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IMMOBILISATION OF PHENANTHROLINE-BIS TRIAZINE (C1-BTPHEN) ON MAGNETIC NANOPARTICLES FOR CO-EXTRACTION OF AMERICIUM(III) AND EUROPIUM(III)

Ashfaq Afsar,[a] Dominic L. Laventine,[a] Laurence M. Harwood,[a,*] Michael J. Hudson,[a] and Andreas Geist[b]

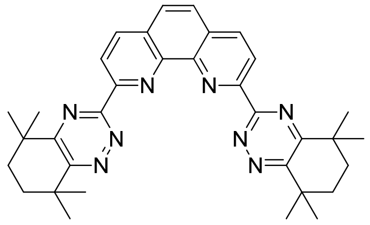
[a]School of Chemistry, University of Reading, Whiteknights, Reading, Berkshire RG6 6AD, UK. E-mail: L.M.Harwood@reading.ac.uk
[b]Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday

Abstract – The present work reports a convenient route for the immobilisation of a phenanthroline-bis triazine (C1-BTPhen) group on the surface of zirconia-coated maghemite (γ-Fe_2O_3) magnetic nanoparticles. The magnetic nanoparticles functionalized with C1-BTPhen were able to co-extract Am(III) and Eu(III) from nitric acid (HNO_3). The extraction efficiency of these C1-BTPhen-functionalized magnetic nanoparticles for both Am(III) and Eu(III) was 20% at 4M HNO_3. The interaction between C1-BTPhen and metal cations is reversible. These functionalized magnetic nanoparticles can be used for the co-extraction of traces of Am(III) and Eu(III).

Recent work has demonstrated the utility of phenanthroline-based molecules for the separation or partitioning of minor actinides from lanthanides.[1-4] There is also a requirement to remove traces of radionuclides from aqueous media. So far inorganic ion exchangers, biological materials and organic ion exchangers have proved to be useful.[5-7]

Numerous examples of ligands for nuclear waste treatment on solid supports have been reported. However, the majority of these examples make use of ligands that form complexes via *O*-, *P*-, and *S*-donor atoms.[1] Ligands are typically coated onto or impregnated into the solid supports, which include polymer resins and membranes, metal oxide microparticles, clays, carbon nano-tubes, amorphous carbon, magnetic nanoparticles (MNPs), and SiO_2-stabilized polymers.[1] More rarely, ligands are covalently attached to the solid supports.[1] Solid supported ligands can be particularly effective at extracting metals at low concentrations and have been applied in the preconcentration or analysis of dilute samples. Additionally solid-supported ligands can be used as adsorbents in extraction chromatography, a purification method that reduces or eliminates the need for organic solvents. To date the only published examples of solid-supported soft *N*-donor ligands for nuclear waste treatment have made use of alkyl-BTP (bis-triazinyl-pyridine) systems.[1] In the light of the Fukushima nuclear incident, interest in such methods has significantly increased. Our work is currently focused on immobilisation of BTPhen (bis-triazinyl-phenanthroline) ligands (which have been developed specifically for selective extraction of minor actinides An(III)) to solid supports and investigate their applications in nuclear waste treatment. It has been shown that CyMe$_4$-BTPhen is highly selective for Am(III) over Eu(III).[8] One of the reasons for the selectivity is that two BTPhen units are able to combine with the Am(III) thereby enclosing the coordination shell of the Am(III). The result is that a hydrophobic exterior is formed. In the case of Eu(III) only one BTPhen unit combines and the resultant complex remains hydrophilic.



CyMe$_4$-BTPhen

Synthesis of mono-dispersed MNPs, particularly iron oxide (Fe_3O_4 or γ-Fe_2O_3) MNPs, provides a new opportunity for the removal of traces of radioactive elements combined with separation of the particles using the ferri-magnetic properties. With particle sizes of less than 40 nm, they offer very large surface areas coupled with high surface activity. The magnetic properties of these MNPs enable them to be separated from solution, making them highly useful in novel separation processes.[9-14]

However, iron oxide MNPs are subject to chemical attack by nitric acid and therefore a suitable protective coating is essential.[15-19] An effective way to solve this problem is to use zirconia (ZrO_2), which has been shown to provide a chemically resistant surface whilst retaining ionic exchange properties.[20-21] Furthermore the free Zr-OH surface groups can allow effective binding of organic functional groups on to the surface of the ZrO_2 coated MNPs. It was proposed that surface modification with alkoxysilanes of the general formula $X\text{-}(CH_2)_n\text{-}SiR_n(OR')_{3-n}$, could be used where X represents the headgroup functionality, $(CH_2)_n$ a flexible spacer, and $Si(OR)_n$ the anchor groups by which (after hydrolysis of the alkoxy group) they can attach to free Zr-OH.[22]

