

## SUPPLEMENTARY INFORMATION

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### **Extraction of minor actinides, lanthanides and other fission products by silica-immobilized BTBP/BTPPhen ligands**

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## 1.0 Experimental Procedures

### General procedure

NMR spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Deuterated chloroform ( $\text{CDCl}_3$ ) and Deuterated DMSO (dimethyl sulfoxide- $\text{d}_6$ ) were used as solvents. Chemical shifts ( $\delta$  values) were reported in parts per million (ppm) with the abbreviations s, d, t, q, qn, sx, dd, ddd and br denoting singlet, doublet, triplet, quartet, quintet, sextet, double doublets, doublet of doublets of doublets and broad resonances respectively. Coupling constants ( $J$ ) are quoted in Hertz.

IR spectra were recorded on a Perkin Elmer RX1 FT-IR instrument.

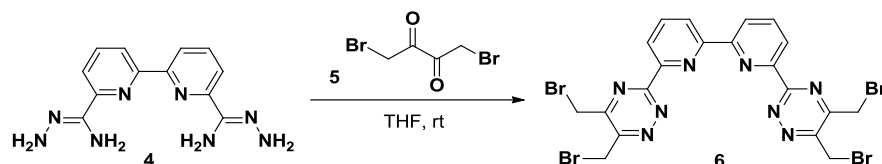
All the melting points were determined on a Gallenkamp melting point apparatus.

Mass spectra ( $m/z$ ) were recorded under conditions of electrospray ionisation (ESI). The ions observed were quasimolecular ions created by the addition of a hydrogen ion denoted as  $[\text{MH}]^+$ . The instrument used was Xcalibur Tune 2.1 (SP1).

The size and morphology of the silica gels at various stages of functionalization were observed by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). For TEM analysis, samples were obtained by placing a drop of colloid solution onto a copper grid and allowing evaporation in air at room temperature.

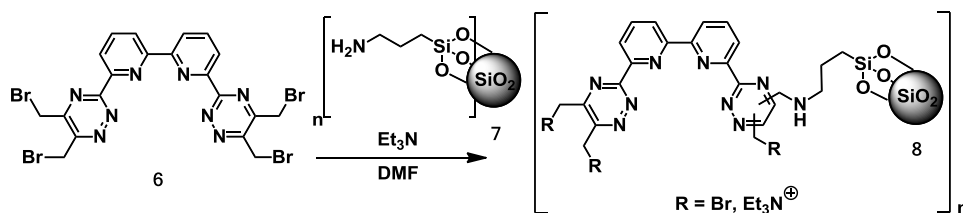
Thermo-gravimetric (TGA) analyses were performed using a TGA-Q50 thermo-gravimetric analyzer.

