SUPPLEMENTARY INFORMATION

Separation of minor actinides from lanthanides using immobilized ligand systems: the role of the counterion

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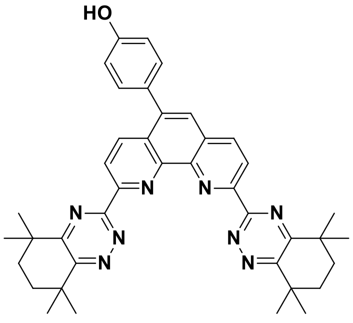
1.0 Experimental Procedures

General procedure

NMR spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Deuterated chloroform ($CDCl_3$) and Deuterated DMSO (dimethyl sulfoxide-d_6) were used as solvents. Chemical shifts (δ 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 $[MH]^+$. The instrument used was Xcalibur Tune 2.1 (SP1). Thermo-gravimetric (TGA) analyses were performed using a TGA-Q50 thermo-gravimetric analyzer.

4-(2,9-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthrolin-5-yl)phenol (6)[1,2]

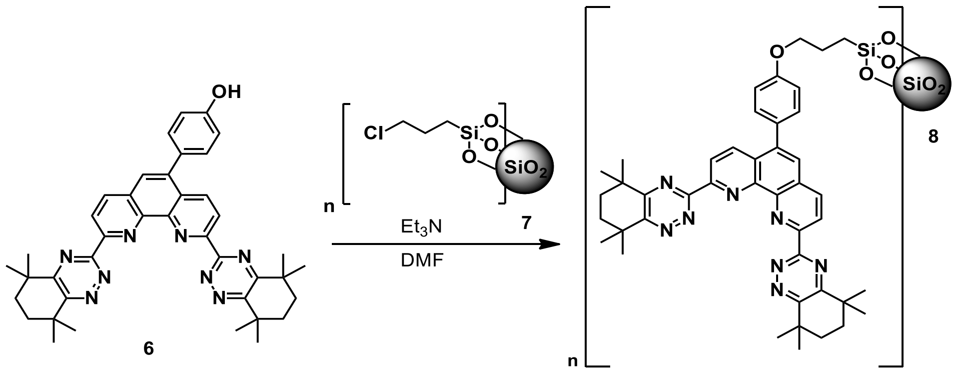


6

A suspension of 5-bromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline[1,2] (0.51 g, 0.8 mmol), tetrakis(triphenylphosphane)palladium(0) (0.04 g, 0.04 mmol, 0.05 eq), (4-hydroxyphenyl)boronic acid (0.13 g, 0.9 mmol, 1.1 eq) and K_2CO_3 (0.15 g, 1.1 mmol, 1.4 eq) in degassed EtOH (75 mL) was heated to reflux for 18 h under nitrogen. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with EtOH (20 mL). The filtrate was evaporated and the solid residue was taken up in DCM (150 mL) and water (100 mL) was added. The organic layer was washed with saturated brine (100 mL) and dried over $MgSO_4$. The filtrate was evaporated and the solid was triturated with Et_2O (100 mL).

The insoluble solid was filtered and washed with Et_2O (50 mL) and allowed to dry in air to afford **6** as a yellow solid (0.31 g, 59 %); Mp (250-252 °C); ^1H NMR (400.1 MHz, $CDCl_3$) δ_H (ppm) = 1.58 (s, 12H), 1.61 (s, 12H), 1.93 (s, 8H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.76 (d, *J* = 8.8 Hz, 1H), 8.87 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C (ppm) = 29.3, 29.9, 33.8, 36.7, 37.6, 115.6, 122.9, 123.7, 127.0, 128.2, 129.5, 129.5, 130.0, 136.3, 137.3, 140.2, 145.3, 146.5, 153.2, 153.3, 157.7, 161.0, 161.3, 163.5, 163.6, 165.2, 165.3; $C_{40}H_{43}N_8O$ $[MH]^+$ requires $^m/_z$ 651.3554; (FTMS + p ESI) MS found $^m/_z$ 651.3553; IR ν_{max} / cm^{-1}= 3399, 2962, 2931, 2865, 1611, 1587, 1514, 1471, 1456, 1389, 1365.

