The effect of pore diameter in the arrangement of chelating species grafted onto silica surfaces with application to uranium extraction

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Supplementary material

Figure S1 Synthesis of TR molecule

Synthesis of 3 (2-chloro-N,N-di(2-ethylhexyl)acetamide):

In a round flask, 2 was added dropwise to a solution of 1 (1 eq), trimethylamine (1 eq) in dichloromethane (0.1 mol.L\(^{-1}\)). The mixture was stirred for 3 hours at room temperature. 3 was extracted from the mixture with dichloromethane. The combed extracts were dried over magnesium sulphate, filtered and evaporated under vacuum to give compound 3 (yield >95%)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 0.85-0.91 (m, 12H) ; 1.23-1.33 (m, 16H) ; 1.55-1.60 (m, 1H) ; 1.67-1.73 (m, 1H) ; 3.18 (d, 2H) ; 3.22-3.32 (m, 2H) ; 4.09 (s, 2H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) (ppm): 10.7; 11.0 ; 23.1; 23.9; 24.0; 28.7; 28.9; 30.4; 30.6 ; 36.8; 38.5 ; 41.6 ; 48.8; 51.7 ; 167.1.

Synthesis of 4 (N;N-di(2-ethylhexyl)carbamoylmethylphosphonate):
This step was based on an Arbuzov reaction. In a round flask, 3 (1 eq) and triethyl phosphite (3 eq) were stirred and heated under reflux at 160°C for 3 hours. After completion of the reaction, the excess triethyl phosphite was distilled off under reduced pressure. 4 can thus be used without further purification.

^1H NMR (400 MHz, CDCl₃) δ (ppm): 0.81-0.86 (m, 12H, CH₃); 1.21-1.32 (m, 22H); 1.51-1.57 (m, 1H); 1.64-1.71 (m, 1H); 3.02 (d, 2H, CO-CH₂-P); 3.21-3.27 (m, 4H); 4.08-4.16 (m, 4H).

^13C NMR (100 MHz, CDCl₃) δ (ppm): 10.6; 11.0; 14.1; 14.2; 16.3; 16.4; 23.1; 23.2; 23.5; 23.9; 28.8; 28.9; 30.4; 30.6; 33.1; 34.5 (d); 37.0; 38.6; 48.9; 52.3; 62.5 (d); 165.2.

^31P NMR (160 MHz; CDCl₃) δ (ppm): 21.8.

Synthesis of 5 (3-(N,N-di(2-ethylhexyl)carbamoyl)-3-(diethoxyphosphono)-ethylpropanoic acid):

A solution of 1 (1 eq.) in anhydrous THF (1 mol/L) was added dropwise to a suspension of sodium hydride (1.5 eq.) in anhydrous THF (2 mol/L). The mixture was stirred for 1 hour at room temperature before cooling at 0°C. Ethyl bromoacetate (1.5 eq.) was slowly added to the cold mixture; after return to room temperature the mixture was stirred for 1h. The mixture was acidified with HCl (1 mol/L) until the solution reached to pH 1; and then extracted with dichloromethane. The combined extracts were dried over magnesium sulphate; filtered and evaporated under vacuum. The excess of ethyl bromoacetate was removed by distillation under vacuum to give the desired compound 2 (yield >95%).

^1H NMR (400 MHz; CDCl₃) δ (ppm): 0.77 – 0.89 (m; 12H); 1.16 – 1.28 (m; 27H); 1.63 – 1.70 (m; 1H); 1.74 – 1.83 (m; 1H); 2.68 – 2.76 (m; 1H); 2.70 – 2.90 (m; 1H); 3.01 – 3.18 (m; 2H); 3.50 – 3.75 (m; 3H); 4.01 – 4.13 (m; 6H).

^13C NMR (100 MHz; CDCl₃) δ (ppm): 10.3; 10.5; 10.6; 10.9; 14.0; 14.1; 16.3; 16.4; 23.1; 23.5; 23.7; 24.0; 28.6; 28.7; 28.8; 28.9; 30.2; 30.3; 30.6; 30.7; 32.7; 37.0; 37.1; 37.2; 37.3; 37.7 – 39.1 (d; J = 132.0 Hz); 38.6; 38.7; 38.9; 50.2; 50.6; 50.9; 51.2; 51.9; 52.4; 60.8; 62.4; 62.5; 63.1; 63.2; 63.3; 167.4; 168.5; 171.3 – 171.5 (dd; J = 18.5 Hz; d = 4.5 Hz).

^31P NMR (160 MHz; CDCl₃) δ (ppm): 23.1.