## 6,6'-bis(5,6-bis(bromomethyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine (**6**)<sup>1,2</sup>



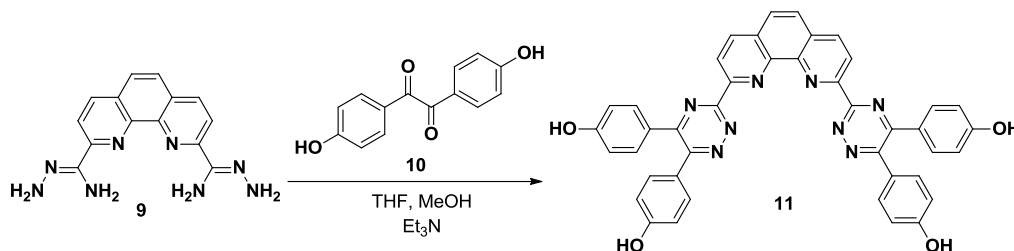
2,2'-Bipyridine-6,6'-dicarbohydrazonamide **4** (10.86 g, 40.2 mmol) was suspended in THF (500 mL) and solid 1,4-dibromobutane-2,3-dione **5** (22.01 g, 90.2 mmol, 2.2 eq) was added. The suspension was stirred at room temperature for 3 days. The insoluble solid was filtered and washed successively with methanol (300 mL), acetone (300 mL) and diethyl ether (300 mL). The solid was allowed to dry in air to afford the title compound **6** as a yellow solid (22.59 g, 82 %). Mp 202–204 °C (decomposed); <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>) δ: 4.82 (s, 4H, 2 × CH<sub>2</sub>Br), 5.04 (s, 4H, 2 × CH<sub>2</sub>Br), 8.13 (t, *J* = 7.8, 2H, 4-H and 4'-H), 8.67 (dd, *J* = 7.8 and 1.0, 2H, 5-H and 5'-H), 8.93 (dd, *J* = 7.8 and 1.0, 2H, 3-H and 3'-H) ppm; <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) δ: 25.7 (2 × CH<sub>2</sub>Br), 27.0 (2 × CH<sub>2</sub>Br), 123.0 (C-3 and C-3'), 124.0 (C-5 and C-5'), 137.3 (C-4 and C-4'), 150.4 (2 × quat), 154.7 (2 × quat), 155.3 (2 × quat), 156.1 (2 × quat), 161.6 (2 × quat) ppm; HRMS (CI) *m/z* 682.8126: calculated for [C<sub>20</sub>H<sub>14</sub>N<sub>8</sub>Br<sub>4</sub> + H]<sup>+</sup> 682.8153; IR  $\nu_{\max}$  / cm<sup>-1</sup> = 3087, 3037, 3014, 1576, 1557, 1517, 1442, 1425, 1406.

## Immobilization of 6,6'-bis(5,6-bis(bromomethyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine (**6**) on silica gel



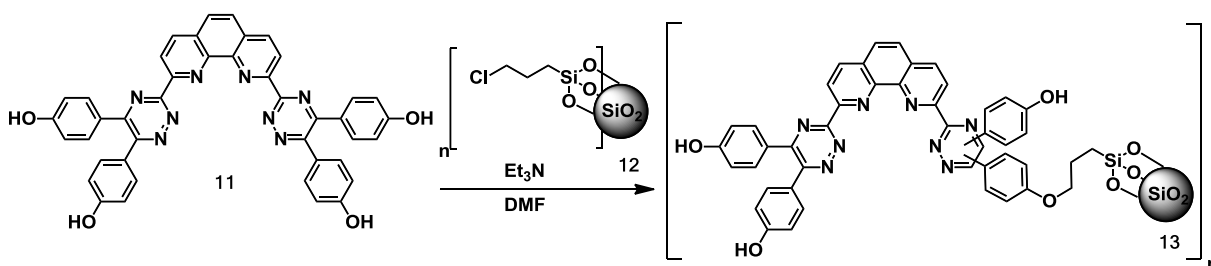
Triethylamine (22 mL, 156.7 mmol) was added to a suspension of aminopropyl-functionalized SiO<sub>2</sub> gel **7** (50 g, ~ 1 mmol/g NH<sub>2</sub> loading) in DMF (500 mL) at 120 °C and stirred for 30 min. 6,6'-bis(5,6-bis(bromomethyl)-1,2,4-triazin-3-yl)-2,2'-bipyridine **6** (17.91 g, 26.1 mmol) was slowly added and the reaction mixture was stirred at 120 °C overnight. BTBP-functionalized SiO<sub>2</sub> gel **8** was collected by filtration and was thoroughly washed with water (3×100 mL) and ethanol (3×100 mL). Finally, the functionalized SiO<sub>2</sub> gel **8** (58.58 g) was allowed to dry at 120 °C.

