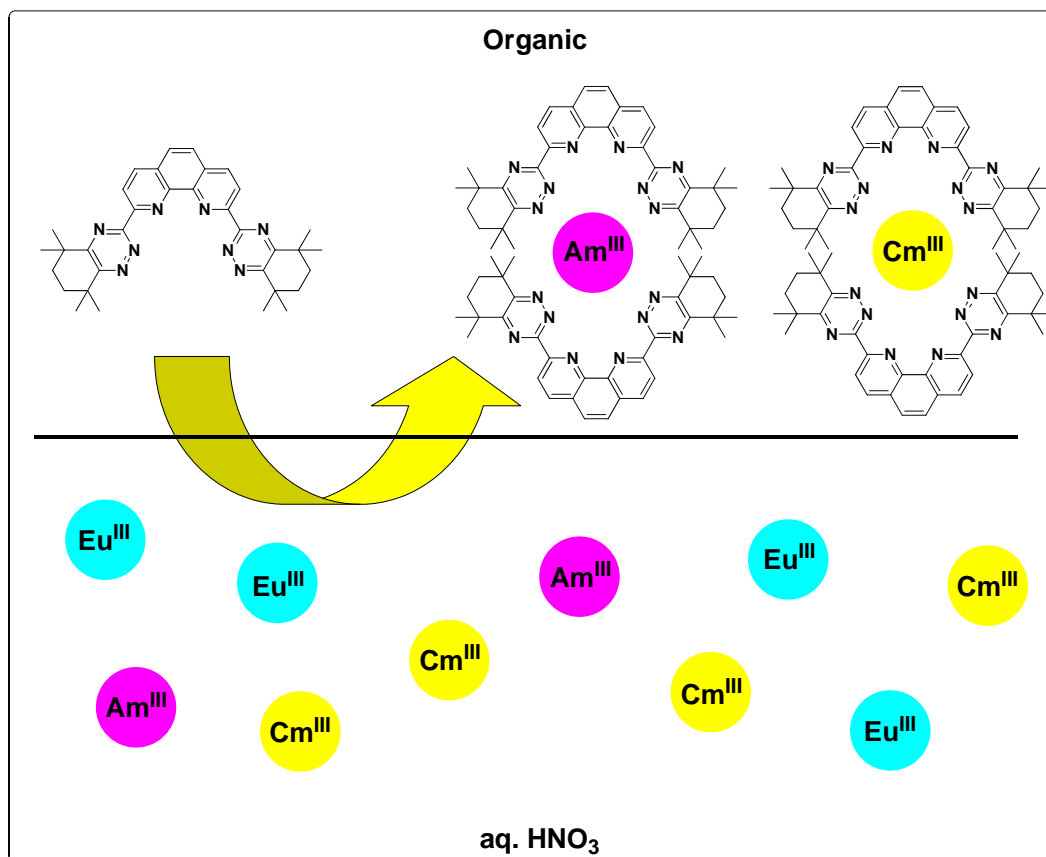
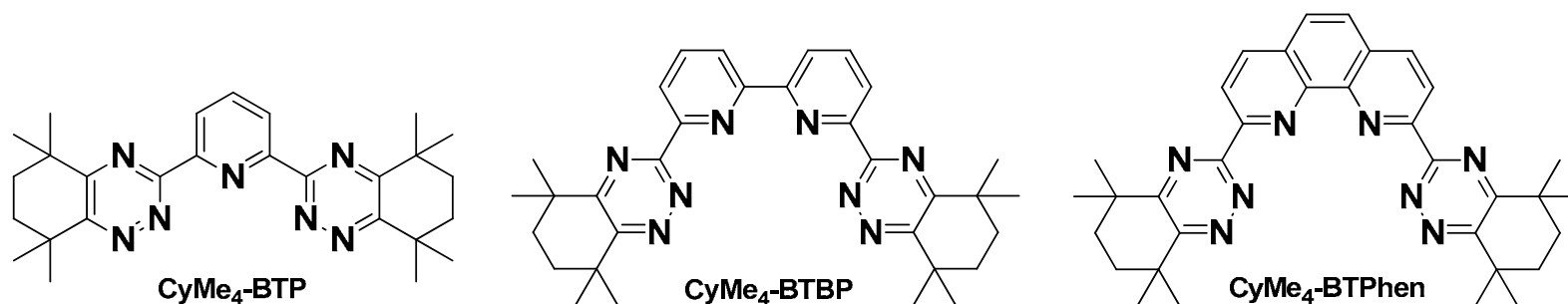


Progress Towards the Development of Ligands for Separating Actinides from Lanthanides

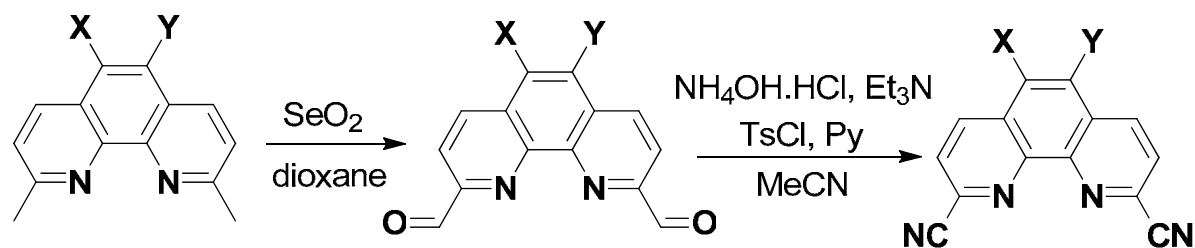
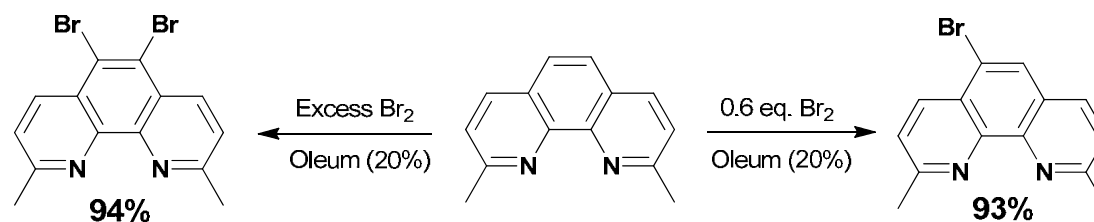
Ashfaq Afsar

Petr Distler, Andreas Geist, L. M. Harwood, Mark E. Hodson, Michael J. Hudson,
Jan John, Dominic M. Laventine, Elizabeth J. Shaw, James Westwood