Synthesis of 6 (3-(N,N-di(2-ethylhexyl)carbamoyl)-3-(ethoxy)hydroxyphosphoryl)-propanoic acid) (TR):

To a solution of 2 in ethanol (0.4 mol/L) was added an aqueous solution of potassium hydroxide (20%; 6 eq). The solution was then heated under reflux for 3 h. After return to room temperature; the mixture was acidified with HCl (1 mol/L) until the solution reached to pH 1; and then extracted with
dichloromethane. The combined extracts were dried over sodium sulphate; filtered and evaporated under vacuum to give the desired compound TR (yield >95%).

$^1$H NMR (400 MHz; CDCl3) δ (ppm): 0.82 – 0.92 (m; 12H); 1.22 – 1.38 (m; 19H); 1.66 – 1.73 (m; 1H); 1.74 – 1.82 (m; 1H); 2.88 – 3.0 (m; 2H); 3.01 – 3.23 (m; 2H); 3.46 – 3.80 (m; 3H); 4.07 – 4.17 (m; 2H); 8.96 (bs; 2H).

$^{13}$C NMR (100 MHz; CDCl3) δ (ppm): 10.3; 10.5; 10.7; 10.8; 14.0; 16.2; 16.3; 23.0; 23.4; 23.6 23.8; 28.5; 28.6; 28.7; 30.2; 30.3; 30.4; 32.9; 37.1; 37.7 – 39.0 (d; J = 132.0 Hz); 38.5; 38.6; 50.4; 50.6; 52.3; 52.8; 62.4 168.8; 174.2 (d; J = 9.0 Hz); 174.4 (d; J = 9.0 Hz).

$^{31}$P NMR (160 MHz; CDCl3) δ (ppm): 24.0.

Nitrogen Adsorption and pore size distribution using BJH model

![Figure S2: Adsorption isotherm of each silica support and pore size distribution of each support calculated by the BJH model.](image-url)
TGA curves

![TGA curve graph](image)

Figure S3: TGA of SBA15 swelled in blue, NH2@SBA15 (in blue) and TR@SBA15 swelled (in red)

SAXS spectra

![SAXS spectra graphs](image)

Figure S4: SAXS spectra from Silica (black), NH2@Silica (blue), TR@Silica (red), for different silica support: A/ MCM41 ; B/ SBA15s ; C/ SBA15
$^{29}$Si MAS NMR

Figure S5 $^{29}$Si MAS NMR spectra of NH$_2$@Silica; silica support: MCM41 (black); SBA15 (red); SBA15s (green); Davisil150 (orange); Vycor (purple)

IR Spectra
Kinetic model: pseudo-second order model

\[ \frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \]

Table S1: Parameters of pseudo-second order model for TR@SBA15 and TR@DAVISIL150 to uranium extraction

<table>
<thead>
<tr>
<th>Material</th>
<th>(k) (g.mol(^{-1}).h(^{-1}))</th>
<th>(q_e) (mmol.g(^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR@SBA15</td>
<td>0.015</td>
<td>19.8</td>
<td>0.999</td>
</tr>
<tr>
<td>TR@DAVISIL150</td>
<td>0.088</td>
<td>15.1</td>
<td>0.999</td>
</tr>
</tbody>
</table>
Thermodynamic models: Langmuir and Freundlich models

Table S2: Parameters of thermodynamic models for all TR@silica materials to uranium extraction

<table>
<thead>
<tr>
<th>Material</th>
<th>$q_{\text{max}}$ (mmol.g$^{-1}$)</th>
<th>$K_l$ (L.mmol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TR@MCM41</td>
<td>0.093</td>
<td>105.7</td>
<td>0.97</td>
</tr>
<tr>
<td>TR@SBA15</td>
<td>0.14</td>
<td>46.2</td>
<td>0.97</td>
</tr>
<tr>
<td>TR@SBA15 s</td>
<td>0.11</td>
<td>54.7</td>
<td>0.97</td>
</tr>
<tr>
<td>TR@DAVISIL 150</td>
<td>0.066</td>
<td>14.05</td>
<td>0.98</td>
</tr>
<tr>
<td>TR@VYCOR</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Langmuir model

$$q_e = \frac{q_{\text{max}} K_l C_e}{1 + K_l C_e}$$

Figure S8: Uranium extraction of SBA15, NH2@SBA15, TR@SBA15.
Figure S9 $^{31}$P (top), and $^{29}$Si (left down) and $^{13}$C (right down) MAS NMR spectra of TR@Silica; silica support: MCM41 (black); SBA15 (red); sSBA15 (green); Davisil150 (orange); Vycor (purple)