### Tetra(4-hydroxyphenyl)BTPhen (**11**)<sup>3-6</sup>



To a suspension of 1,10-phenanthroline-2,9-dicarbohydrazonamide (0.60 g, 2 mmol) in THF (100 mL) and MeOH (100 mL) was added 4,4'-dihydroxybenzil **10** (1.10 g, 4.6 mmol, 2.3 eq). Triethylamine (50 mL, 356.2 mmol) was added and the mixture was heated at 81 °C for 3 days. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with DCM (25 mL). The filtrate was evaporated and the solid was triturated with MeOH (100 mL). The insoluble solid was filtered and washed with further MeOH (50 mL) and Et<sub>2</sub>O (50 mL) and allowed to dry in air to afford the ligand **11** as a yellow solid (0.99 g, 69 %); Mp 280–282 °C (decomposed); <sup>1</sup>H NMR (400.1 MHz, DMSO-*d*<sub>6</sub>) δ<sub>H</sub> (ppm) = 6.78-6.93 (m, 8H), 7.51-7.71 (m, 8H), 8.11 (s, 2H), 8.58 (d, *J* = 8.0 Hz, 2H), 8.61 (d, *J* = 8.0 Hz, 2H); <sup>13</sup>C NMR (100.6 MHz, DMSO-*d*<sub>6</sub>) δ<sub>C</sub> (ppm) = 115.4, 122.9, 125.5, 126.1, 127.7, 129.5, 130.7, 131.6, 137.7, 145.5, 152.6, 154.6, 155.3, 159.0, 159.6, 160.5; C<sub>42</sub>H<sub>27</sub>O<sub>4</sub>N<sub>8</sub> [MH]<sup>+</sup> requires *m/z* 707.2150; (FTMS + P ESI) MS found *m/z* 707.2153; IR ν<sub>max</sub> / cm<sup>-1</sup> = 3206, 1608, 1590, 1483, 1442, 1377, 1276, 1240, 1169.

### Immobilization of tetra(4-hydroxyphenyl)BTPhen (**11**) on silica gel

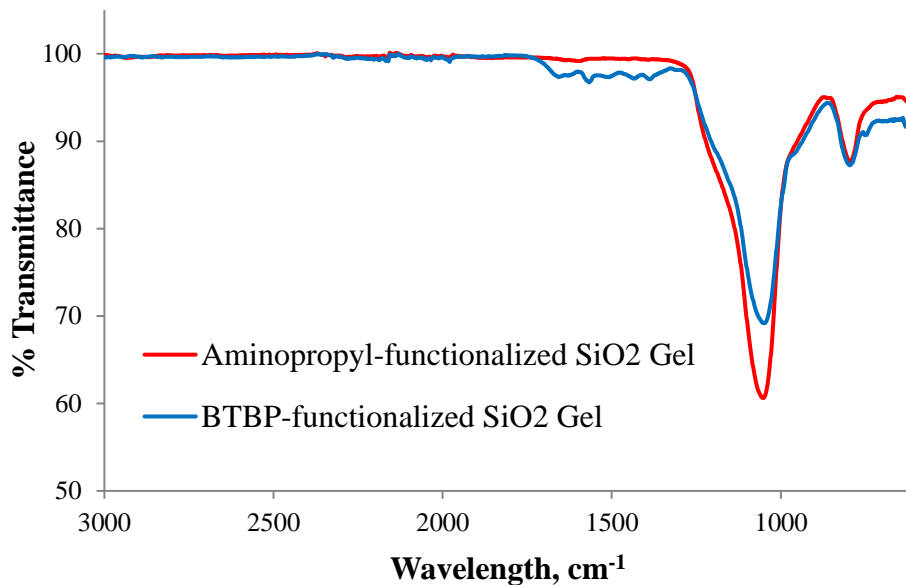


Sodium hydride (60 % dispersion in mineral oil, 0.24 g, 6 mmol, 2 eq) was added to a solution of tetra(4-hydroxyphenyl)BTPhen **11** (2.11 g, 3.0 mmol) in DMF (100 mL) at 120 °C and stirred for 30 min. Chloropropyl-functionalized SiO<sub>2</sub> gel **12** (4.04 g, ~ 2.5 mmol/g loading) was slowly added and the reaction mixture was stirred at 120 °C overnight. BTPhen-functionalized SiO<sub>2</sub> gel **13** was

