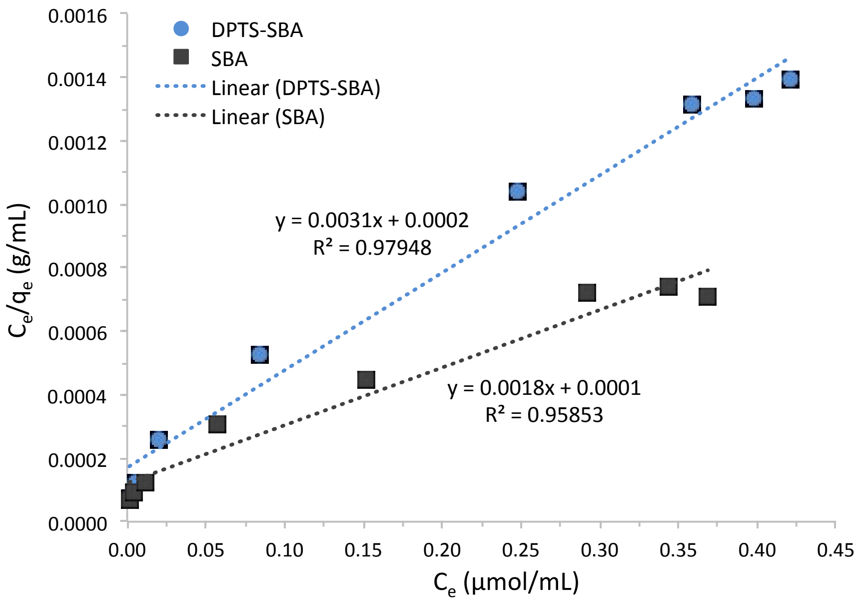

Figure S6. U(VI) Langmuir isotherm fit for DPTS-SBA and SBA. Solution conditions: 3 M $NaNO_3$, pH 4.

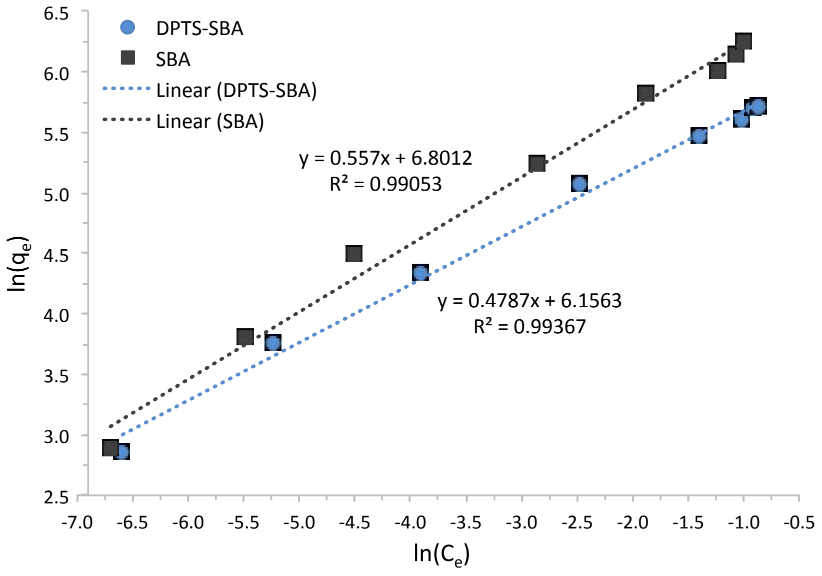

Figure S7. U(VI) Freundlich isotherm fit for DPTS-SBA and SBA. Solution conditions: 3 M $NaNO_3$, pH 4.

Table S1. U(VI) Isotherm Fit Parameters

Langmuir adsorption model			Freundlich adsorption model		
	SBA	DPTS-SBA		SBA	DPTS-SBA
q_m (μmol/g)	551 ± 47	326 ± 19	K_F ($\mu mol^{(1-1/n)}$ $mL^{1/n}$ g^{-1})	899 ± 74	472 ± 26
K_{eq} (mL/μmol)	15 ± 4	18 ± 5	n	1.80 ± 0.07	2.09 ± 0.07
R^2	0.9585	0.9795	R^2	0.9905	0.9937

References

1 A. Katiyar, S. Yadav, P. G. Smirniotis and N. G. Pinto, *J. Chromatogr. A*, 2006, **1122**, 13–20.