In this study, the C1-BTPhen **10** covalently attached to ZrO_2 coated γ-Fe_2O_3 MNPs have been assessed for their ability to co-extract Am(III) and Eu(III) from highly acidic solutions. The γ-Fe_2O_3 MNPs were synthesized by a coprecipitation method.[23] Then ZrO_2 was coated on the surface of γ-Fe_2O_3 MNPs by a sol-gel method.[23] After this, the ZrO_2 surface was further modified with 3-iodopropyltrimethoxysilane

(3-IPTMS). The presence of iodo-functional group allowed immobilisation of C1-BTPhen **10** onto the MNPs by a simple SN2 reaction via the C-5 4-hydroxyphenyl substituent on the phenanthroline.

The structure of γ-Fe_2O_3 MNPs **1** was characterised by X-ray diffraction. Figure 1 shows the XRD pattern, which corresponds to pure maghemite or γ-Fe_2O_3.[24]

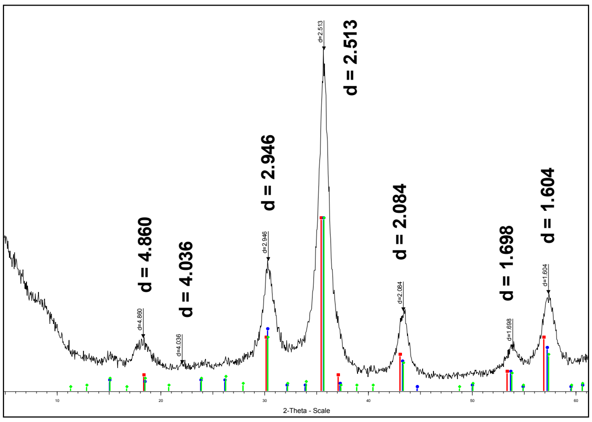


Figure 1. X-Ray powder diffraction pattern of γ-Fe_2O_3 MNPs **1** overlapping the theoretical pattern for maghemite

The TEM images of γ-Fe_2O_3 MNPs **1** and ZrO_2-coated MNPs **2** in Figure 2 were taken for the particles dispersed in methanol and dried on a copper grid at room temperature. Figure 2(a) shows the predominantly spherical morphology of the γ-Fe_2O_3 MNPs **1** with an average diameter of *ca.*15 nm that formed as aggregates as shown in Figure 2(b). In the case of zirconia-coated MNPs **2** [Figure 2(c)], the thickness of the zirconia coating was found to be *ca.*40~45 nm. Zirconia has an iso-electric point of pH 4-11[25] with the result that, in the acidic media used, the particles are protonated and have a net positive charge. The repulsion between the positively charged particles ensures that there is no aggregation.

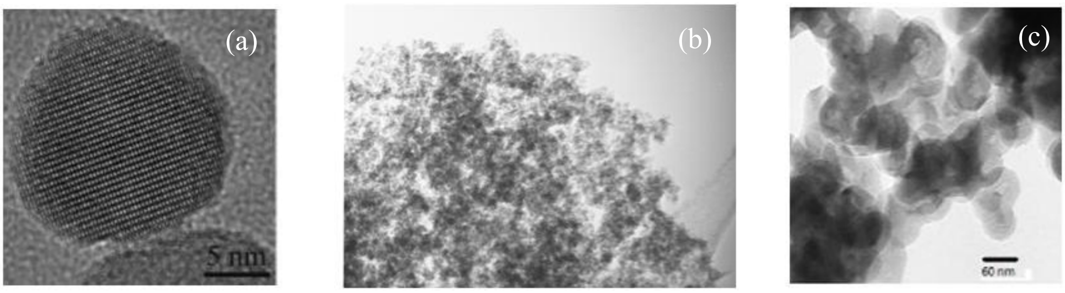


Figure 2. TEM images of (a, b) γ-Fe_2O_3 MNPs **1** and (c) ZrO_2-coated MNPs **2**

The presence of γ-Fe_2O_3 MNPs **1** can be seen by two strong FT-IR bands at 630 and 580 cm^{-1} (Figure 3), which are characteristic of Fe-O stretching vibrations. The absorption band at 960 cm^{-1} is assigned to stretching modes associated with Zr-O-Si groups. The band at 1080 cm^{-1} is due to the stretching mode of the Si-O bonds, and the presence of C1-BTPhen ligand was confirmed by (C=C) aromatic vibrations that appeared in the range 1500-1600 cm^{-1}.