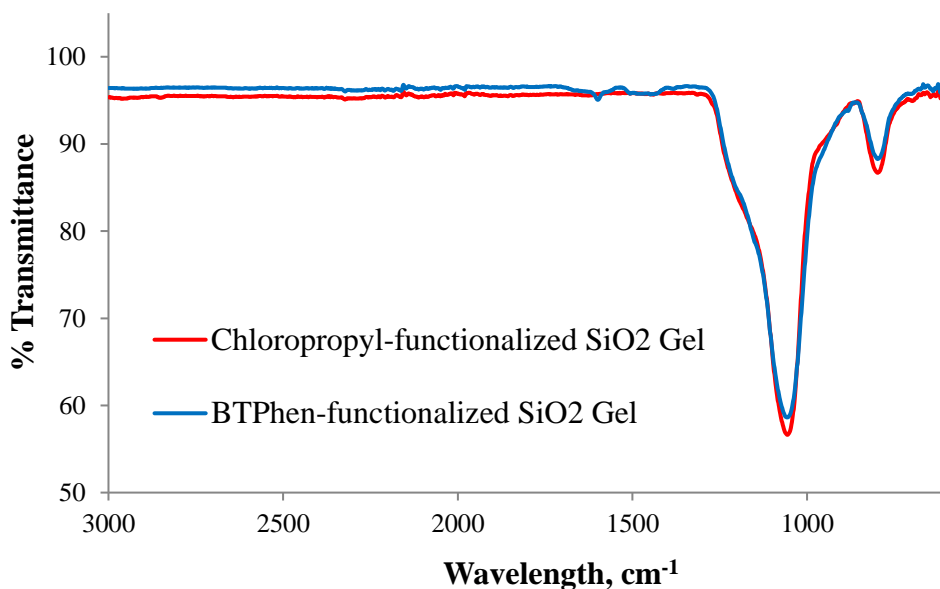
collected by filtration and was thoroughly washed with water (1×100 mL) and ethanol (1×100 mL). Finally, the product (3.95 g) was allowed to dry at 120 °C.

## 2.0 Characterization

### FT-IR spectra

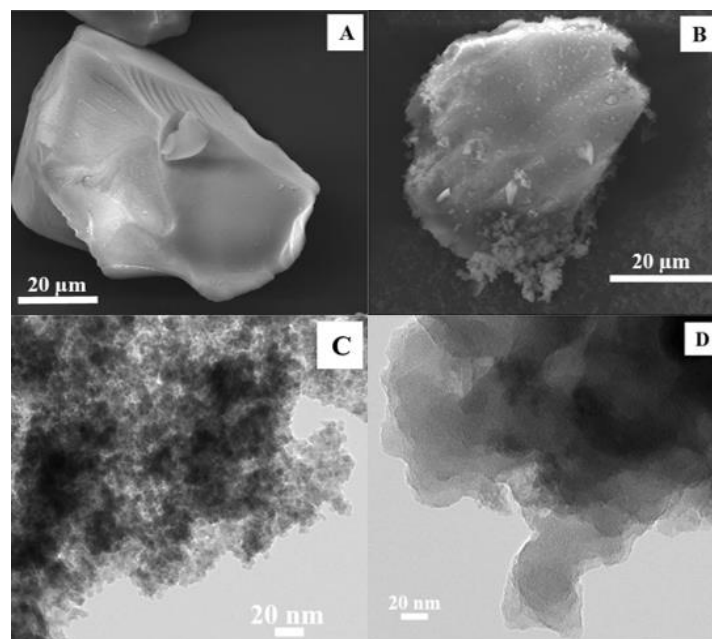


**Figure S1.** FR-IR spectra of aminopropyl-functionalized SiO<sub>2</sub> gel **7** and BTBP-functionalized SiO<sub>2</sub> gel **8**.

