

## 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

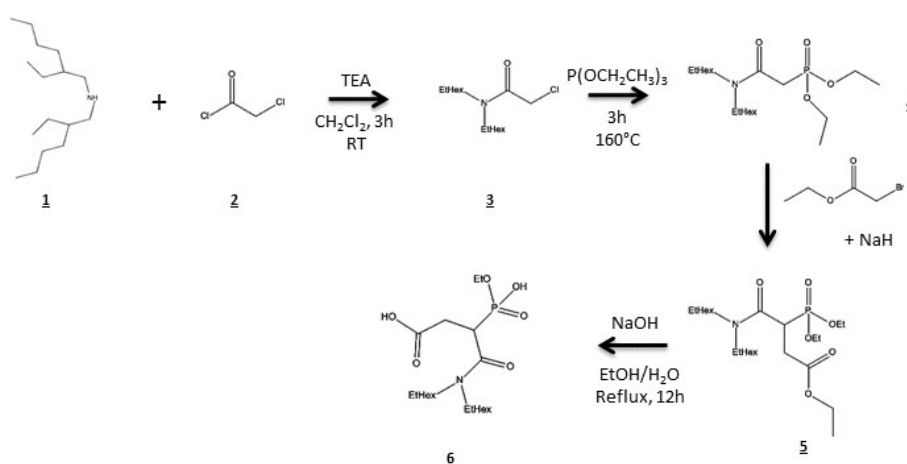


Figure S1 Synthesis of TR molecule

#### 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<sup>-1</sup>). 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%)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(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).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (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 a 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.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ (ppm): 0.81-0.86 (m, 12H, CH<sub>3</sub>) ; 1.21-1.32 (m, 22H) ; 1.51-1.57 (m, 1H) ; 1.64-1.71 (m, 1H) ; 3.02 (d, 2H, CO-CH<sub>2</sub>-P) ; 3.21-3.27 (m, 4H) ; 4.08-4.16 (m, 4H).

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (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.

$^{31}\text{P NMR}$  (160 MHz;  $\text{CDCl}_3$ )  $\delta$  (ppm): 21.8.

### Synthesis of **5** (3-(N;N-di(2-éthylhexyl)carbamoyl)-3-(diéthoxy)phosphono)-ethylpropanoate):

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%).

$^1\text{H NMR}$  (400 MHz;  $\text{CDCl}_3$ )  $\delta$ (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).

$^{13}\text{C NMR}$  (100 MHz;  $\text{CDCl}_3$ )  $\delta$  (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).

$^{31}\text{P NMR}$  (160 MHz;  $\text{CDCl}_3$ )  $\delta$  (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%).

$^1\text{H NMR}$  (400 MHz;  $\text{CDCl}_3$ )  $\delta$  (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).

$^{13}\text{C NMR}$  (100 MHz;  $\text{CDCl}_3$ )  $\delta$  (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).

$^{31}\text{P NMR}$  (160 MHz;  $\text{CDCl}_3$ )  $\delta$  (ppm): 24.0.