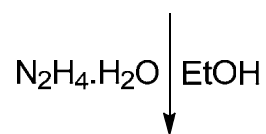
Bis(1,2,4-triazine) Ligands



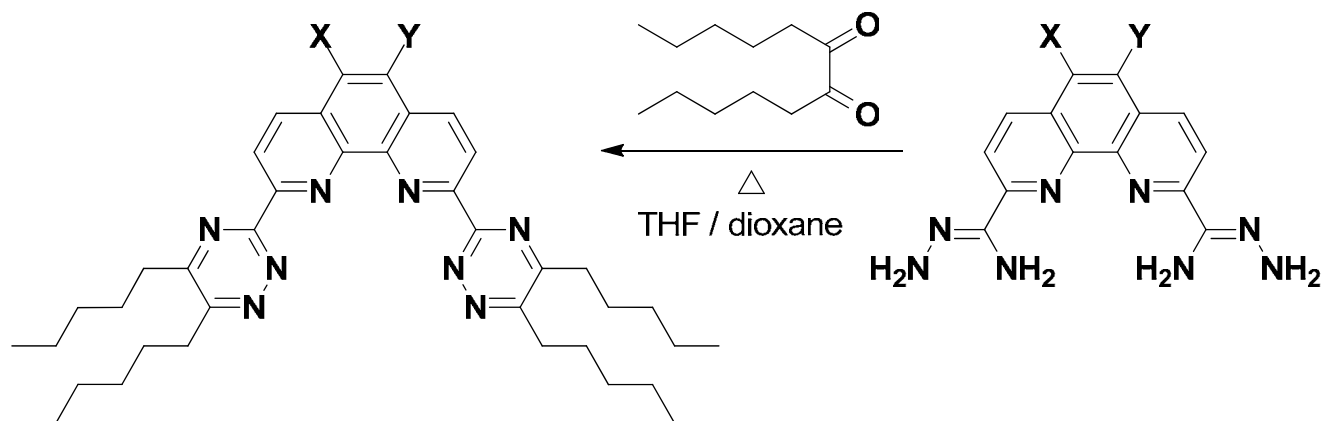
Electronic Modulation



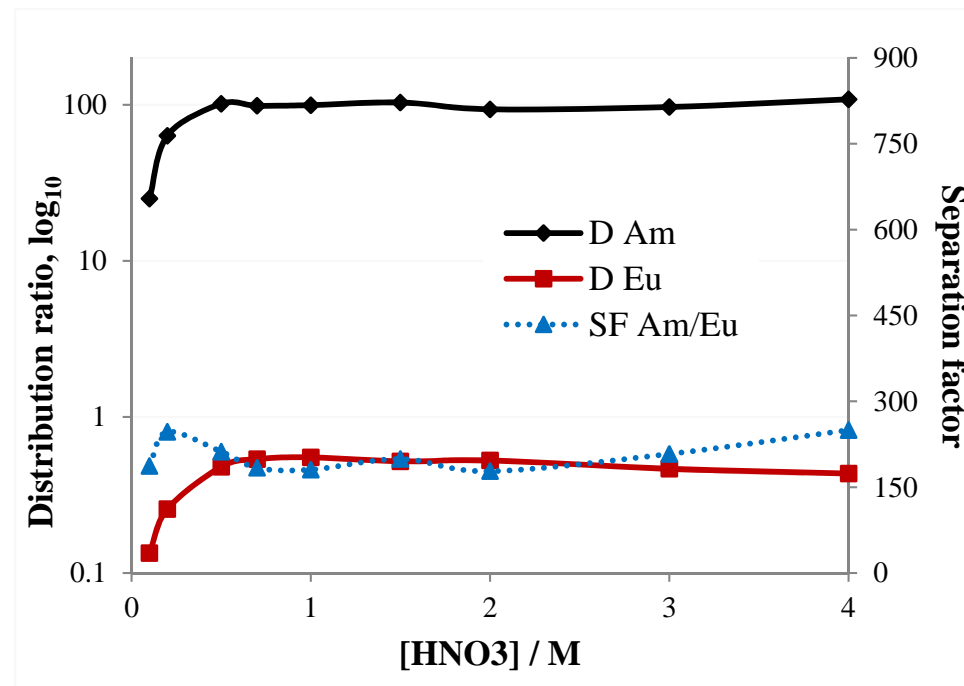
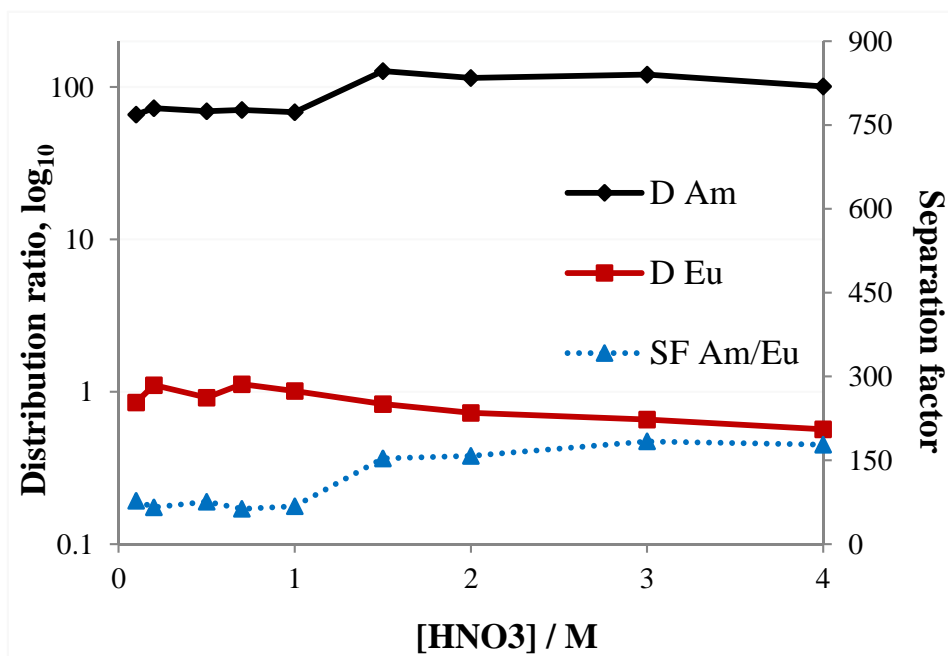
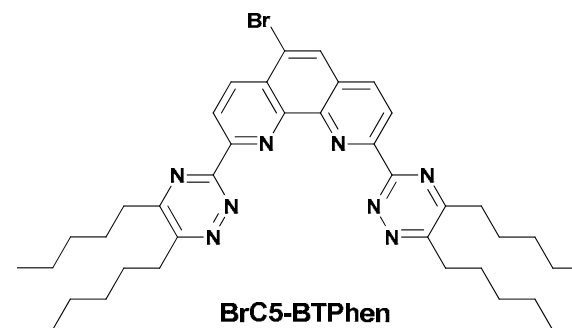
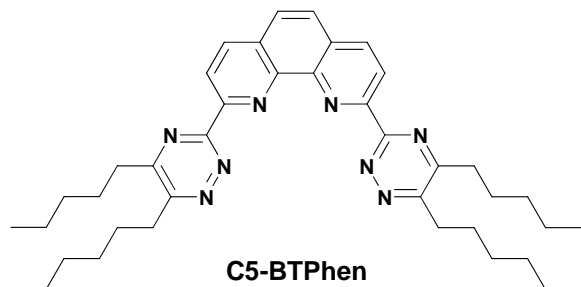
X=Y=H
X=Br, Y=H
X=Y=Br