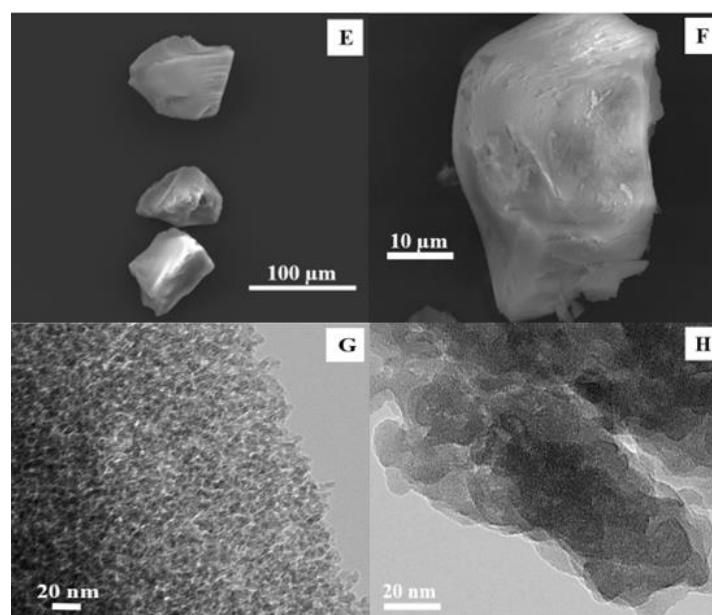


**Figure S2.** FR-IR spectra of chloropropyl-functionalized SiO<sub>2</sub> gel **12** and BTPPhen-functionalized SiO<sub>2</sub> gel **13**.

## SEM/TEM images



**Figure S3.** SEM images (A, B) and TEM images (C, D) of aminopropyl-functionalized SiO<sub>2</sub> gel **7** (A, C) and BTBP-functionalized SiO<sub>2</sub> gel **8** (B, D).



**Figure S4.** SEM images (E, F) and TEM images (G, H) of chloropropyl-functionalized SiO<sub>2</sub> gel **12** (E, G) and BTPPhen-functionalized SiO<sub>2</sub> gel **13** (F, H).

## Elemental Analysis

**Table S1** Results of elemental analysis for aminopropyl-functionalized SiO<sub>2</sub> gel **7** and BTBP-functionalized SiO<sub>2</sub> gel **8**.

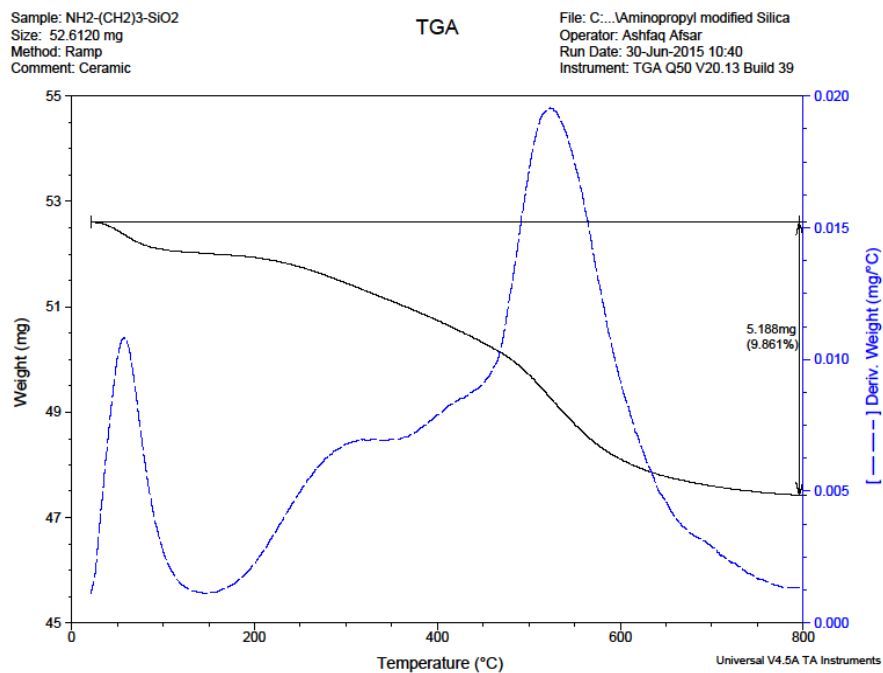
	Aminopropyl Modified SiO <sub>2</sub> Gel	BTBP Modified SiO <sub>2</sub> Gel
<b>C (%)</b>	5.04	14.43
<b>H (%)</b>	1.50	1.92
<b>N (%)</b>	1.63	5.48
<b>Br (%)</b>	-	2.68