### Nitrogen Adsorption and pore size distribution using BJH model

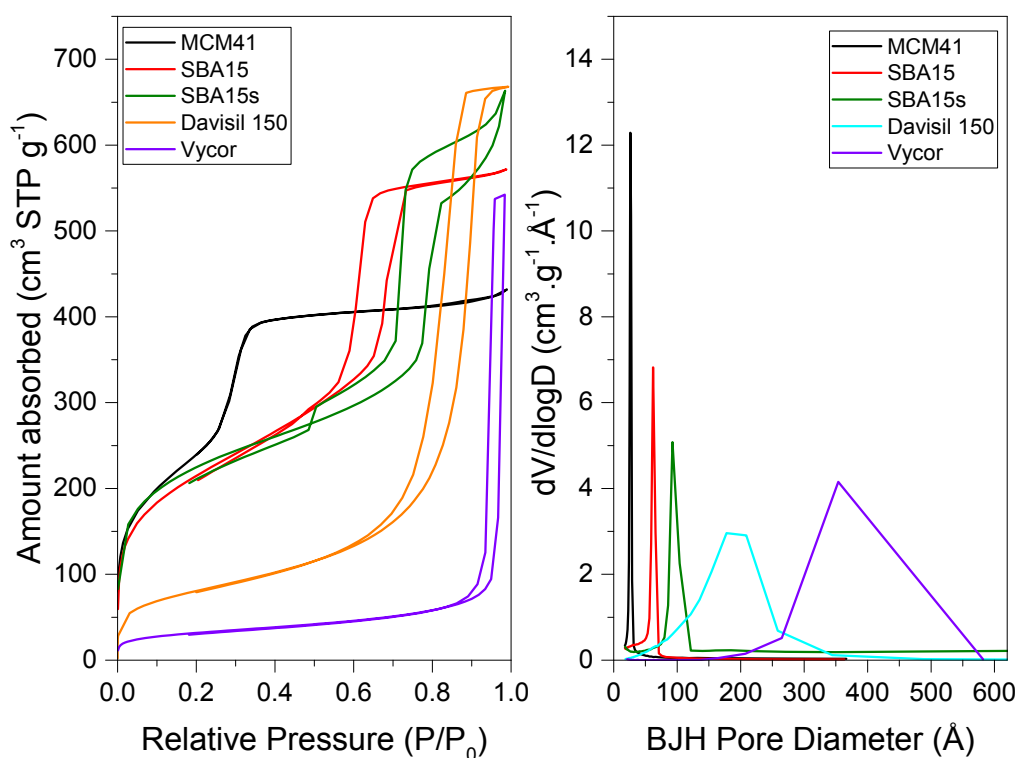


Figure S2: Adsorption isotherm of each silica support and pore size distribution of each support calculated by the BJH model.

## TGA curves

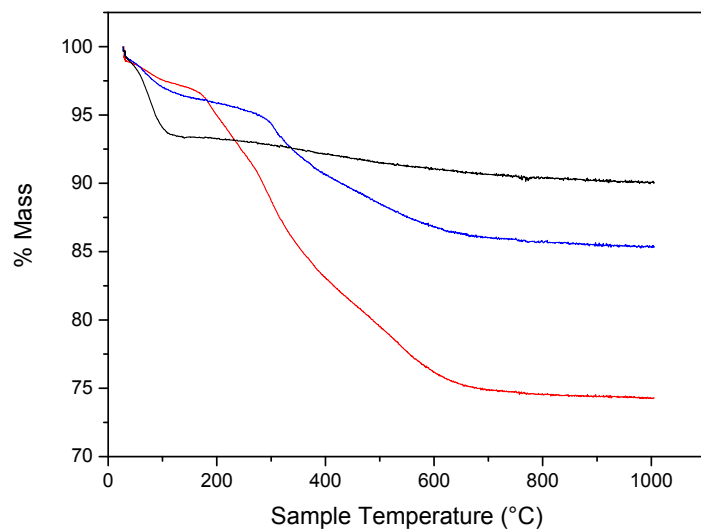


Figure S3: TGA of SBA15 swelled in blue, NH<sub>2</sub>@SBA15 (in blue) and TR@SBA15 swelled (in red)

## SAXS spectra

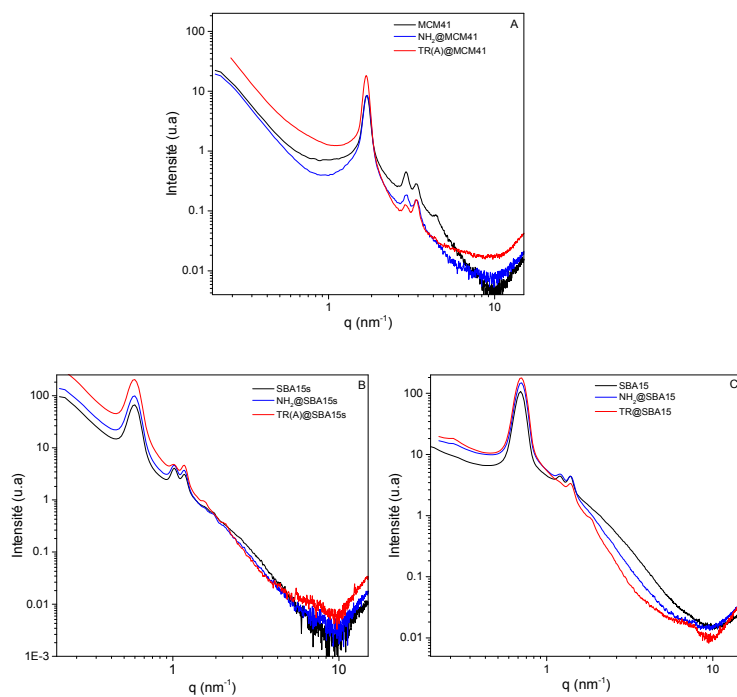


Figure S4: SAXS spectra from Silica (black), NH<sub>2</sub>@Silica (blue), TR@Silica (red), for different silica support: A/ MCM41 ; B/ SBA15s ; C/ SBA15

