

Electronic Supporting Information

**Novel mesoporous silicas bearing phosphine oxide ligands with  
different alkyl chains for the binding of uranium in strong HNO<sub>3</sub>  
media**

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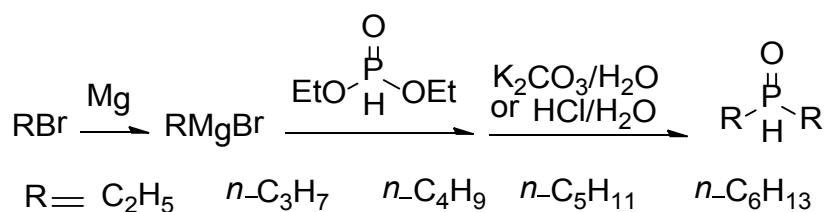
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## 1 Synthesis of secondary phosphine oxides

All reagents and chemicals were of A.R. grade and used without further purification unless otherwise noted. Solvents for chemical synthesis were purified according to the standard procedures. Anhydrous THF and toluene were distilled from Na/benzophenone. Saturated solutions of sodium chloride, sodium bicarbonate, and sodium carbonate were prepared from the respective solids.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a JNM-ECA 600M spectrometer with chemical shifts reported as ppm (tetramethylsilane as internal standard).  $^{31}\text{P}$  NMR chemical shifts were calibrated vs. external 85% aq.  $\text{H}_3\text{PO}_4$ .

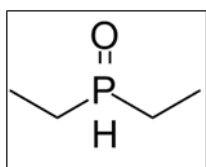


Dialkylphosphine oxides were prepared according to the method of Hays<sup>1, 2</sup>. For example, the dipentylphosphine oxide was synthesized in the following way:

Granular magnesium (13.2 g, 0.55 mol, 3.3 equiv) and a crystal of iodine were added under Ar to a 1000 mL RB flask. Corresponding bromoalkane (0.55 mol, 3.3 equiv) in 200 mL dry THF was then added one-tenth, with stirring to initiate the reaction. After the mixture had refluxed, add bromoalkane THF solution dropwise at speed to keep a moderate boiling. Then the mixture was stirred at room temperature for 2 h. The resulting black Grignard solution was cooled to 0°C, and a solution of diethylphosphite (0.18 mol, 1.0 equiv) in 150 mL THF was then added dropwise over 2 h. Then the cool bath was removed, and the mixture stirred over night at ambient temperature, then cooled to 0 °C again. 0.1 mol/L HCl (g, 0.55mol, equiv) aqueous solution (100 mL) was then added dropwise over 2 h with stirring at 25-35 °C. Then diethyl ether was added and the upper organic phase was decanted from the gel and saved. To the remaining gel was added  $\text{CH}_2\text{Cl}_2$ , and the mixture agitated and then

filtered through a Celite pad. The filtrate phases were separated, and the organic phase combined with the first organic phase, washed with sodium chloride solution, dried with  $\text{MgSO}_4$ , and the solvents removed in vacuo. The residue solid was recrystallized with hexane, give as colorless crystal (94%).

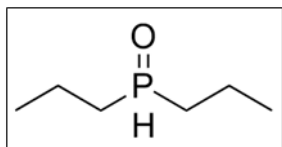
### Diethylphosphine Oxide



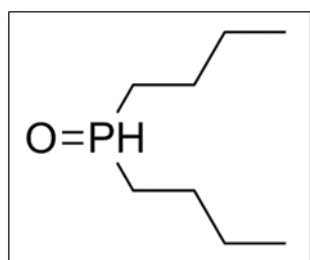
$^{31}\text{P}$  NMR (243 MHz, chloroform-*d*)  $\delta$  42.15 (d,  $^1J_{\text{PH}} = 445.0$  Hz).  $^1\text{H}$  NMR (600 MHz, chloroform-*d*)  $\delta$  6.79 (d,  $^1J_{\text{HP}} = 445.8$  Hz, 1H), 1.84 (m, 4H), 1.23 (dt,  $J = 18.6, 7.7$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz, chloroform-*d*)  $\delta$  20.63 (d,  $^1J_{\text{CP}} = 66.0$  Hz), 5.67

(d,  $^2J_{\text{CP}} = 4.2$  Hz).