**Table S2** Results of elemental analysis for chloropropyl-functionalized SiO<sub>2</sub> gel **12** and BTPhen-functionalized SiO<sub>2</sub> gel **13**.

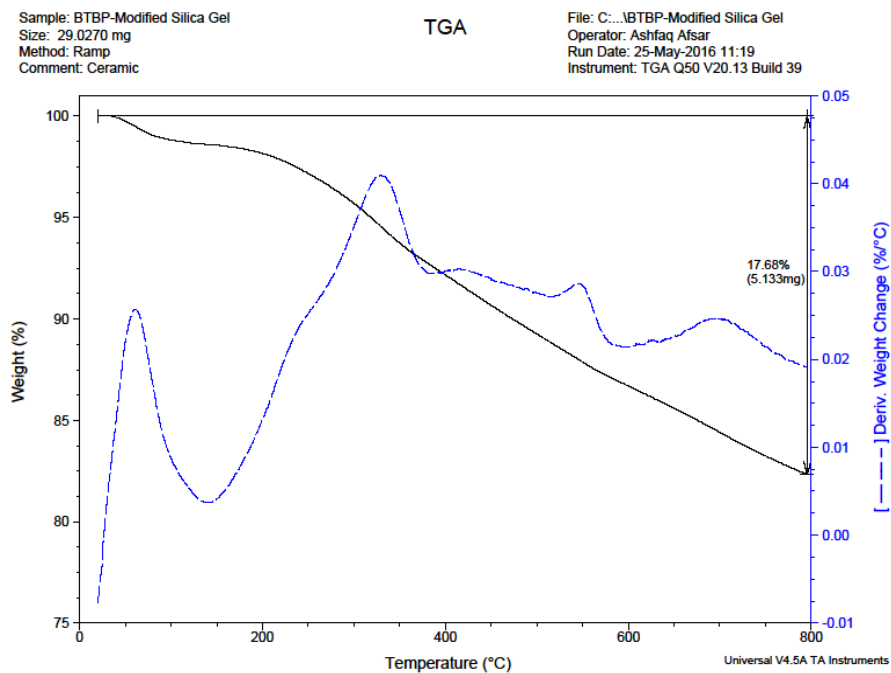
	Chloropropyl Modified SiO <sub>2</sub> Gel	BTPhen Modified SiO <sub>2</sub> Gel
<b>C (%)</b>	5.05	8.10
<b>H (%)</b>	1.22	1.28
<b>N (%)</b>	-	1.08
<b>Cl (%)</b>	3.61	0.49