F. W. Lewis, L. M. Harwood, M. J. Hudson *et al.*, *J. Am. Chem. Soc.*, 2011, **133**(33), 13093-13102.



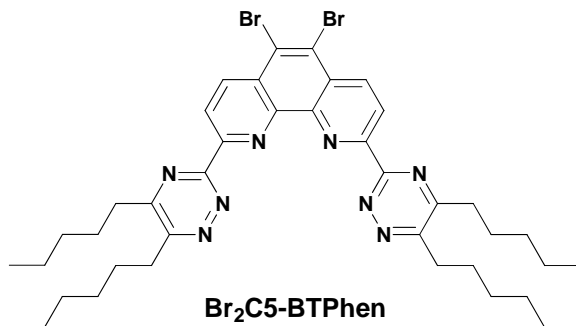
Screening Results



$SF_{Am/Eu} = ca. 180$ at 4 M HNO_3

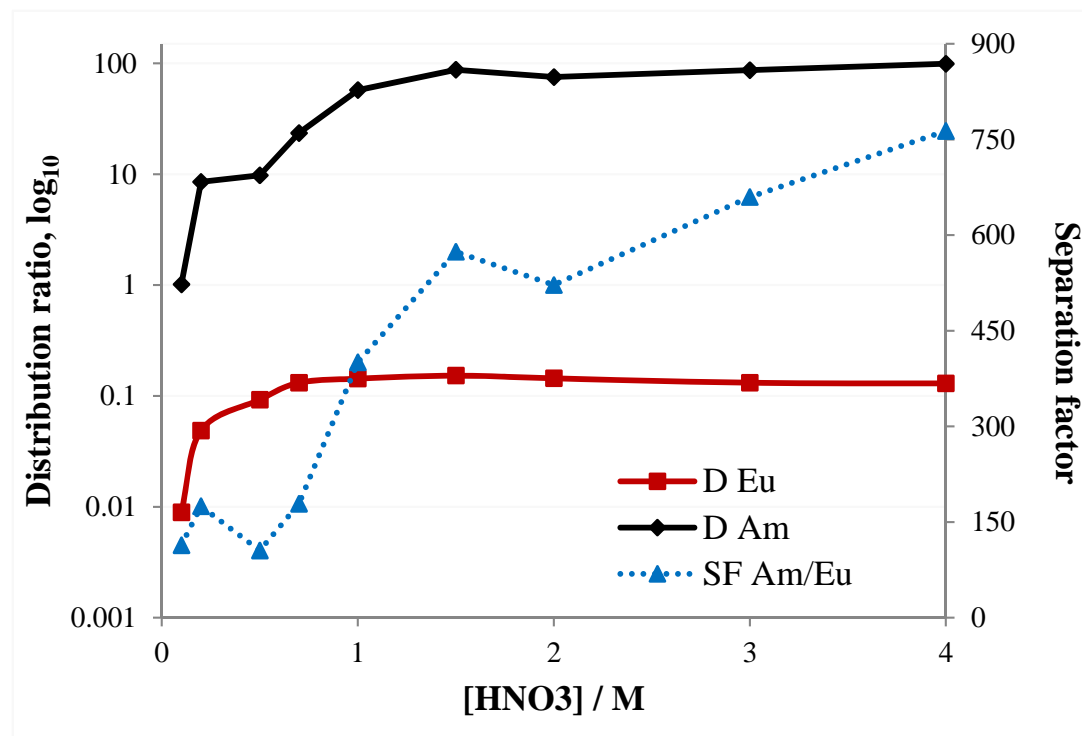
$SF_{Am/Eu} = ca. 250$ at 4 M HNO_3

Screening Results

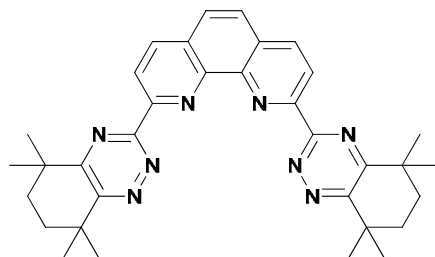


$SF_{Am/Eu} = ca. 800$ at 4 M HNO₃

D_{Eu} value approximately one order of magnitude lower than that of C₅-BTPhen

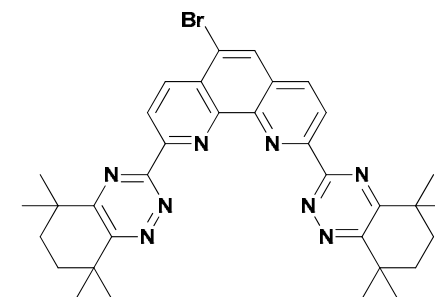


Screening Results

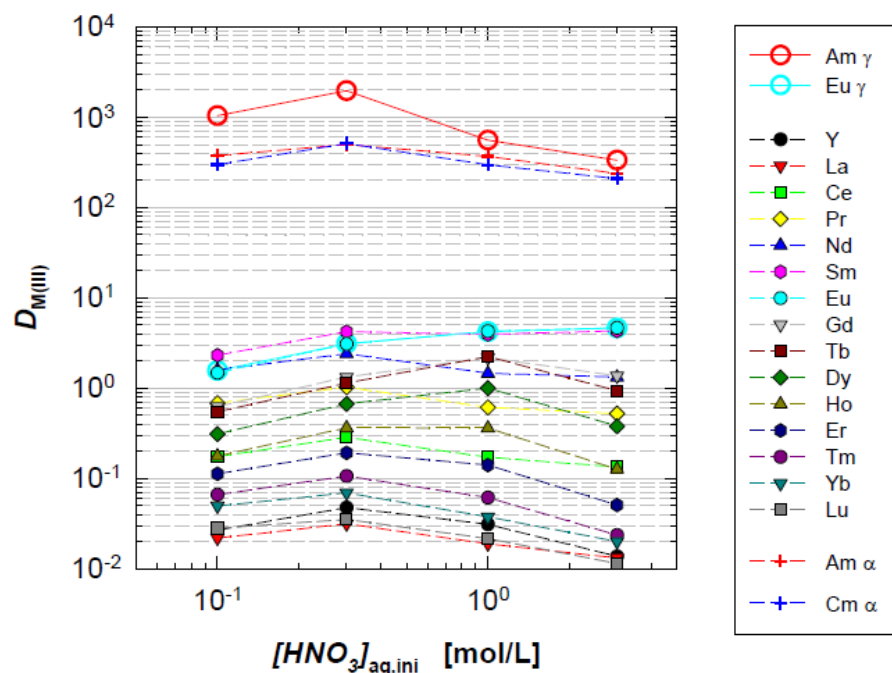


CyMe₄-BTPPh

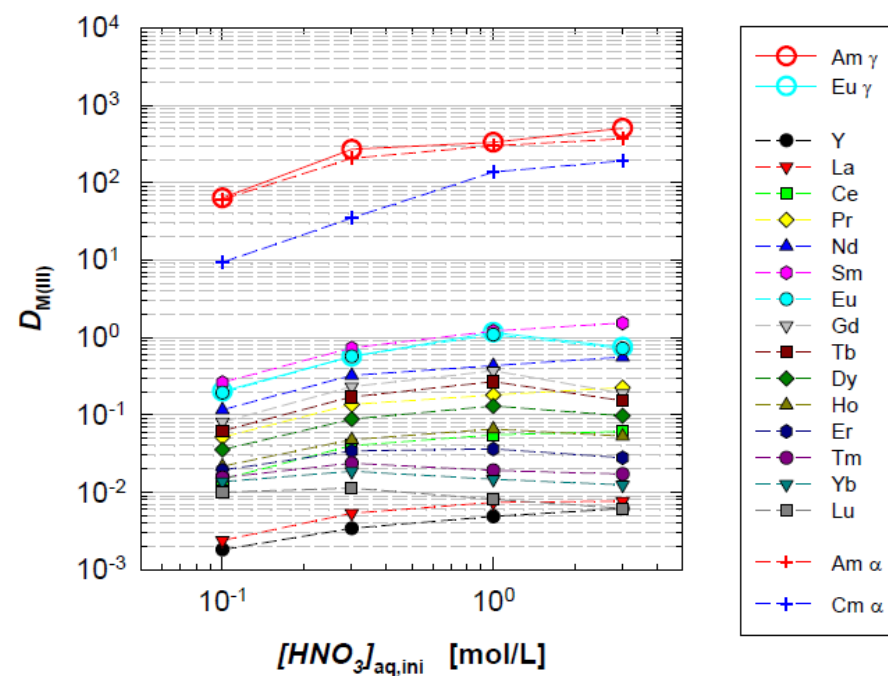
Ligand in 1-octanol (0.01 M)
²⁴¹Am(III) + ¹⁵²Eu(III) + ²⁴⁴Cm(III)
 in HNO₃ of varied concentrations
 Contact time = 60 mins at 22 °C