Immobilization of (4-hydroxyphenyl) functionalized CyMe$_4$-BTPhen ligand (6) on silica gel



Sodium hydride (60 % dispersion in mineral oil, 0.10 g, 2.5 mmol, 3 eq) was added to a solution of tetra(4-hydroxyphenyl)BTPhen **6** (0.50 g, 0.8 mmol) in DMF (25 mL) at 120 °C and stirred for 30 min. Chloropropyl-functionalized SiO_2 gel **7** (0.32 g, ~ 2.5 mmol/g loading) was slowly added and the reaction mixture was stirred at 120 °C overnight. BTPhen-functionalized SiO_2 gel **8** was collected by filtration and was thoroughly washed with water (50 mL) and ethanol (50 mL). Finally, the product (0.38 g) was allowed to dry at 120 °C.

2.0 Characterization

FT-IR spectra

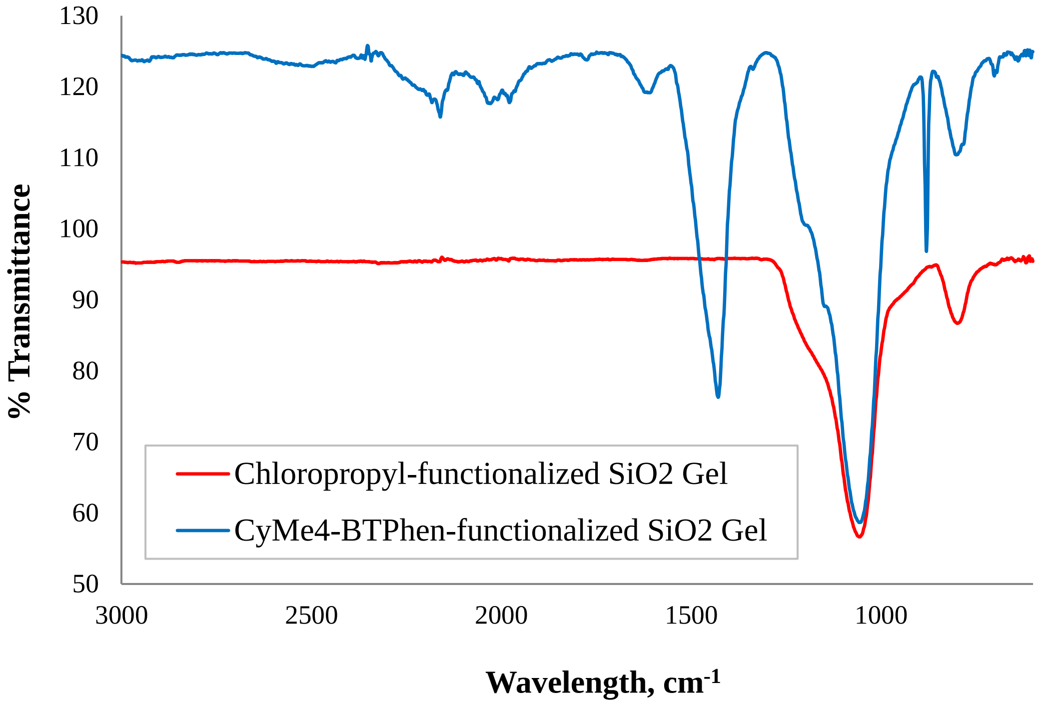


Figure S1. FR-IR spectra of chloropropyl-functionalized SiO_2 gel **7** and $CyMe_4$-BTPhen-functionalized SiO_2 gel **8**.

Elemental Analysis (EA)

Table S1 Results of elemental analysis for chloropropyl-functionalized SiO_2 gel **7** and $CyMe_4$-BTPhen -functionalized SiO_2 gel **8**.