### Di-*n*-propylphosphine oxide



$^{31}\text{P}$  NMR (243 MHz, chloroform-*d*)  $\delta$  36.60 (d,  $^1J_{\text{PH}} = 453.9$  Hz).  $^1\text{H}$  NMR (600 MHz, DMSO-*d*6)  $\delta$  6.72 (d,  $^1J_{\text{HP}} = 442.2$  Hz, 1H), 1.77 – 1.69 (m, 4H), 1.54 – 1.44 (m, 4H),

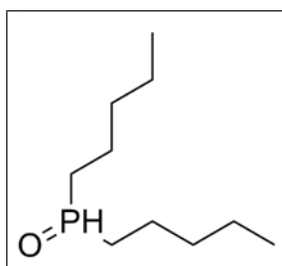


0.89 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz, DMSO-*d*6)  $\delta$  27.77 (d,  $^1J_{\text{CP}} = 64.8$  Hz), 24.08 (d,  $^2J_{\text{CP}} = 3.7$  Hz), 23.68 (d,  $^3J_{\text{CP}} = 13.3$  Hz), 14.08 (s).

### Di-*n*-butylphosphine oxide

$^{31}\text{P}$  NMR (243 MHz, chloroform-*d*)  $\delta$  34.91 (d,  $^1J_{\text{PH}} = 447.4$  Hz).  $^1\text{H}$  NMR (600 MHz, DMSO-*d*6)  $\delta$  6.72 (d,  $^1J_{\text{HP}} = 442.2$  Hz, 1H), 1.77 – 1.69 (m, 4H), 1.54 – 1.44 (m, 4H), 1.39 (m,  $J = 14.6, 7.1$  Hz, 4H), 0.89 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz, DMSO-*d*6)  $\delta$  27.77 (d,  $^1J_{\text{CP}} = 64.8$  Hz), 24.08 (d,  $^2J_{\text{CP}} = 3.7$  Hz), 23.68 (d,  $^3J_{\text{CP}} = 13.3$  Hz), 14.08 (s).

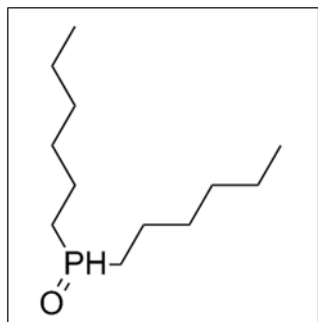
### Di-*n*-pentylphosphine oxide



$^{31}\text{P}$  NMR (243 MHz, chloroform-*d*)  $\delta$  35.64 (d,  $^1J_{\text{PH}} = 445.6$  Hz).  $^{13}\text{C}$  NMR (151 MHz, DMSO-*d*6)  $\delta$  32.70 (d,  $^1J_{\text{CP}} = 13.2$  Hz), 27.99 (d,  $^2J_{\text{CP}} = 64.6$  Hz), 22.23 (s), 21.63 (d,  $^4J_{\text{CP}} = 3.6$  Hz), 14.26 (s).  $^{13}\text{C}$  NMR (151 MHz, benzene-*d*6)  $\delta$  32.82 (d,  $^1J_{\text{CP}} = 13.6$  Hz), 28.24 (d,  $^2J_{\text{CP}} = 65.2$  Hz), 22.19 (s), 21.46 (d,  $^4J_{\text{CP}} = 2.9$  Hz), 13.79 (s).  $^1\text{H}$  NMR (600 MHz,

DMSO-*d*6)  $\delta$  6.70 (d,  $^1J_{\text{HP}} = 441.9$  Hz, 1H), 1.77 – 1.67 (m, 4H), 1.57 – 1.41 (m, 4H), 1.38 – 1.24 (m, 8H), 0.86 (t,  $J = 7.2$  Hz, 6H).