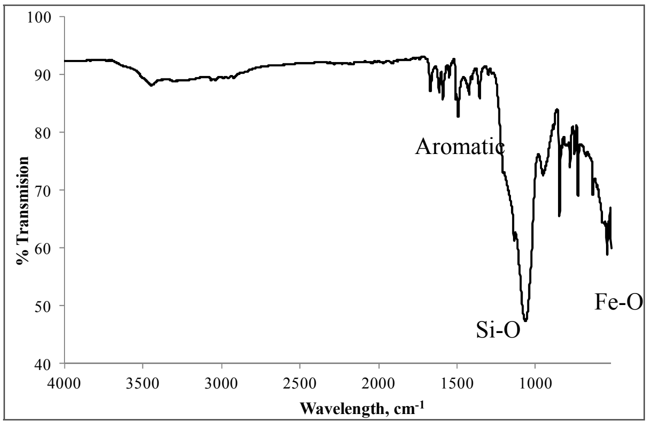


Figure 3. FT-IR spectrum of C1-BTPhen-MNPs **11**

Suspensions of the C1-BTPhen-MNPs **11** in octanol were contacted with HNO_3 solutions containing ^{241}Am and ^{152}Eu radiotracers. Little extraction of ^{241}Am and ^{152}Eu was shown by the un-functionalized ZrO_2-coated MNPs **2** (Figure 4a) over the range of 1M to 4M HNO_3. In this range of acidity the surface hydroxyl groups of the zirconia are protonated giving rise to a positively charged surface and the consequent repulsion of M(III) cations.

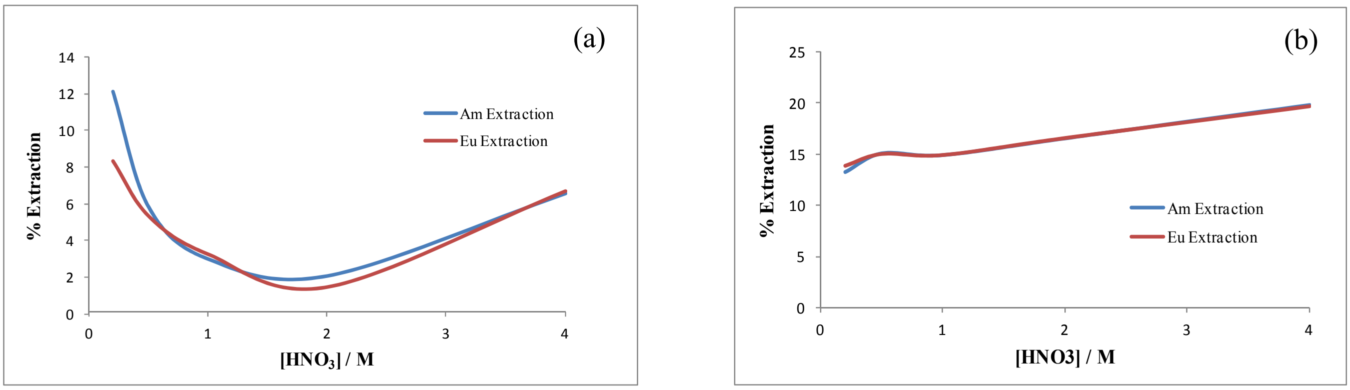


Figure 4. % Extraction of Am(III) and Eu(III) by (a) ZrO_2-coated MNPs **2** and (b) C1-BTPhen-MNPs **11** in octanol as a function of [HNO_3]

On the other hand, significant extraction (15-20%) of both Am(III) and Eu(III) was observed when using C1-BTPhen-MNPs **11** (Figure 4b). The lack of selectivity may arise because only one BTPhen moiety combines with the metal(III) cations, because the linker is too short to allow two BTPhen groups to bind to the Am(III) as is the case in the solvent extraction.

In summary, we have prepared C1-BTPhen-MNPs **11**, which are the first examples of the immobilisation of BTPhen ligand on to the solid support. These MNPs **11** exhibited some affinity for both Am(III) and Eu(III) and successfully extracted 20% of these cations from 4M HNO_3 solutions in which these MNPs

11 were stable. These findings may lead to the development of various BTPhen ligands onto the solid support and may provide a potential platform for developing a new route for lanthanides/actinides extraction from nuclear waste.