BrCyMe₄-BTPPh

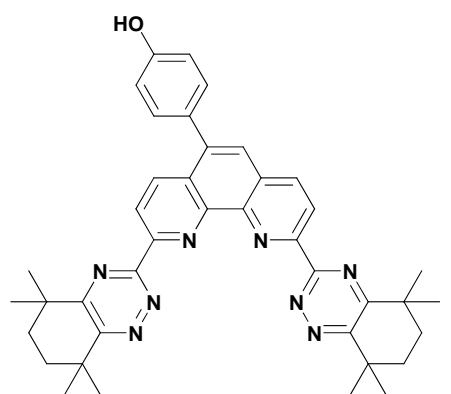
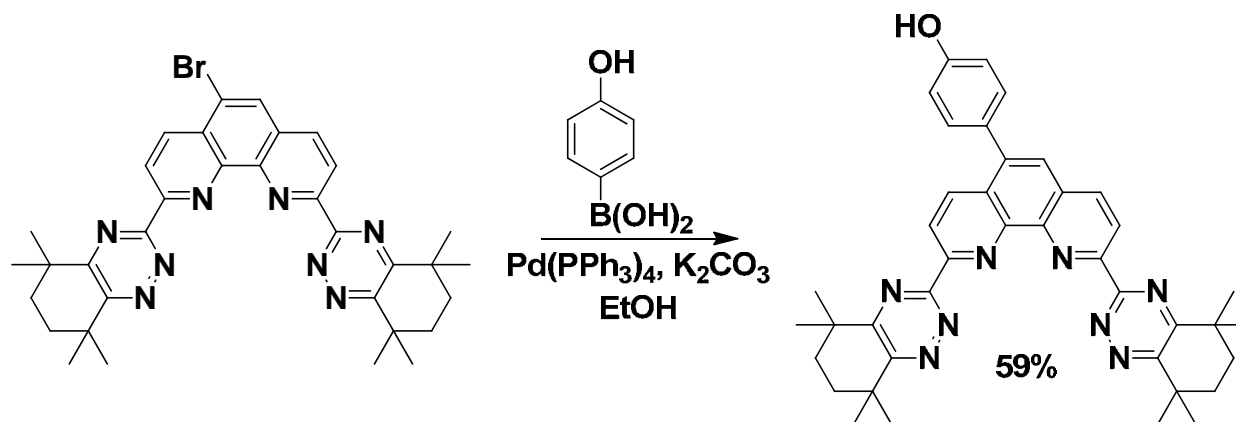


$D_{Am} = ca. 335$, $D_{Eu} = ca. 5$
 $SF_{Am/Eu} = ca. 70$ at 3 M HNO₃



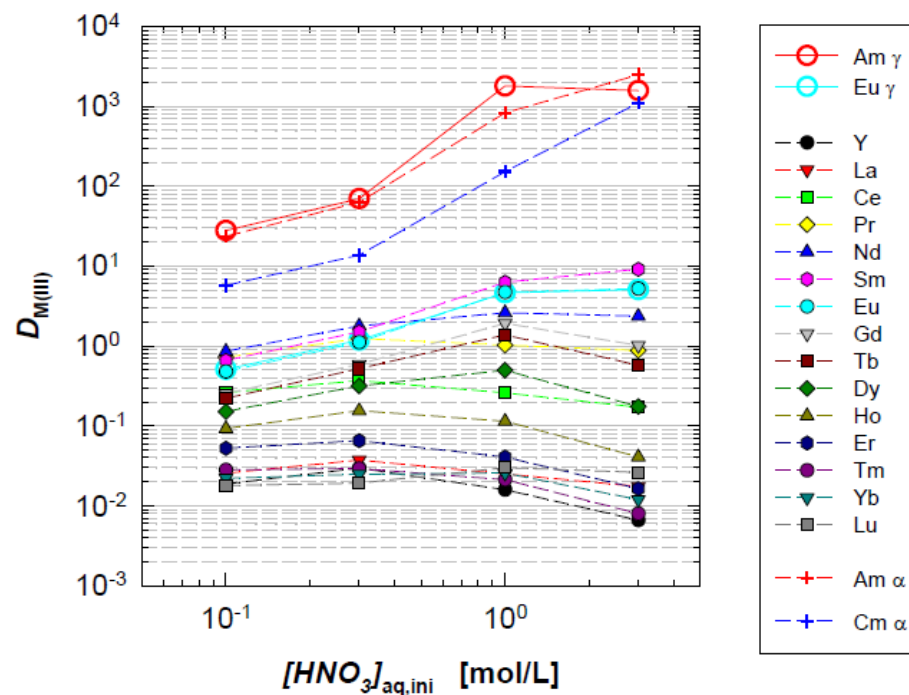
$D_{Am} = ca. 508$, $D_{Eu} < 1$
 $SF_{Am/Eu} = ca. 680$ at 3 M HNO₃

Screening Results

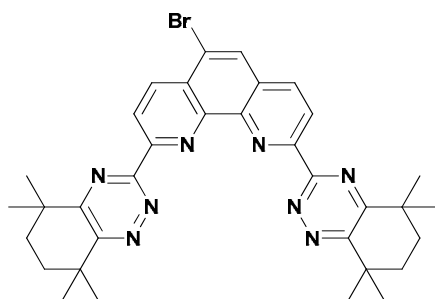


5-(4-hydroxyphenyl)-CyMe4-BTPhen

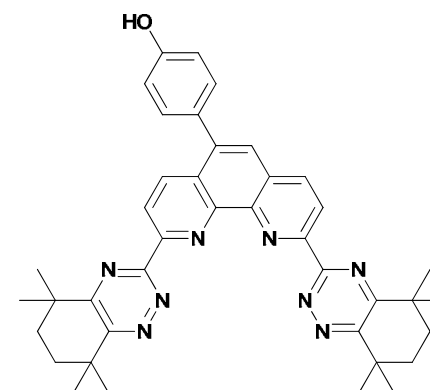
$D_{Am} = ca. 1581$, $D_{Eu} = ca. 5$
 $SF_{Am/Eu} = ca. 320$ at 3 M HNO_3



