**Electronic Supplementary Information**

Phosphonate-functionalized large pore 3-D cubic mesoporous (KIT-6) hybrid as highly efficient actinide extracting agent

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**Experimental Section**

*Synthesis of ordered mesoporous SBA-15/KIT-6 silica materials.* High quality mesoporous KIT-6 silica material was obtained in large quantities following the method reported by Kleitz *et al.* [F. Kleitz, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136; F. Kleitz, F. Bérubé, R. Guillet-Nicolas, C.-M. Yang and M. Thommes, *J. Phys. Chem. C*, 2010, 114, 9344]. Briefly, 9.0 g of Pluronic P123 (EO20PO70EO20, Sigma-Aldrich) was dissolved in 325 g of distilled water and 17.40 g HCl (37 %) under vigorous stirring. After complete dissolution, 9.0 g of n-butanol (BuOH, Aldrich, 99%) was added. The mixture was left under stirring at 35°C for 1 h, after which 19.35 g of tetaethoxysilane (TEOS, Acros, 99 %) were added at once to the homogeneous clear solution. The molar composition of the starting reaction mixture is TEOS/P123/HCl/H2O/BuOH = 1/0.017/1.83/195/1.31. This mixture was left under stirring at 35 °C for 24 h, followed by an aging step at 80 °C for 48 h under static conditions. The resulting solid products were then filtered and dried for 48 h at 100 °C. For comparison purpose, 2-D hexagonal SBA-15 was synthesized following the method proposed by Choi *et al.* [M. Choi, W. Heo, F. Kleitz and R. Ryoo, *Chem. Commun.*, 2003, 1340]. This synthesis of SBA-15 is briefed as follows: 13.9 g of Pluronic P123 was dissolved in 252 g of distilled water and 7.7 g HCl
(37%). After complete dissolution, 25.0 g of TEOS was added at once. The mixture was left under stirring at 35 °C for 24 h, followed by hydrothermal treatment at 100 °C for 48 h under static conditions. In both cases, for template removal, the as-synthesized silica powders were first shortly slurried in an ethanol-HCl mixture and subsequently calcined at 550 °C for 2 hours.

**Grafting of 2-diethylphosphatoethyl) triethoxysilane on mesoporous KIT-6 and SBA-15 silicas.** For surface modification of both supports, 1 g of the given activated mesoporous silica (treated overnight at 150 °C under vacuum) was dispersed in 50 mL of dry toluene. Then, 6 mmol of (2-diethylphosphatoethyl) triethoxysilane (DPTS, Gelest, 98%) was added at once to the dispersion in toluene under nitrogen atmosphere at room temperature. The resulting mixture was left under further stirring for 24 h under reflux conditions. After cooling to room temperature, the suspended solid product was filtered, washed thoroughly with 20 mL of toluene and ethanol three times, and then dried at 70 °C overnight in air.

**Characterization**

N$_2$ adsorption-desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2010 analyzer. Before the sorption measurements, the samples were outgassed for 6 h at 80 °C. Specific surface area, $S_{BET}$, were determined using the BET equation in the range 0.05 ≥ $P/P_0$ ≥ 0.20 and the total pore volume was measured at $P/P_0 = 0.95$. Pore size distributions were calculated using non-local density functional theory (NLDFT) methods applying the cylindrical pore model. TG-DTA measurements were performed using a Netzsch STA 449C thermogravimetric analyzer, under air flow of 20 mL/min with a heating rate of 10 °C/min. FTIR-ATR spectra were recorded using a Nicolet Magna FTIR spectrometer with a narrow band MCT detector and a diamond ATR Golden-Gate accessory (Specac Ltd., London). The spectra were obtained from 128 scans with a resolution of 4 cm$^{-1}$. Solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were obtained on a Bruker DRX300 MHz NMR spectrometer. $^{29}$Si MAS NMR spectrum was measured at 59.60 MHz using 7 mm rotors spinning at 4 kHz. $^{31}$P spectra were measured at 121.4 MHz using 4 mm rotors spinning at 8 kHz. The 75.4 MHz $^{13}$C CP-MAS spectra were obtained using a 7 mm rotor spinning at 4 kHz. The chemical shifts are reported in ppm relative to tetramethylsilane (TMS) for $^{29}$Si and $^{13}$C and
relative to phosphoric acid for $^{31}\text{P}$. Low angle X-ray diffraction (XRD) measurements were conducted on a Siemens D5000 X-ray diffractometer using Cu radiation. Transmission electron microscopy (TEM) was performed using a JEOL JEM1230 at an accelerating voltage of 80kV with a LaB6 filament. X-ray photoelectron spectroscopy (XPS) measurements were performed with a KRATOS Axis-Ultra instrument (UK) using a monochromatic $K_{\alpha}$ Al X-ray source at 300W. Survey spectra used for determining the elemental composition were collected at a pass energy of 160 eV with a step size of 1 eV.