### Di-*n*-hexylphosphine oxide



$^{31}\text{P}$  NMR (243 MHz, DMSO-*d*6)  $\delta$  32.85 (d,  $^1J_{\text{PH}} = 440.4$  Hz).  $^1\text{H}$  NMR (600 MHz, DMSO-*d*6)  $\delta$  6.68 (d,  $^1J_{\text{HP}} = 441.6$  Hz, 1H), 1.72 – 1.66 (m, 4H), 1.54 – 1.39 (m, 4H), 1.33 (dt,  $J = 14.3, 7.0$  Hz, 4H), 1.28 – 1.19 (m, 8H), 0.84 (t,  $J = 6.9$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz, DMSO-*d*6)  $\delta$  31.37 (s), 30.19 (d,  $^2J_{\text{CP}} = 13.1$  Hz), 28.09 (d,  $^3J_{\text{CP}} = 64.9$  Hz), 22.42 (s), 21.93 (d,  $J = 3.5$  Hz), 14.39 (s).

## 2 Synthesis of mesoporous silicas

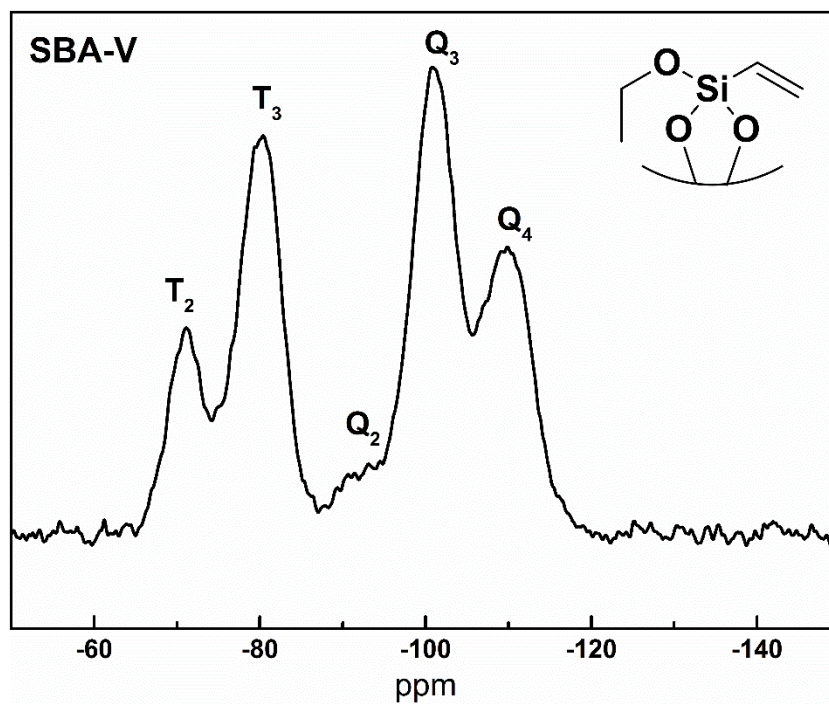
Small angle X-ray diffraction (SAXD) patterns were recorded on a Rigaku D/max-2400 X-ray powder diffractometer using Cu-K $\alpha$  radiation. Infrared (IR) spectra were recorded by Nicolet Nexus 470 fourier transform infrared spectrometer with KBr disk method. Solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were obtained on a Bruker AV300 NMR spectrometer.  $^{29}\text{Si}$  MAS NMR spectrum was measured at 59.63 MHz using 7 mm rotors spinning at 5 kHz.  $^{31}\text{P}$  spectra were measured at 121.49 MHz using 4 mm rotors spinning at 7 kHz. The 75.47 MHz  $^{13}\text{C}$  CP-MAS spectra were obtained using a 7 mm rotor spinning at 6.5 kHz. The chemical shifts are reported in ppm relative to tetramethylsilane for  $^{29}\text{Si}$  and  $^{13}\text{C}$  and relative to phosphoric acid for  $^{31}\text{P}$ . Elemental analyses were performed on a Flash EA 1112 Element Analyzer. The nitrogen adsorption/desorption isotherms were measured at 77 K using a Surface Area and Porosity Analyzer (Nava 3200e). Prior to nitrogen sorption experiments, the samples were outgassed at 373 K for 4 h. Thermogravimetry curves were recorded with a thermal analysis instrument (TA SDT Q600) at a heating rate of 20 °C/min in N $_2$  atmosphere. Transmission electron microscopy (TEM) was performed using a Hitachi HT7700 at an accelerating voltage of 80 kV.