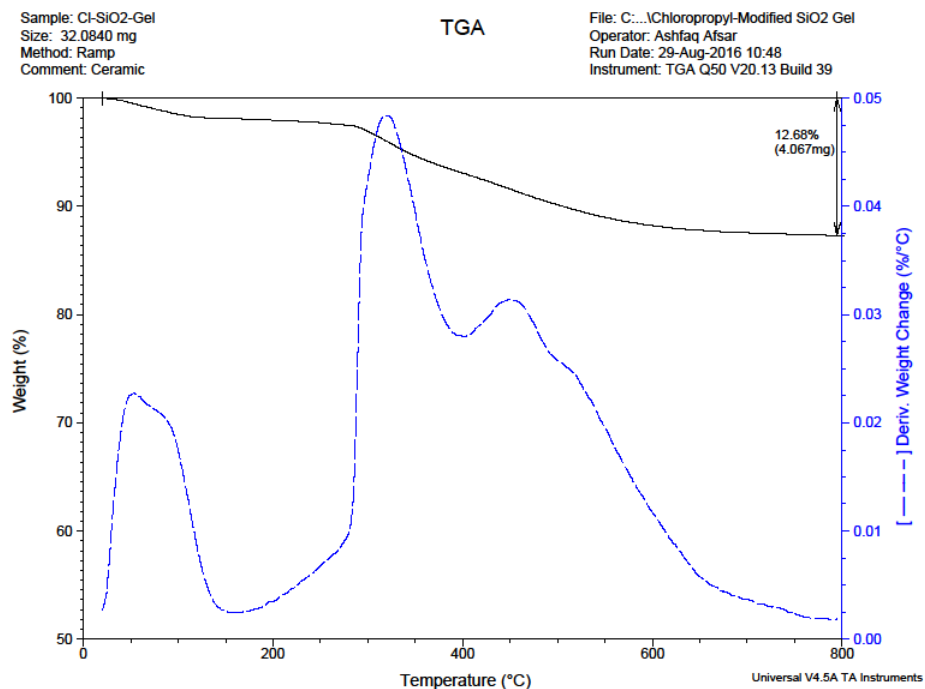
## Thermal-gravimetric analysis



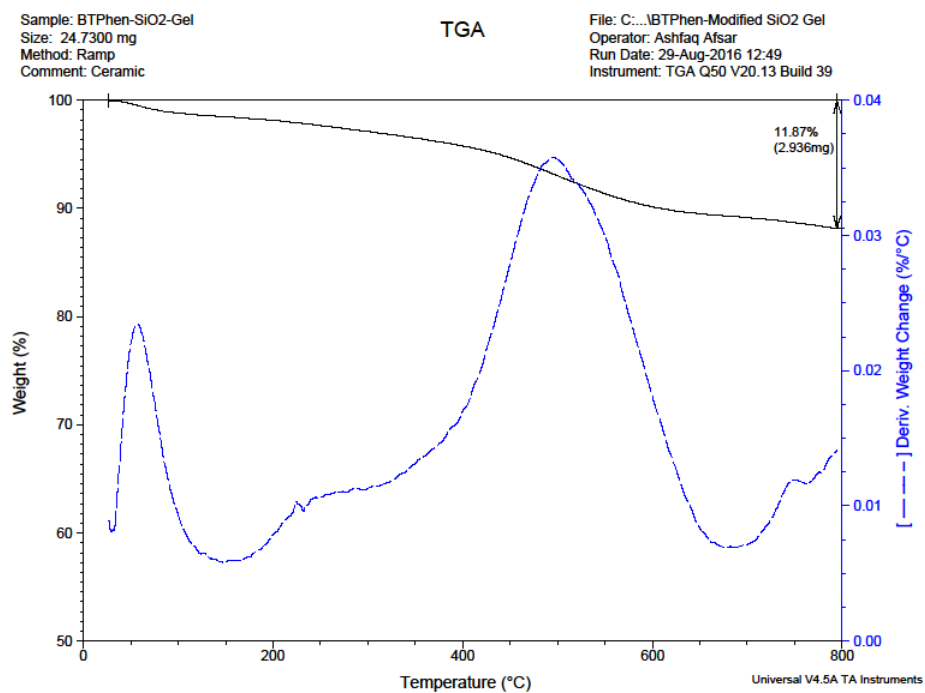
**Figure S5.** TGA curve of aminopropyl-functionalized SiO<sub>2</sub> gel 7.