## $^{29}\text{Si}$ MAS NMR

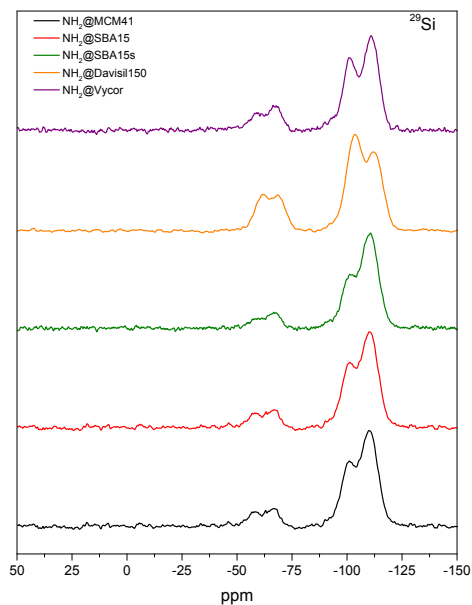


Figure S5  $^{29}\text{Si}$  MAS NMR spectra of NH<sub>2</sub>@Silica; silica support : MCM<sub>41</sub> (black); SBA<sub>15</sub> (red); SBA<sub>15s</sub> (green); Davisil<sub>150</sub> (orange); Vycor (purple)

## IR Spectra

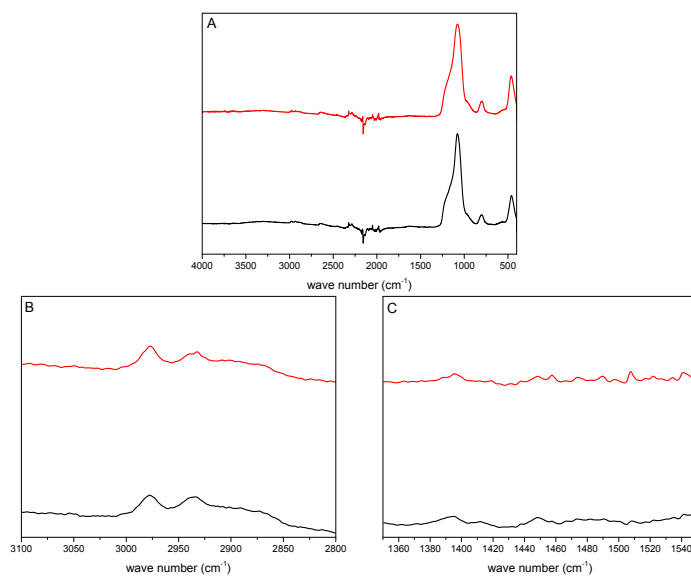


Figure S6 IR spectra of NH<sub>2</sub>@Silica; SBA15 (black); Davisil (orange)

**Kinetic model: pseudo-second order model**

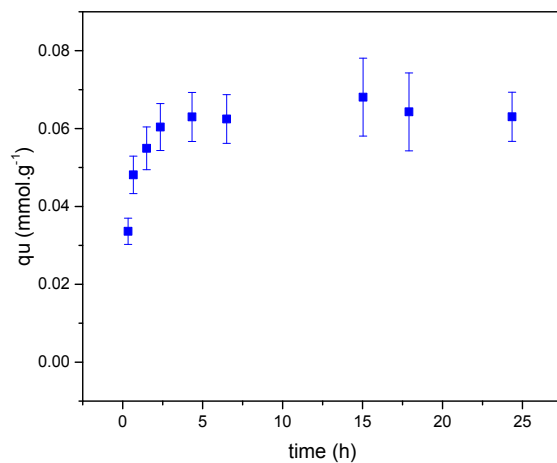


Figure S7: Plot of uranium extracted versus time for TR@SBA15 and TR@DAVISIL150

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

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

Material	k (g.mol <sup>-1</sup> .h <sup>-1</sup> )	q <sub>e</sub> (mmol.g <sup>-1</sup> )	R <sup>2</sup>
TR@SBA15	0.015	19.8	0.999
TR@DAVISIL150	0.088	15.1	0.999

## Thermodynamic models: Langmuir and Freundlich models

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

<b>Langmuir model</b>			
$q_e = \frac{q_{max}K_l C_e}{1 + K_l C_e}$			
Material	$q_{max}$ (mmol.g <sup>-1</sup> )	$K_l$ (L.mmol <sup>-1</sup> )	R <sup>2</sup>
<b>TR@MCM41</b>	0.093	105.7	0.97
<b>TR@SBA15</b>	0.14	46.2	0.97
<b>TR@SBA15 s</b>	0.11	54.7	0.97
<b>TR@DAVISIL 150</b>	0.066	14.05	0.98
<b>TR@VYCOR</b>	-	-	-

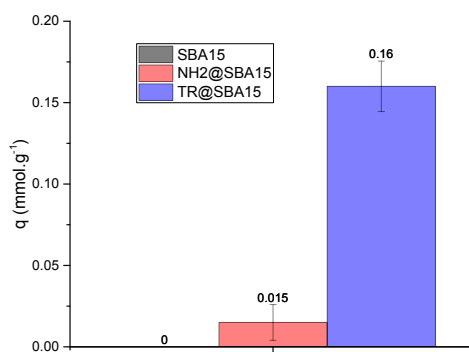


Figure S8 : Uranium extraction of SBA15, NH2@SBA15, TR@SBA15.