Vinyl-Functionalized mesoporous silica (SBA-V) was synthesized using poly(ethylene glycol)-b-poly(propylene glycol)-b-poly(ethylene glycol) (P123, MV=5800, Aldrich) as the surfactant by a similar method with Nie et al<sup>3</sup>. In a typical synthesis, the tetraethoxysilane (TEOS, Aldrich) were added to an aqueous HCl solution under stirring before P123 was dissolved to the mixture, followed by the addition of the vinyltriethoxysilane (TEVS, TCI) 4 h later. The molar ratio of 1 TEOS: 0.433 TEVS: 0.017 P123: 162 H $_2$ O: 5.86 HCl was used. The resulting viscous mixture was left under stirring at 35 °C for 20 h, followed by an aging step at 100 °C for 24 h. After filtered, the product was washed well with a large quantity of water. The surfactant was removed by acid/solvent extraction, using a solution of 500 mL of ethanol and 30mL g of aqueous HCl (37%) per 10 g of sample. This mixture was

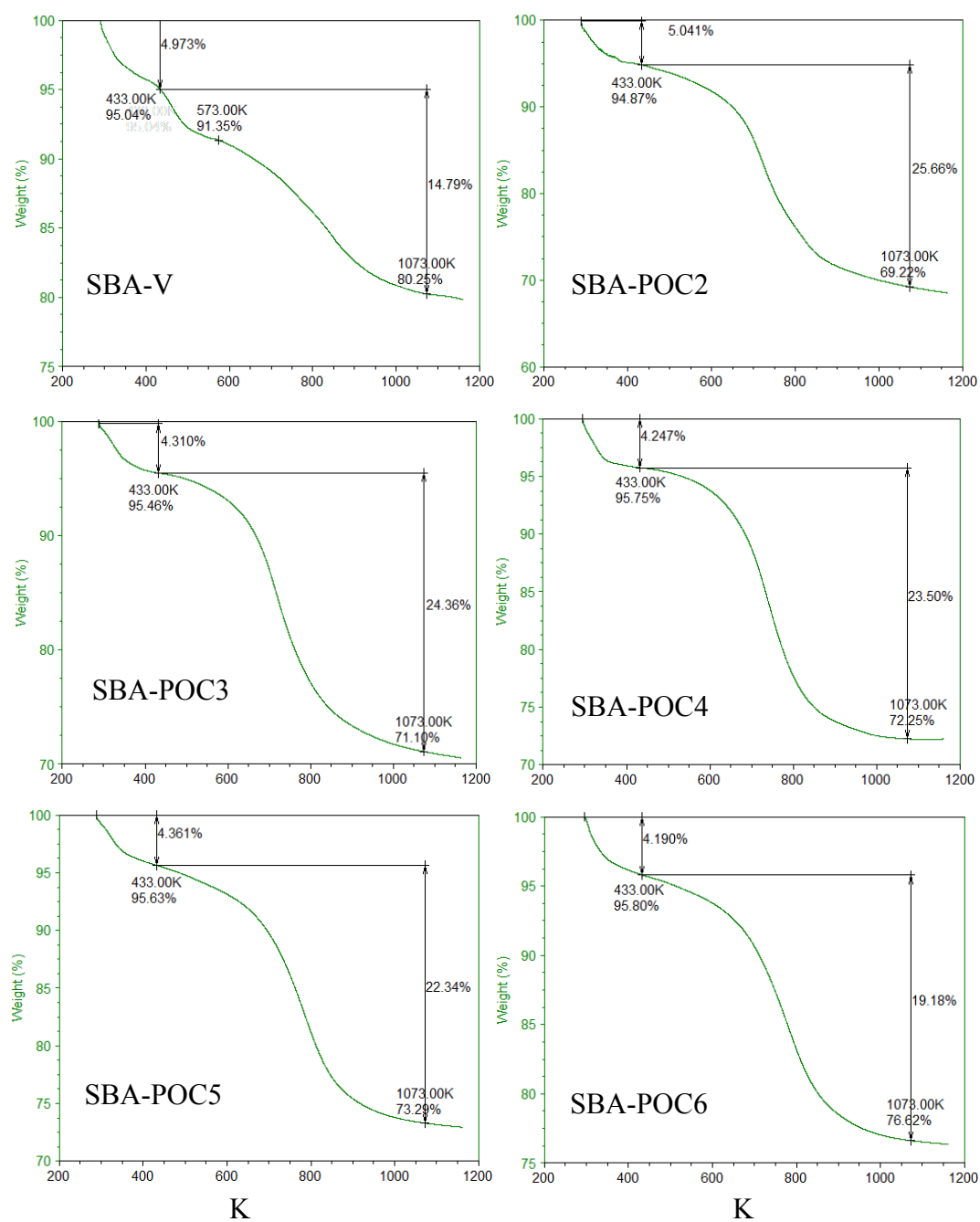
refluxed for 12h, and then repeated one. The solution was filtered, washed with water and ethanol until the pH was neutral, and dried in vacuum for 24 h at 60 °C.