EXPERIMENTAL

Materials. Iron(III) chloride, iron(II) chloride tetrahydrate, sodium hydroxide pallets, ammonium hydroxide (35%), zirconium (IV) isopropoxide isopropanol complex, 3-iodopropyltrimethoxysilane (3-IPTMS), ethanol and dimethylformamide (DMF) were purchased from Sigma-Aldrich. All chemicals were of analytical grade and used as received without further purification. Degassed deionized water was used throughout the experiment.

Characterization. The structure of the precipitated powders was investigated by X-ray powder diffraction (XRD) with a Siemens D5000 diffractometer, using a monochromatized X-ray beam with nickel-filtered Cu Kα radiation. 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 to evaporate in air at room temperature.

Extraction studies. All the extraction studies were carried out in the Institute of Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology (Germany). 500 µL of solutions of C1-BTPhen-MNPs **11** (10 mmol/L) in 1-octanol and 500 µL of solutions of ^{241}Am(III) + ^{152}Eu(III) (1 kBq/mL each) in nitric acid of varied concentrations were shaken for 90 min on an orbital shaker at 2500/min in 2 mL glass screw-cap vials at *T*= 20 °C. Phases were separated by centrifugation, and 300 µL of each organic and aqueous phase were taken for analysis on a gamma counter (Packard Cobra Auto Gamma 5003).

Synthesis of Iodo functionalized ZrO_2-Coated γ-Fe_2O_3 MNPs (3). γ-Fe_2O_3 MNPs **1** were prepared by the chemical co-precipitation method (Figure 5).[23]

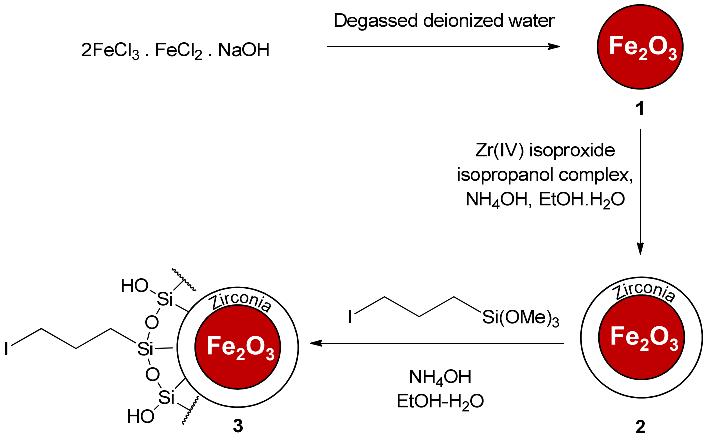


Figure 5. Synthesis of iodo-functionalized zirconia coated γ-Fe_2O_3 MNPs **3**

Complete precipitation of Fe_2O_3 was achieved under alkaline conditions, while maintaining a molar ratio of Fe^{2+}:Fe^{3+} = 1:2 under nitrogen. To obtain 0.8 g of γ-Fe_2O_3 MNPs **1**, $FeCl_2 \cdot 4H_2O$ (0.8 g) and $FeCl_3$ (1.3 g) dissolved in degassed deionized water 40 mL were added dropwise into 2M NaOH solution (200 mL) with vigorous stirring. After 1 h, the resulting γ-Fe_2O_3 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-Fe_2O_3 MNPs **1** were coated with ZrO_2 using a sol-gel method (Figure 6).[23] Typically, 0.7 g of γ-Fe_2O_3 MNPs **1** were dispersed in a mixed solution of degassed EtOH (400 mL) and degassed deionized water (100 mL) by sonication for 10 min. Ammonium hydroxide (35%, 36 mL) and zirconium (IV) isopropoxide isopropanol (1 g) were consecutively added to reaction mixture and the reaction was allowed to proceed at room temperature for 2 h under continuous sonication. 3-IPTMS (6.3 mL) was then added and the reaction was allowed to proceed for further 3 h. The resultant functionalized particles **2** were obtained by magnetic separation and thoroughly washed with degassed EtOH (2×100 mL). Finally the resultant solid was dried at 120 °C.

Synthesis of C1-BTPhen with a 4-hydroxyphenol linker (10). The C1-BTPhen ligand with a 4-hydroxyphenol linker **10** was synthesized as shown in Figure 6.