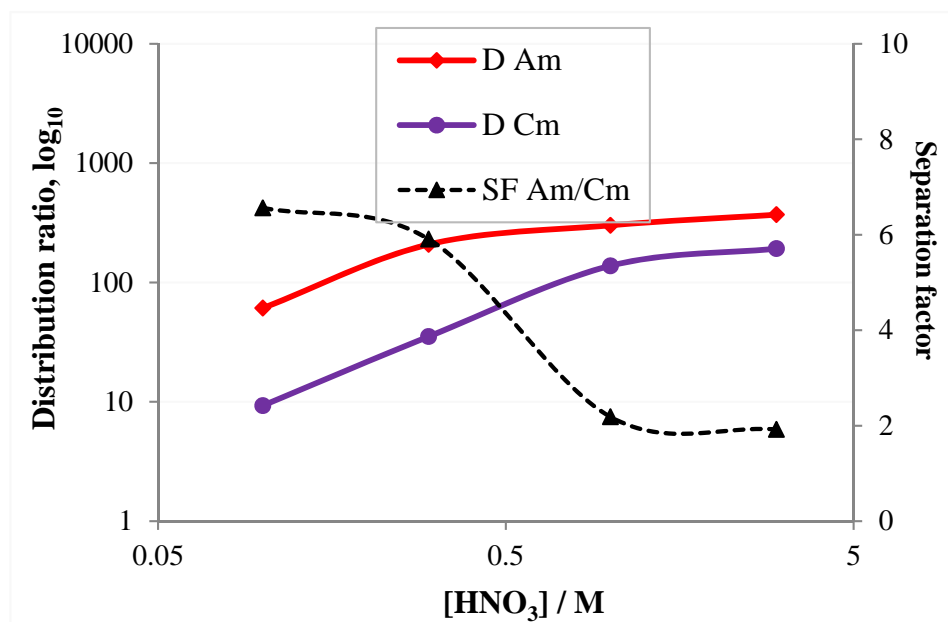
Am(III)/Cm(III) Separation



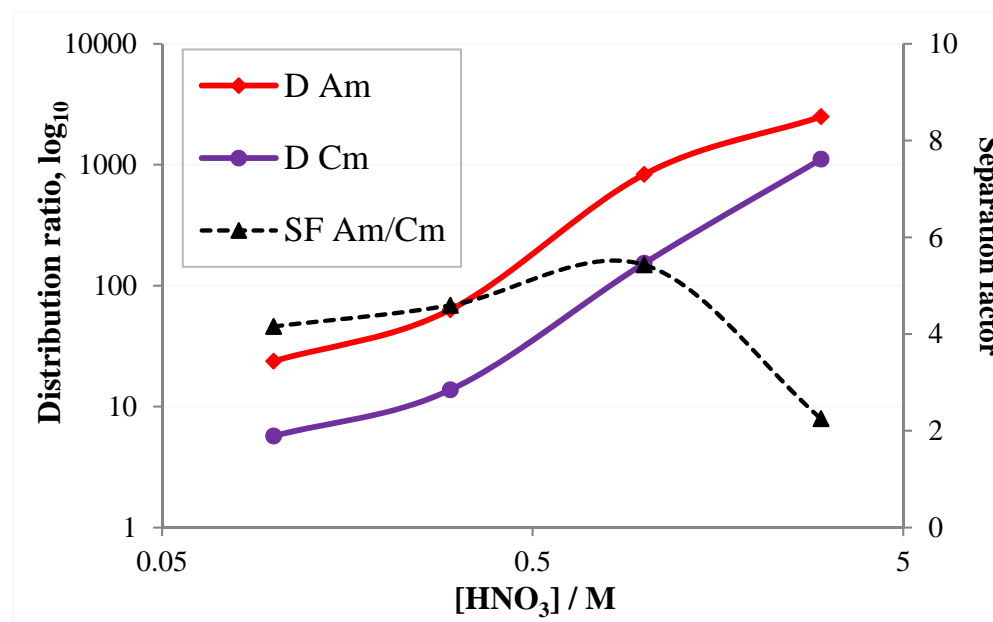
BrCyMe₄-BTPhen



5-(4-hydroxyphenyl)-CyMe₄-BTPhen

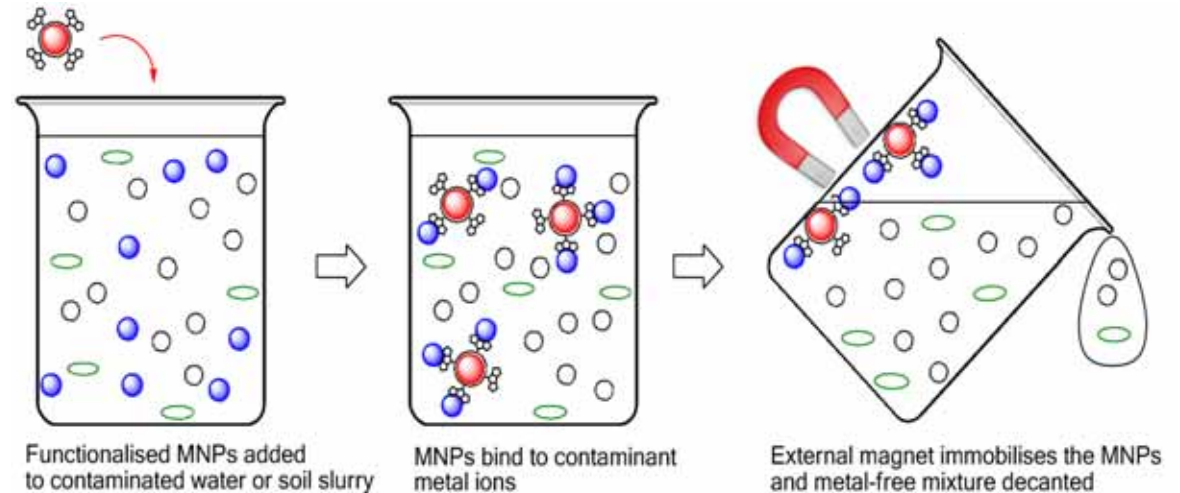


max SF_{Am/Cm} = ca. 7 at 0.1 M HNO₃



max SF_{Am/Cm} = ca. 5 at 1 M HNO₃

Ligands Immobilized on Magnetic Nanoparticles



Liquid-liquid extraction

- Requires substantial tankage and reagents
- Generates significant quantities of secondary waste
- Not suitable for low concentrations

Immobilized ligands

- Efficient separation of particles
- Simple, versatile and compact
- Minimized secondary waste
- Suitable for low concentrations (legacy wastes)
- Good kinetics

Ligands Immobilized on Magnetic Nanoparticles

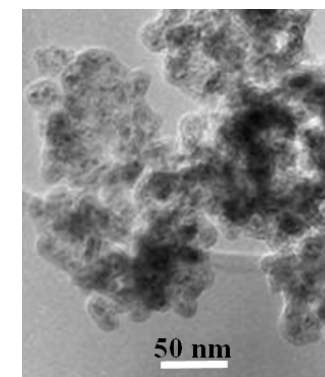
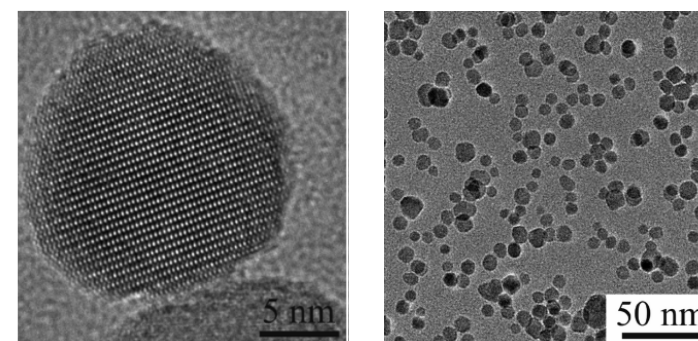
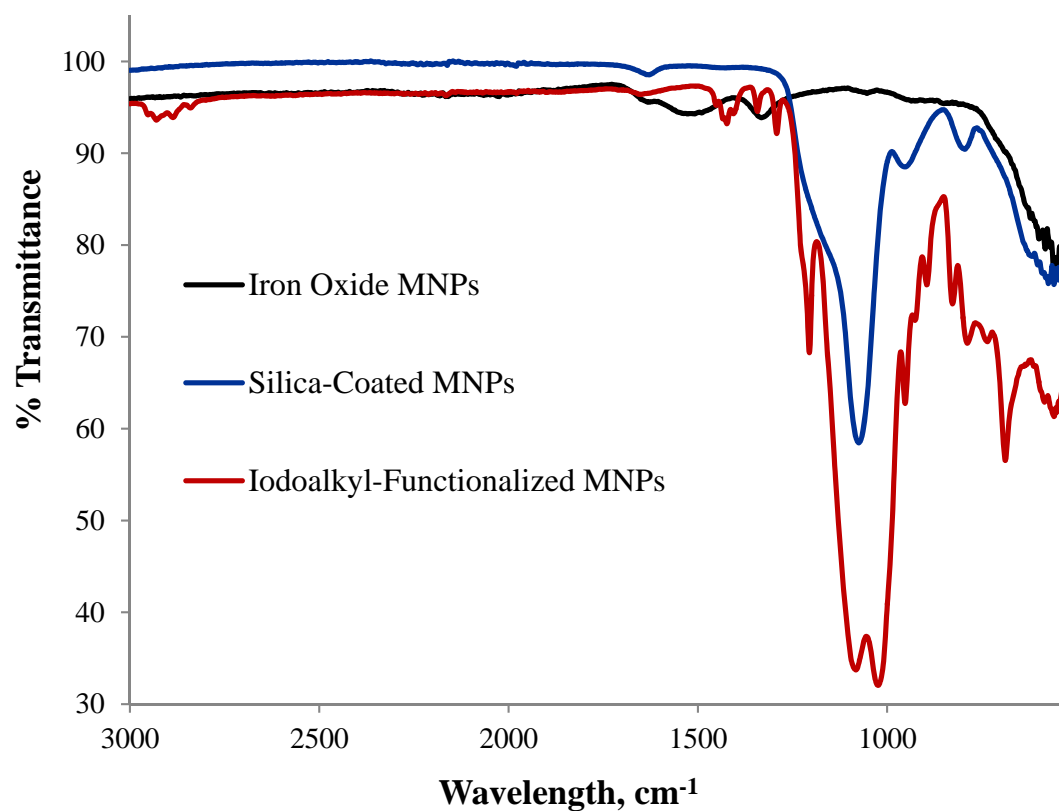
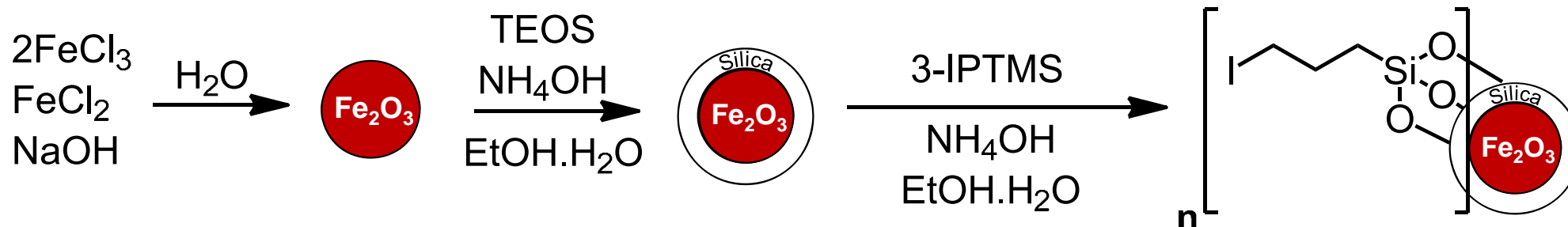


