SUPPLEMENTARY INFORMATION

Effective separation of Am(III) and Eu(III) from HNO₃ solutions using CyMe₄-BTPhen-functionalized silica-coated magnetic nanoparticles

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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 (CDCl₃) and Deuterated DMSO (dimethyl sulfoxide-d₆) 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 as Nujol_® mulls (N) 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).

The size and morphology of the MNPs at various stages of functionalization were observed by Philips/FEI CM20 transmission electron microscopy and 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.

Iodoalkyl-functionalized silica coated magnetic nanoparticles (3)



Complete precipitation of Fe₂O₃ was achieved under alkaline conditions, while maintaining a molar ratio of Fe²⁺:Fe³⁺ = 1:2 under nitrogen. To obtain 0.7 g of γ -Fe₂O₃ MNPs **1**, FeCl₂.4H₂O (0.8 g, 4 mmol) and FeCl₃ (1.3 g, 8 mmol) dissolved in degassed deionized water 40 mL were added dropwise into 2M NaOH solution (200 mL) with vigorous stirring. After 1 hour, the resulting γ -Fe₂O₃ MNPs **1** were separated by putting the vessel on a neodymium magnet and decaying the supernatant. The MNPs **1** were washed with degassed deionized water (2×100 mL) and 0.01M HCl (17 %, 100 mL) to remove unreacted iron salts. γ -Fe₂O₃ MNPs **1** were coated with SiO₂ using a solgel method. Typically, 0.7 g of γ -Fe₂O₃ MNPs **1** were dispersed in a mixed solution of degassed ethanol (400 mL) and degassed deionized water (100 mL) by sonication for 10 min. NH₄OH (35 %, 36 mL) and tetraethyl orthosilicate (3.6 mL, 16 mmol) were consecutively added to reaction mixture and the reaction was allowed to proceed at room temperature for 2 h under continuous sonication. 3-iodopropyltrimethoxysilane (6.3 mL, 32 mmol) was then added and the reaction was allowed to proceed for further 3 h. The resultant functionalized particles **3** were obtained by magnetic separation and thoroughly washed with degassed ethanol (2×100mL). Finally the resultant yellow powder (2.3 g) was dried at 120 °C.

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 (4)



To a suspension of 5-bromo-1,10-phenanthroline-2,9-dicarbohydrazonamide (1.47 g, 3.9 mmol) in 1,4-dioxane (200 mL) was added 3,3,6,6-tetramethylcyclohexane-1,2-dione (1.72 g, 10.2 mmol, 2.6 eq). Triethylamine (6 mL, 42.7 mmol) was added and the mixture was heated under reflux for 3

days. After allowing the solution to cool to room temperature, the solvent was evaporated and the remaining semi-solid residue was triturated with ice-cold Et₂O (400 mL). The insoluble solid was filtered and washed with further ice-cold Et₂O (400 mL) and allowed to dry in air to afford the **4** as a yellow solid (1.23 g, 49 %); Mp (197-200 °C); ¹H NMR (400.1 MHz, CDCl₃) $\delta_{\rm H}$ (ppm) = 1.54 (s, 12H), 1.56 (s, 12H), 1.90 (s, 8H), 8.29 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.86 (d, *J* = 8.4 Hz, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.95 (d, *J* = 9.4 Hz, 1H); ¹³C NMR (100.6 MHz, CDCl₃) $\delta_{\rm C}$ (ppm) = 29.3, 29.8, 33.6, 33.8, 36.7, 37.5, 122.0, 124.0, 124.1, 128.9, 129.8, 130.6, 136.3, 137.3, 146.0, 146.9, 154.4, 154.7, 161.1, 161.3, 163.3, 163.4, 165.0, 165.1; C₃₄H₃₇N₈Br [MH]⁺ requires ^m/_z 637.2397 and 639.2377; (FTMS + p ESI) MS found ^m/_z 637.2392 and 639.2371; IR v_{max} / cm⁻¹= 3531, 3486, 2959, 2927, 2865, 1644, 1609, 1510, 1475, 1452, 1439.

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 (5)



A suspension of 5-bromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3yl)-1,10-phenanthroline (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 K₂CO₃ (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 MgSO₄. The filtrate was evaporated and the solid was triturated with Et₂O (100 mL). The insoluble solid was filtered and washed with Et₂O (50 mL) and allowed to dry in air to afford **5** as a yellow solid (0.31 g, 59 %); Mp (250-252 °C); ¹H NMR (400.1 MHz, CDCl₃) $\delta_{\rm H}$ (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); ¹³C NMR (100.6 MHz, CDCl₃) $\delta_{\rm C}$ (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; C₄₀H₄₃N₈O [MH]⁺ requires m/_z 651.3554; (FTMS + p ESI) MS found m/_z 651.3553; IR $v_{\rm max}$ / cm⁻¹= 3399, 2962, 2931, 2865, 1611, 1587, 1514, 1471, 1456, 1389, 1365.