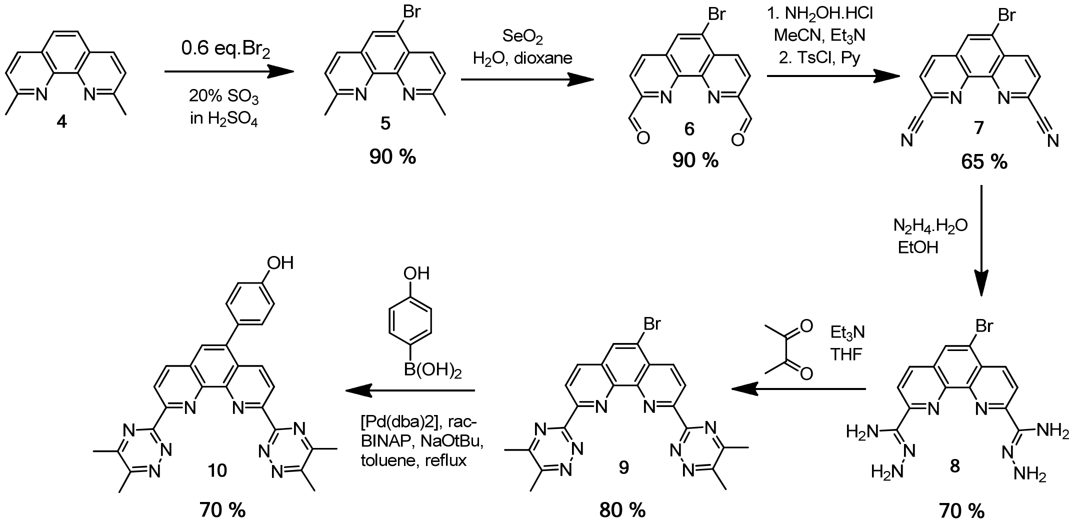


Figure 6. Synthesis of C1-BTPhen with a 4-hydroxyphenol linker **10**

Firstly, regioselective bromination[26] of 2,9-dimethyl-1,10-phenanthroline **4** was carried out with 0.6 equivalent of bromine in the presence of fuming H_2SO_4 (20% SO_3). The key intermediate, dihydrazide **8** was then synthesized through a modification of our previously reported procedure[8] in which benzylic oxidation of **5** with SeO_2 gave the dialdehyde **6** which was then converted to the dioxime. This was not isolated, but elimination achieved by direct treatment with *p*-toluenesulfonyl chloride and pyridine to afford the dinitrile **7**. The reaction of the dinitrile **7** with hydrazine hydrate in EtOH gave the bis-aminohydrazide **8** and the condensation of **8** with commercially available 2,3-butanedione in THF at reflux afforded 5 bromo-C1-BTPhen ligand **9** as a brown solid in 80% yield. Finally replacement of the bromine with a 4-hydroxyphenol linking group was successfully achieved via Suzuki coupling with 4-hydroxyphenylboronic acid.[27]

Synthesis of C1-BTPhen functionalized ZrO_2-Coated MNPs (11). Immobilisation of C1-BTPhen on MNPs was carried out in DMF in the presence of potassium hydroxide as shown in Figure 7.

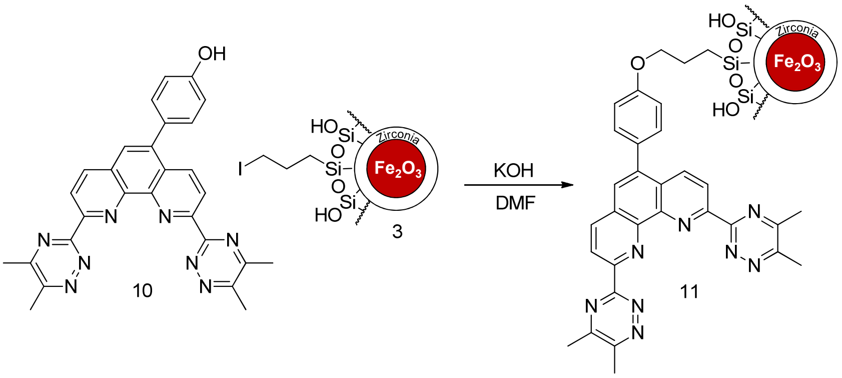


Figure 7. Immobilisation of C1-BTPhen on MNPs **11**

The C1-BTPhen ligand with a 4-hydroxyphenol linker **10** (0.3 g, 1.1 eq.) was dissolved in DMF (100 mL) and the pH of the solution was adjusted to 11 with 10 M KOH. The solution was heated to 120 °C with stirring. Iodo-functionalized ZrO_2-coated MNPs **3** (0.2 g) were slowly added and the reaction mixture was stirred at 120 °C overnight. C1-BTPhen functionalized MNPs **11** were separated by an external magnet and were thoroughly washed with degassed EtOH (2×100 mL). Finally, the product (0.2 g) was allowed to dry at 120 °C.

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