Nanoparticles dispersed in water (colloidal solution).

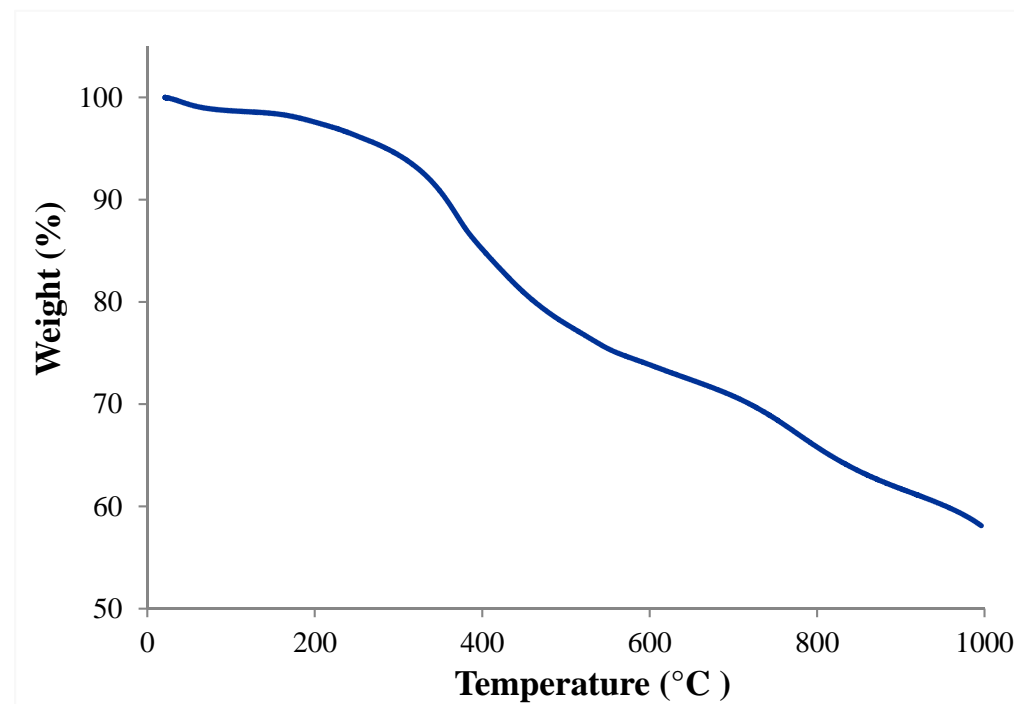
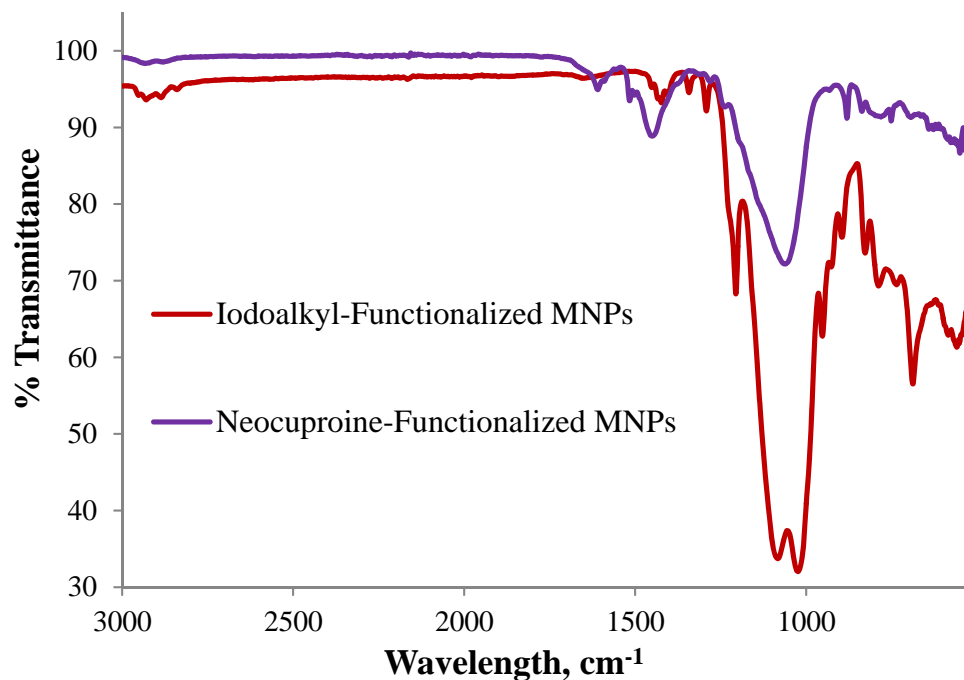
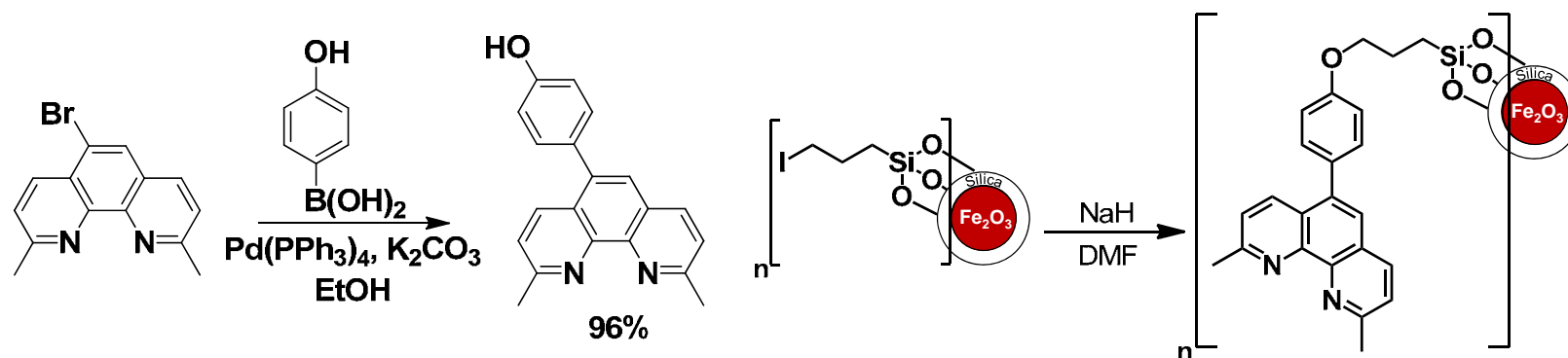


Nanoparticles extracted on application of magnetic field.