**Figure S6.** TGA curve of BTBP-functionalized SiO<sub>2</sub> gel 8.



**Figure S7.** TGA curve of chloropropyl-functionalized SiO<sub>2</sub> gel **12**.



**Figure S8.** TGA curve of BTPPhen-functionalized SiO<sub>2</sub> gel **13**.

### 3.0 Extraction Data

#### General Procedure

ICP-MS analysis was run on a Thermo-Fisher iCAP Q ICP-MS with Rh as the internal standard. Standard solutions were prepared using a stock solution of 2% HNO<sub>3</sub> spiked with 5 ppb Rh. Standards were made using various metal mixes purchased from Sigma-Aldrich as TraceCERT (Traceable Certified Reference Materials). Standards used to calibrate the ICP-MS were 10, 25, 50 and 100 ppb. A 3.8 cm diameter glass column was loaded with 10 g of BTBP-functionalized SiO<sub>2</sub> gel **8** and rinsed with 100 mL 2% HNO<sub>3</sub> blank solution. A solution of 100 mL of 100 ppb metal mix solution was eluted through the column at a rate of 10 mL per minute and fractions of 10 mL were collected and 2 mL aliquots were taken from each fraction for measurement using the ICP-MS. An average of three readings was taken.

The aqueous solutions for the solid phase extraction experiments were prepared by spiking nitric acid solutions (0.001 – 4 M) with stock solutions of <sup>241</sup>Am and <sup>152</sup>Eu and then adding 1 mL of spiked aqueous solution to 14 mg of BTBP-functionalized SiO<sub>2</sub> gel **8** or 17 mg of BTPPhen-functionalized SiO<sub>2</sub> gel **13**. The suspension was sonicated for 10 min and shaken at 1800 rpm for 90 min. After centrifuging for 10 min, aliquots of the supernatant were separated and taken for gamma measurements. The weight distribution ratios is defined as  $D_w = (A_0 - A)/A \cdot V/m$ , where  $A_0$  and  $A$  were initial and final number of counts in the taken standard/aliquot,  $V$  is a volume of an aqueous phase shaken and  $m$  is a mass of the material **8** or **13**. The separation factor is  $SF_{Am/Eu} = D_{wAm} / D_{wEu}$ . All extraction experiments were carried out in duplicate and error bars in the figures represent standard deviations.

**Table S3.** Extraction of Am(III) and Eu(III) by BTBP-functionalized SiO<sub>2</sub> gel **8** as a function of nitric acid concentration.

c(HNO <sub>3</sub> )	D(Am)			D(Eu)			SF(Am/Eu)		
0.001	0.361	+/-	0.015	0.011	+/-	0.011	32	+/-	17
0.1	1.301	+/-	0.028	0.007	+/-	0.007	193	+/-	171
1	0.259	+/-	0.014	0.006	+/-	0.006	46	+/-	45
4	0.049	+/-	0.012	0.007	+/-	0.007	8	+/-	7

**Table S4.** Extraction of Am(III) and Eu(III) by BTPPhen-functionalized SiO<sub>2</sub> gel **13** as a function of nitric acid concentration.

<b>c(HNO<sub>3</sub>)</b>	<b>D<sub>g</sub>(Am)</b>			<b>D<sub>g</sub>(Eu)</b>			<b>SF(Am/Eu)</b>		
0.001	94	+/-	3	136	+/-	5	0.69	+/-	0.04
0.1	4883	+/-	974	630	+/-	51	7.7	+/-	1.7
1	250	+/-	12	4.2	+/-	0.4	60	+/-	6
4	28	+/-	1	≈ 0.2			≈ 140		

## 4.0 References

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