Alkyl phosphine oxide modified mesopores silica SBA-POC $m$  was synthesized by the PH addition reaction. Specifically, 1 g SBA-V, 0.1 g AIBN and 0.05 mol R<sub>2</sub>PH(O) were refluxed in anhydrous toluene at 125 °C for 12 h under Ar atmosphere. After filtration, the products were washed by ethanol and water for several times and dried in vacuum at 60 °C for 24 h, the functionalized products were obtained.

3 Fig.S1  $^{29}\text{Si}$  MAS NMR spectrum of SBA-V

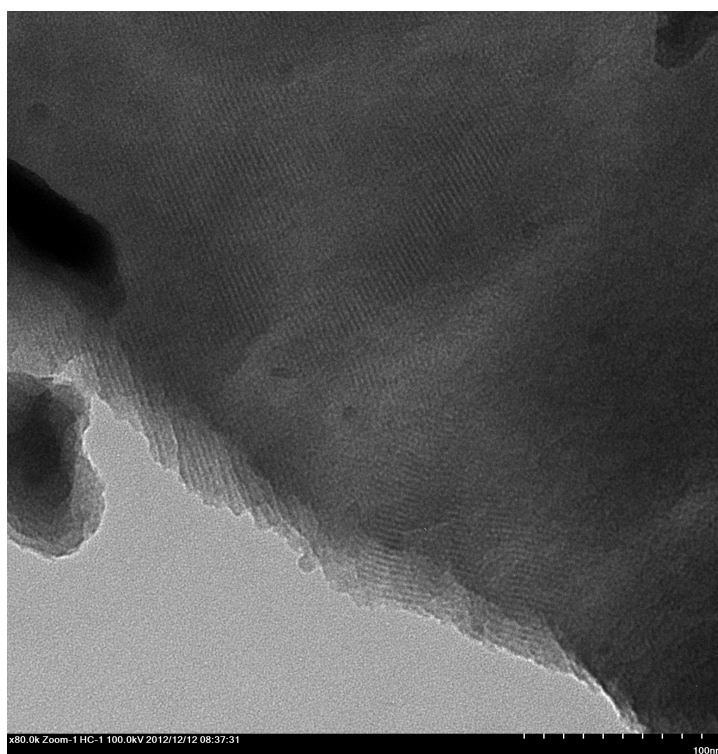
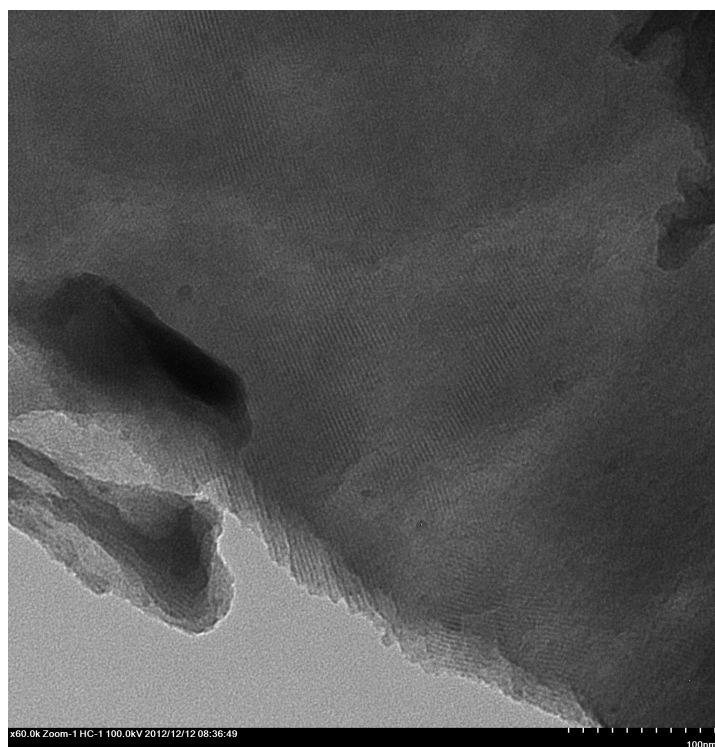


4 Fig. S2 Thermogravimetric(TG) curves





**5 Fig.S3 The transmission electron microscopy photographs of SBA-POC3**



## 6 Batch adsorption

Deionized water used in all experiments was obtained from the Milli-Q water purification system. Solutions of U(VI) were prepared by dissolving uranium oxide in HNO<sub>3</sub> and further diluted with deionized water. The pH of solutions was adjusted by adding small volumes of diluted nitric acid or sodium hydroxide solutions. The batch experiments were carried out in a thermostatic water bath at 25°C.