**Batch extraction experiments**

Solutions of U(VI) and Th(IV) in HNO₃ were prepared from radioactive standards from NIST. The U/TEVA resins were purchased from Eichrom, USA (Lisle, IL). Competition studies were performed with a mixture of 1 μg L⁻¹ of U(VI), Th(IV) and a multi-element solution (Multi-element solution 2A, SPEX, Metuchen, USA) consisting in the following cations: Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, K, Li, Mg, Mn, Na, Ni, Pb, Rb, Se, Sr, Tl, U, V and Zn. The solution/solid ratio was fixed to 200 (V/m). All extraction experiments except the extraction of U(VI) with the commercial resin (1.8 M HNO₃) were performed at pH=4. Samples were stirred in an orbital shaker for 30 min. Subsequently, the supernatant was filtered through a 0.2 μm syringe filter. The initial and final concentrations of the actinides in solutions were determined by ICP-MS measurements and distribution coefficients ($K_d$) were calculated by the following formula [D. T. Pierce and J. X. Zhao, *Trace Analysis with Nanomaterials*, 2010, Germany: Wiley-VCH (p.191)]:

$$K_d (\text{mL/g}) = \frac{(C_i-C_f)}{C_f} \times \frac{V_{\text{solute}} (\text{mL})}{m_{\text{solid}}(\text{g})}$$

where $C_i$ and $C_f$ are the initial and final concentration. Batch experiments were done in triplicates.

Adsorption kinetics study of U(VI) on KIT-6-P was performed under similar conditions as the batch extractions. The studied contact times were set for 1, 2, 3, 5, 10 and 30 min, in duplicates.
**Table S1** Physicochemical parameters of parent and functionalized silica samples derived from \( \text{N}_2 \) physisorption, thermogravimetric analysis and XPS.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface area ( S_{\text{BET}} ) (m(^2)/g)</th>
<th>Pore size ( \text{NLDFT}_{\text{ads}} ) (nm)</th>
<th>Pore size ( \text{NLDFT}_{\text{des}} ) (nm)</th>
<th>Total pore volume (cm(^3)/g)</th>
<th>Weight loss (%)</th>
<th>P/Si (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KIT-6</td>
<td>1128</td>
<td>7.3</td>
<td>7.9</td>
<td>1.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KIT-6-P</td>
<td>846</td>
<td>6.8</td>
<td>7.0</td>
<td>0.93</td>
<td>9.4</td>
<td>3.99</td>
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<tr>
<td>SBA-15</td>
<td>1038</td>
<td>8.5</td>
<td>9.1</td>
<td>1.46</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SBA-15-P</td>
<td>653</td>
<td>8.2</td>
<td>8.5</td>
<td>0.91</td>
<td>8.6</td>
<td>5.07</td>
</tr>
</tbody>
</table>
**Fig. S1** Representative TEM image of the reference 2-D hexagonal SBA-15-P hybrid.
Fig. S2 TG-DTA curves of KIT-6-P and SBA-15-P measured under air flow, as indicated.
Fig. S3 FTIR spectra of KIT-6 and KIT-6-P, as indicated.
**Fig. S4** Solid state $^{29}$Si MAS NMR spectrum of KIT-6-P.
**Figure S5** Solid state $^{13}$C CP/MAS A) and $^{31}$P MAS NMR B) spectra of SBA-15-P.