	Chloropropyl Modified SiO_2 Gel	**$CyMe_4$-BTPhen Modified SiO_2 Gel**
C (%)	5.05	11.64
H (%)	1.22	2.00
N (%)	-	1.40
Cl (%)	3.61	< 0.10

Thermal-gravimetric analysis (TGA)

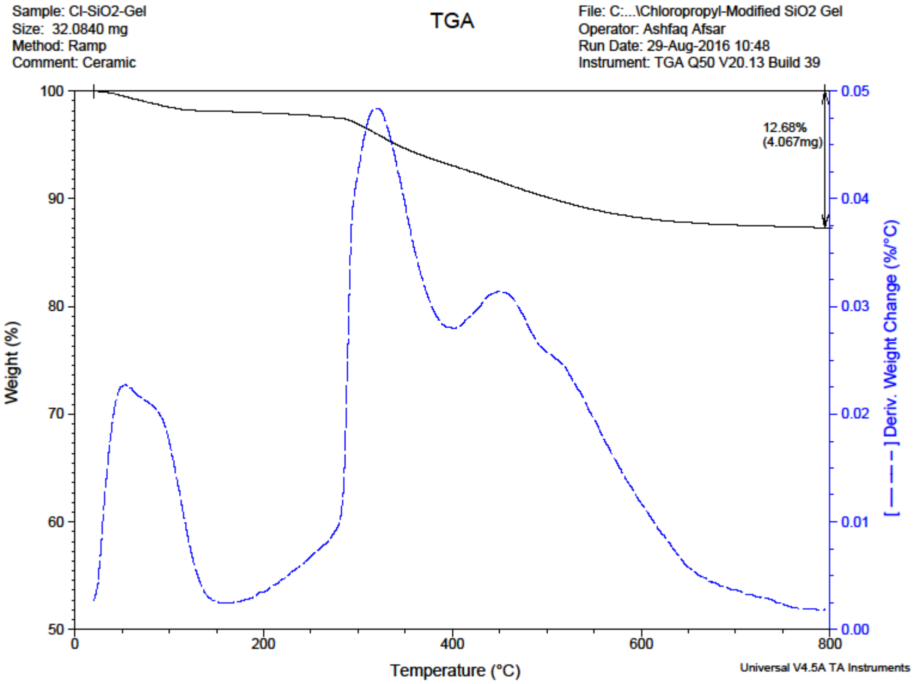


Figure S2. TGA curve of chloropropyl-functionalized SiO_2 gel **7**.

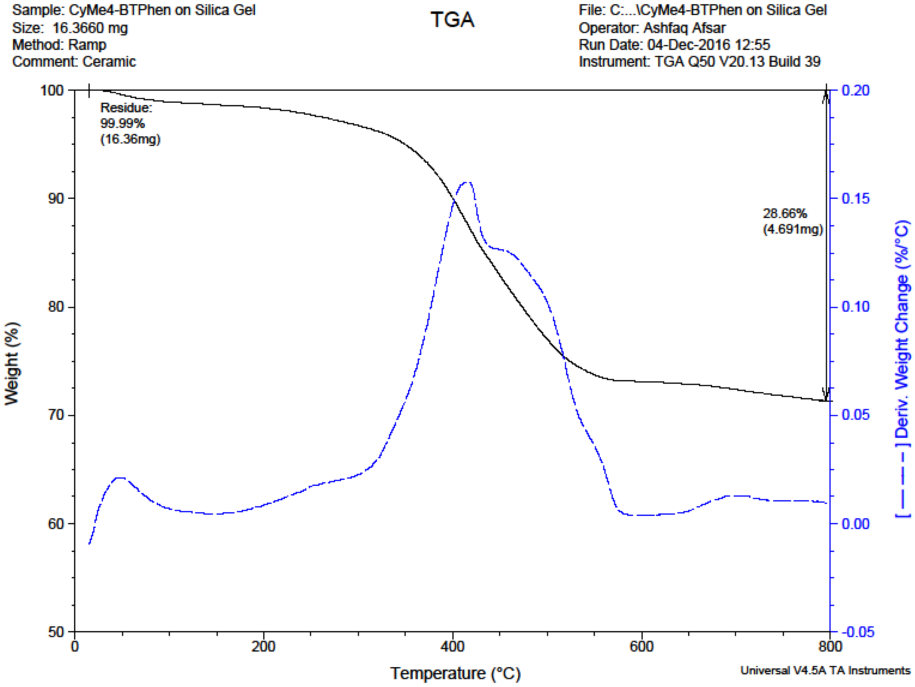


Figure S3. TGA curve of $CyMe_4$-BTPhen-functionalized SiO_2 gel **8**.