In a typical experiment, 10mg of sorbent was added into 10 mL U(VI) solution in a flask (the solid-liquid ratio is thus 1 g/L) stirring for 24 h. The solution was separated by filtration with 0.22 μm filter membrane and then used for analysis. Batch experiments were done in triplicates, with the uncertainty within 5%.

The initial and final concentrations of the U(VI) in solutions were determined by Arsenazo III Spectrophotometric Method at wavelength of 652 nm with a quartz cuvette of 1 cm path length, and adsorption capacity ( $Q_e$ , mg/g) were calculated by the following formula:

$$Q_e = \frac{(C_i - C_f) \times V_{\text{solution}}}{m_{\text{sorbent}}}$$

where  $C_i$  and  $C_f$  are the initial and final concentration.  $m_{\text{sorbent}}$  and  $V_{\text{solution}}$  designate the weight of the mesoporous silicas and the volume of the U(VI) solution used in the adsorption experiment, respectively.

## References

1. H. R. Hays, *The Journal of Organic Chemistry*, 1968, **33**, 3690-3694.
2. C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 4277-4280.
3. Q. Wei, H.-Q. Chen, Z.-R. Nie, Y.-L. Hao, Y.-L. Wang, Q.-Y. Li and J.-X. Zou, *Mater. Lett.*, 2007, **61**, 1469-1473.

## 7 Copies of 31P, 1H and 13C NMR spectra for secondary phosphine oxides