Immobilisation of (5) on silica coated magnetic nanoparticles (6)



Sodium hydride (60 % dispersion in mineral oil, 0.03 g, 0.9 mmol, 1.3 eq) was added to a solution of 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 **5** (0.46 g, 0.7 mmol) in DMF (100 mL) at 120 °C and stirred for 30 min. Iodoalkyl-functionalized SiO₂-coated MNPs **3** (0.72 g) were slowly added and the reaction mixture was stirred at 120 °C overnight. CyMe₄-BTPhen-functionalized MNPs **6** were separated by an external magnet and were thoroughly washed with degassed ethanol (3×100mL). Finally, the product (0.24 g) was allowed to dry at 120 °C.

¹H and ¹³C NMR spectra



Figure S1. ¹H and ¹³C NMR spectra of 5-BrCyMe₄-BTPhen 4.



Figure S2. ¹H and ¹³C NMR spectra of 5-phenol-CyMe₄-BTPhen 5.

FT-IR spectra



Figure S3. FR-IR spectra of Fe_2O_3 1, SiO_2 -coated Fe_2O_3 2, and iodoalkyl-functionalized SiO_2 -coated MNPs 3.



Figure S4. FT-IR spectra of iodoalkyl-functionalized SiO₂-coated MNPs **3** and CyMe₄-BTPhen-functionalized SiO₂-coated MNPs **6**.

TEM images



Figure S5. TEM images of (a, b) γ -Fe₂O₃ MNP **1** and (b) iodoalkyl-functionalized SiO₂-coated MNPs **3**.

Dynamic light scattering data



Figure S6. Size distribution of γ -Fe₂O₃ MNPs **1**.



Thermal-gravimetric analysis



Figure S8. TGA curve of SiO₂-coated Fe₂O₃ MNPs 2.



Figure S9. TGA curve of iodoalkyl-functionalized SiO₂-coated Fe₂O₃ MNPs 3.



Figure S10. TGA curve of CyMe₄-BTPhen-functionalized SiO₂-coated MNPs 6.

2.0 Extraction Results

General Procedure

The aqueous solutions for the solvent extraction experiments were prepared by spiking nitric acid solutions (0.745 mL) (0.001 – 4 M) with stock solutions of 5 µL of ²⁴¹Am (\approx 400 Bq/µL), 3 µL of ¹⁵²Eu (\approx 1.000 Bq/µL), and 7 µL of ²⁴⁴Cm (\approx 300 Bq/µL) and then adding 600 µL of spiked aqueous solution to 18 mg of CyMe₄-BTPhen-functionalized MNP **6**. 150 µL of each labelled solution was taken as a standard (to allow mass balance calculations) for γ - measurements and 10 µL was taken as a standard for α - measurements. The suspension was sonicated for 10 min and shaken on a Heidolph Reax shaker at 1800 rpm for 90 min. After centrifuging for 10 min, aliquots of the aqueous solutions (supernatant) were separated and taken for measurements. Activity measurements of ²⁴¹Am, ¹⁵²Eu and ²⁴⁴Cm were performed with a γ -ray spectrometer EG&G Ortec (USA) with a PGT (USA) HPGe detector and α -ray spectrometer Octete plus Ortec (Germany) with ion-implanted-silicon ultra α -detector (USA). The distribution ratios, *D*, were calculated as the ratio between the radioactivity (α - and γ - emissions) of each isotope in the standard solution and the supernatants after removal of the MNP **6** complexes. The separation factor is *SF*_{Am/Eu} = *D*_{Am} / *D*_{Eu} or *SF*_{Am/Cm} = *D*_{Am} / *D*_{Cm}. All extraction experiments were carried out in duplicate and error bars in the figures represent standard deviations.

Table S1. Ex	xtraction of Am	(III) and	l Eu(III) b	y MNP 6 a	as a function	of nitric acid	concentration.
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[HNO ₃]	D _{Am} *			L		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 S2. Extraction of Am(III) and Cm(III) by MNP 6 as a function of nitric acid concentration.

[HNO ₃]	D _{Am} **			D	:	SF _{Am/Cm}			
0.001	1212.9	±	204.4	1117.4	H	195.6	1.1	±	0.3
0.1	2348.8	±	525.7	1561.1	H	331.5	1.5	±	0.5
1	690.7	±	88.2	444.1	Ŧ	50.7	1.6	±	0.3
4	69.6	±	4.8	31.4	±	2.9	2.2	±	0.4

* calculated from the results of gamma measurement

** calculated from the results of alpha measurement