3.0 Extraction Data

General Procedure

The aqueous solutions for the immobilized ligand extraction experiments were prepared by spiking nitric acid (HNO_3) and perchloric acid ($HClO_4$) solutions (0.001 – 4 M) with stock solutions of ^{241}Am and ^{152}Eu and then adding 1 mL of the spiked aqueous solution to an accurately weighed amount of CyMe$_4$-BTPhen-functionalized SiO_2 gel **8** or CyMe$_4$-BTPhen-functionalized SiO_2-coated MNPs **4**. The suspensions were 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 are defined as $D_w = (I_0 - I)/I \cdot V/m$, where I_0 and I were initial and final count rates in the taken standard/aliquot, V is a volume of an aqueous phase shaken and m is a mass of the material **8** or **4**. 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 S2. Extraction of Am(III) and Eu(III) by CyMe$_4$-BTPhen-functionalized SiO_2 gel **8** as a function of nitric acid concentration.

c(HNO_3)	**D_{wAm}**			**D_{wEu}**			**$SF_{Am/Eu}$**		
0.001	183	+/-	6	165	+/-	6	1.11	+/-	0.05
0.1	11630	+/-	2033	5618	+/-	720	2.1	+/-	0.4
1	3813	+/-	384	63.9	+/-	2.3	60	+/-	6
4	354	+/-	12	< 2.3			> 154		

Table S3. Extraction of Am(III) and Eu(III) by CyMe$_4$-BTPhen-functionalized SiO_2 gel **8** as a function of perchloric acid concentration.

c($HClO_4$)	**D_{wAm}**			**D_{wEu}**			**$SF_{Am/Eu}$**		
0.001	221	+/-	9	145	+/-	5	1.50	+/-	0.10
0.1	6864	+/-	1298	312	+/-	14	22.0	+/-	2.6
1	285	+/-	13	2.4	+/-	0.9	119	+/-	27
4	< 2.0			< 2.1			≈ 1		

Table S4. Extraction of Am(III) and Eu(III) by CyMe$_4$-BTPhen-functionalized SiO$_2$-coated MNPs **4** as a function of nitric acid concentration.[1]

c(HNO$_3$)	D_{wAm}			D_{wEu}			$SF_{Am/Eu}$		
0.001	1162.8	±	79.1	701.4	±	32.4	1.7	±	0.1
0.1	1857.0	±	153.5	101.1	±	2.3	18.4	±	1.6
1	623.1	±	31.2	9.6	±	0.6	65.2	±	5.0
4	55.4	±	1.5	0.03	±	0.4	1675.6	±	335.1

Table S5. Extraction of Am(III) and Eu(III) by CyMe$_4$-BTPhen-functionalized SiO$_2$-coated MNPs **4** as a function of perchloric acid concentration.

c(HClO$_4$)	D_{wAm}			D_{wEu}			$SF_{Am/Eu}$		
0.001	40	+/-	1	23	+/-	1	1.75	+/-	0.06
0.1	153	+/-	6	18	+/-	1	8.4	+/-	0.3
1	2.5	+/-	0.7	< 1.9			> 1.3		
4	All Am in aqueous phase			All Eu in aqueous phase			N/A		

Table S6. Extraction of Am(III) and Eu(III) by CyMe$_4$-BTPhen-functionalized SiO$_2$ gel **8** as a function of perchloric acid / nitric acid concentration.

c(HNO$_3$)	*c(HClO$_4$)*	*c(H$^+$)*	*c(NO$_3^-$)*	*c(ClO$_4^-$)*	D_{wAm}			D_{wEu}			$SF_{Am/Eu}$		
0.001	0.001	0.001	0.0005	0.0005	297	+/-	9	116	+/-	2	2.6	+/-	0.1
0.1	0.1	0.1	0.05	0.05	7856	+/-	1114	1354	+/-	70	5.8	+/-	0.9
1	1	1	0.5	0.5	1513	+/-	96	22	+/-	0.7	69	+/-	5
2	2	2	1	1	631	+/-	28	5.1	+/-	0.5	124	+/-	14

4.0 References

1 A. Afsar, L. M. Harwood, M. J. Hudson, P. Distler and J. John, *Chem. Commun.*, 2014, **50**, 15082–15085.

2 A. Afsar, L. M. Harwood, M. J. Hudson, J. Westwood and A. Geist, *Chem. Commun.*, 2015, **51**, 5860–5863.