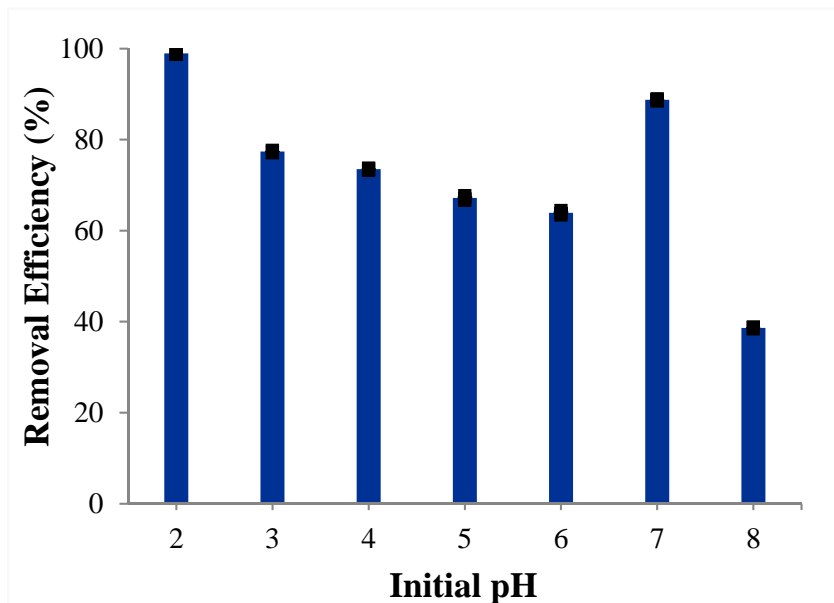
Core-shell MNPs synthesis



Immobilisation of Neocuproine

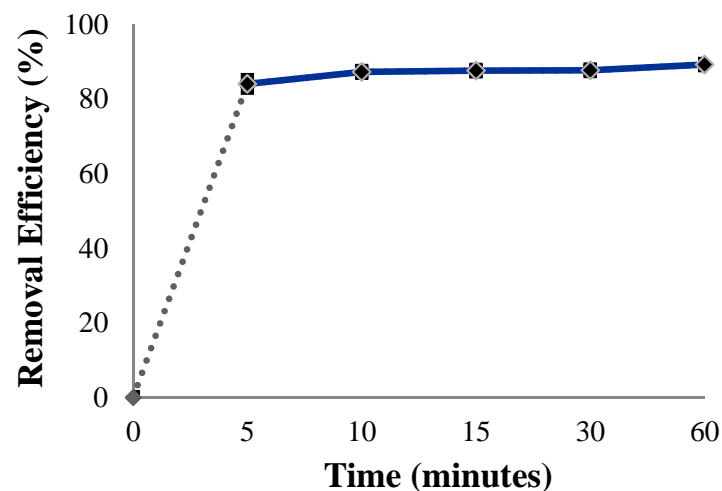
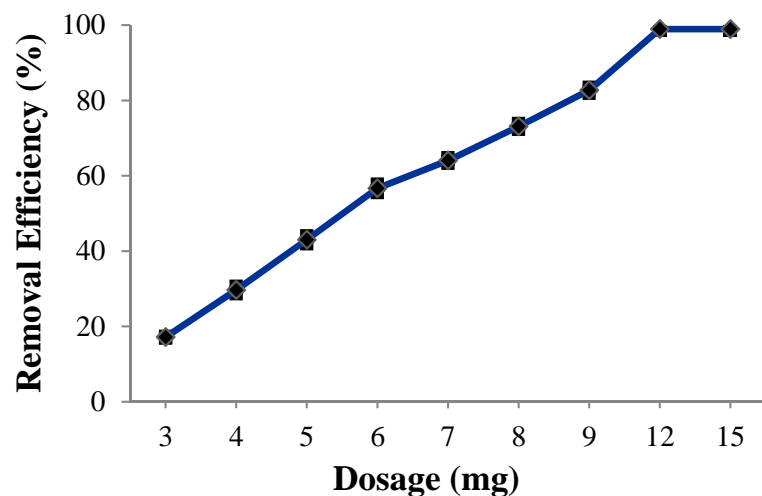


Extraction Results

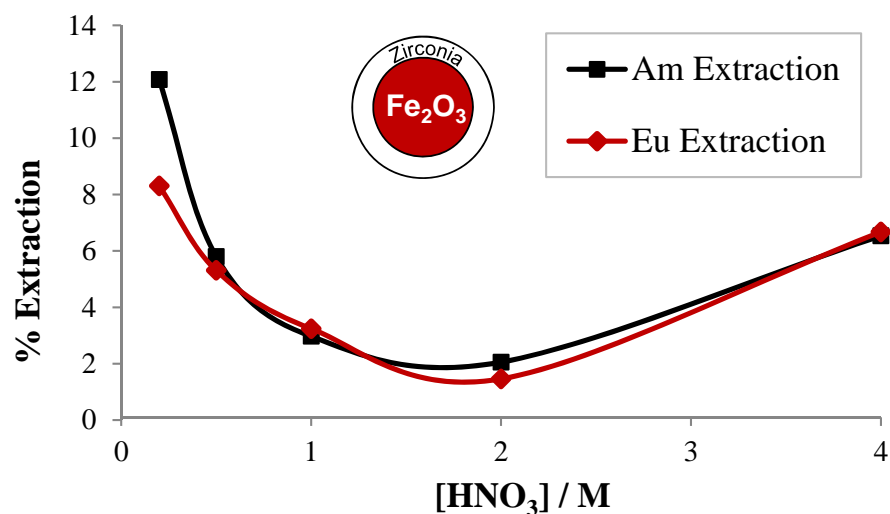
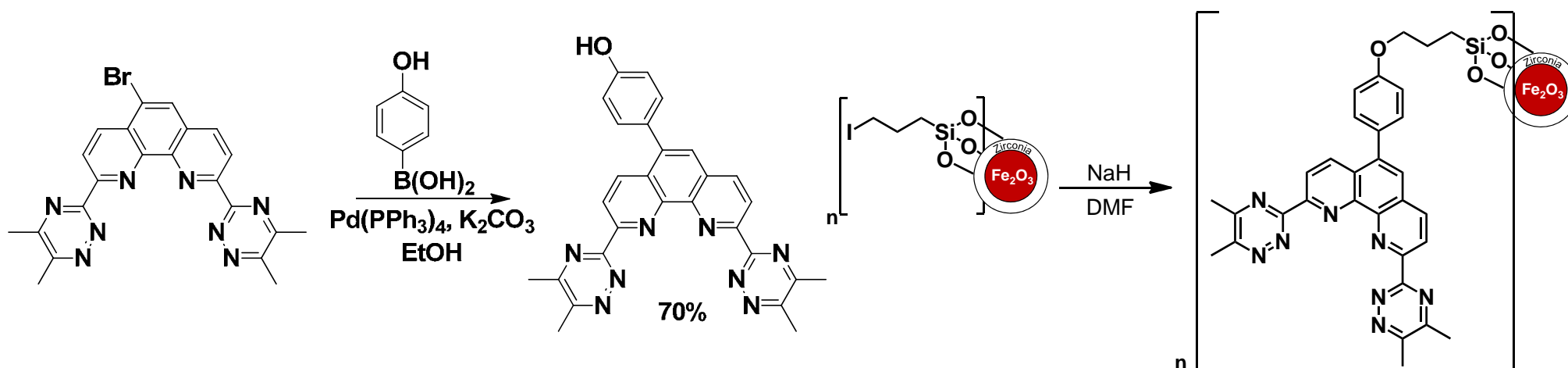


12 ppm of Cu(II) solutions (12 mL)
12 mg of MNPs
Shaking at 2500/min
Separated by neodymium magnet