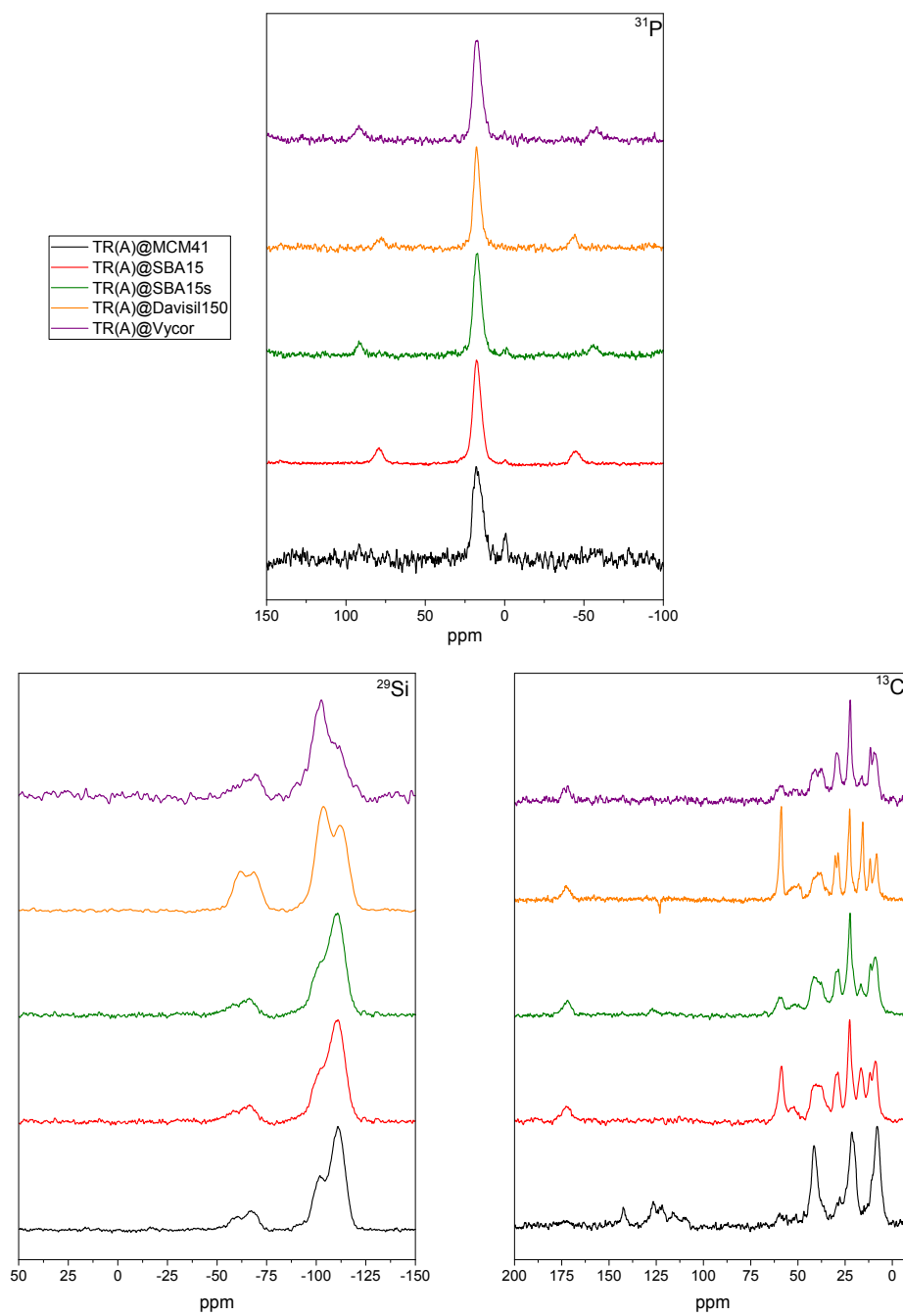


Figure S9  $^{31}\text{P}$  (top), and  $^{29}\text{Si}$  (left down) and  $^{13}\text{C}$  (right down) MAS NMR spectra of TR@Silica; silica support : MCM41 (black); SBA15 (red); sSBA15 (green); Davisil150 (orange); Vycor (purple)