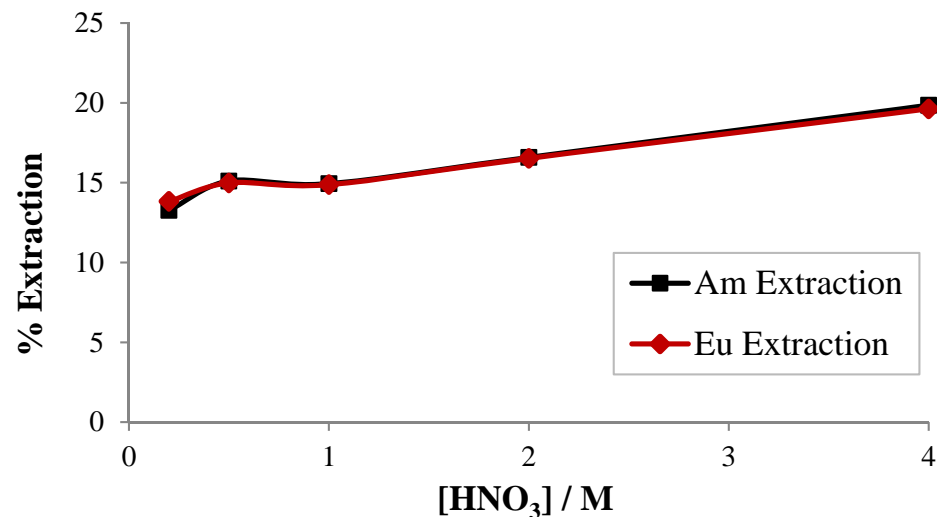
Removal %		
SiO ₂ -coated MNPs	Iodoalkyl-functionalized SiO ₂ -coated MNPs	Neocuproine functionalized MNPs
17	30	99



Immobilisation of C1-BTPPhen

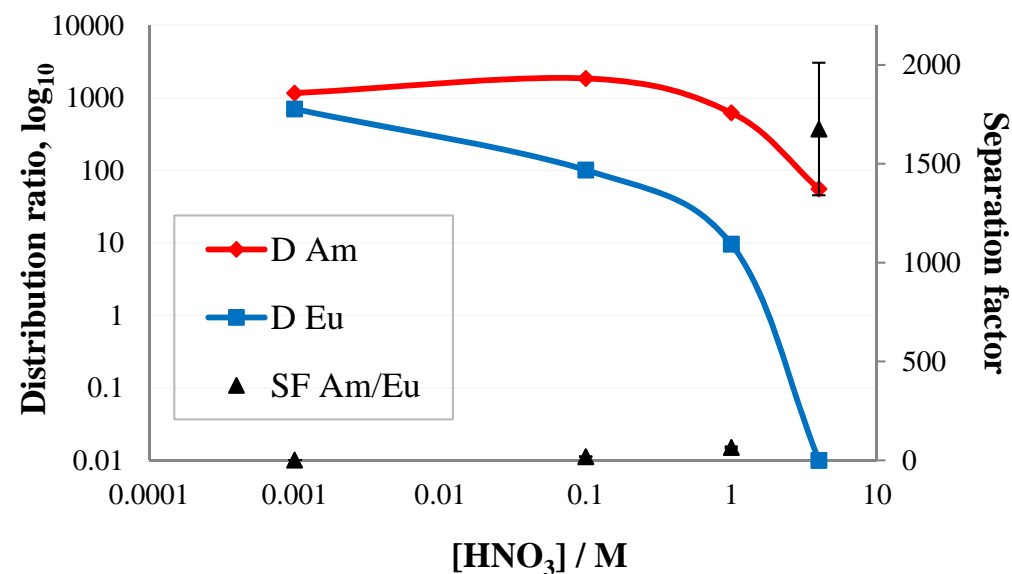
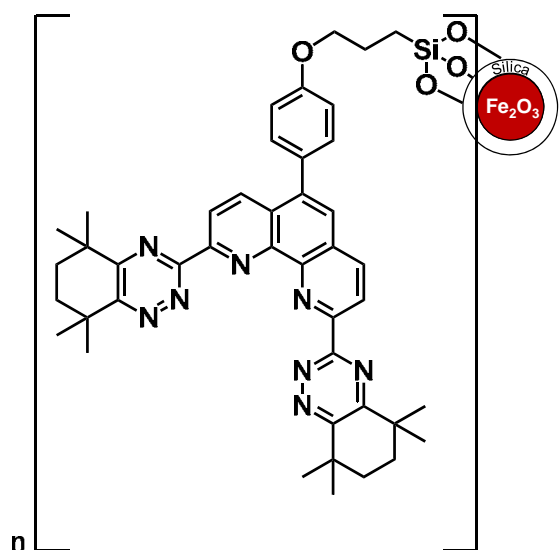


$^{241}\text{Am}(\text{III}) + ^{152}\text{Eu}(\text{III})$ in HNO_3 of varied concentrations
+18 mg of MNPs
Sonication time (10 min), shaking at 1800/min (90 min), separated by centrifugation (10 min)

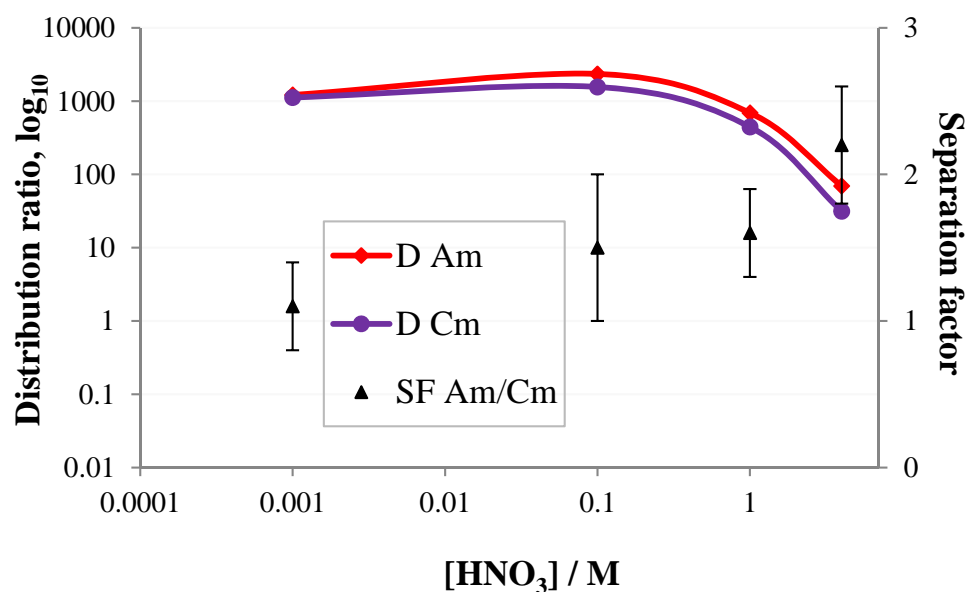


15-20% extraction observed
But lack of selectivity

Immobilisation of CyMe₄-BTPPhen



²⁴¹Am(III) + ¹⁵²Eu(III) + ²⁴⁴Cm(III) in HNO₃ of varied concentrations +18 mg of MNPs
Sonication time (10 min), shaking at 1800/min (90 min), separated by centrifugation (10 min)



At 0.001 M HNO₃, $D > 700$ for both Am(III) and Eu(III), but no significant selectivity ($SF_{Am/Eu} = 1.7$)

At 4 M HNO₃, $D_{Eu} \sim 0$, excellent selectivity ($SF_{Am/Eu} > 1600$)

Achievements and Conclusions



Adding substituents to the phenanthroline backbone at the 5- and 5,6-positions of BTPHens, enable these ligands to be fine-tuned in order to enhance the selectivity of Am(III) from Ln(III) and Cm(III).

Iron oxide (Fe_2O_3) MNPs coated with silica and functionalized with CyMe_4 -BTPhen have the ability to selectively extract Am(III) from Eu(III) at 4M HNO_3 solutions. These MNPs also show a small but significant selectivity for Am(III) over Cm(III).

We propose that this technology may well prove effective for polishing the raffinate from SANEX type processes and for remediation of contaminated water and soils. Future targets: Co(II), Cs(I) and Sr(II).

Acknowledgments



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Jan John (CTU Prague)
Petr Distler (CTU Prague)



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OK dragon! Come out of that cave and fight!!