



## Appendix 8

# Separation of trivalent actinides and lanthanides with some substituted oligopyridines and triazines in synergy with 2-bromodecanoic acid\*

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## Abstract

The separation of trivalent actinides and lanthanides with some substituted oligopyridines and triazines in synergy with 2-bromodecanoic acid was studied. All ligands, except the quinolinyl-derivatives, showed high metal extraction and good separation factors for trivalent actinides over lanthanides. The substituted di-pyridyltriazines and the quaterpyridine showed the highest distribution ratios and quater- and quinquepyridine the highest separation factors, at low nitric acid concentration. The basicity of the different ligands were determined by non-aqueous titration in acetonitrile media and was related to the metal extraction. The substituted di-pyridyltriazines, which showed the highest metal extraction also showed the lowest basicity.

Keywords: Separation, Actinides, Lanthanides, Non-aqueous titration, Basicity.

## Introduction

In future reprocessing of spent nuclear fuel, transmutable actinides are considered to be separated from the fission product /1/. One of the major problems in this reprocessing is the separation of the trivalent actinides from the lanthanides, because of their similar chemical properties /2/. Previous studies on tri-pyridyltriazines (TPTZ) showed that these ligands had potential to separate trivalent actinides and lanthanides /3/. Batch extraction experiments were performed to investigate the possibility of trivalent actinide-lanthanide separation by solvent extraction with a synergistic mixture of substituted oligopyridine or triazine and 2-bromodecanoic acid. Both extraction and separation ability were studied and the basicity of the different ligands was also determined by non-aqueous titration. The extraction and separation was put in relation to the basicity of the ligands.

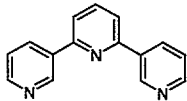
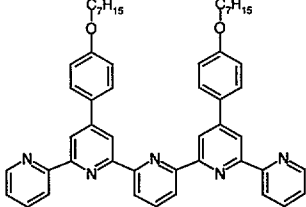
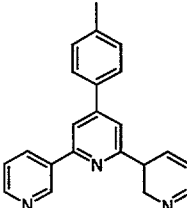
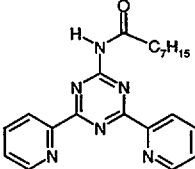
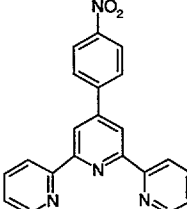
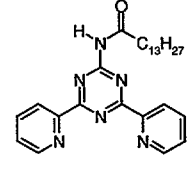
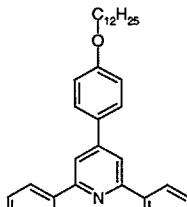
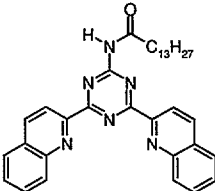
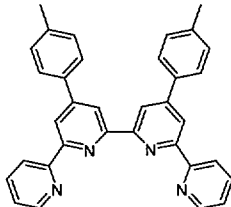
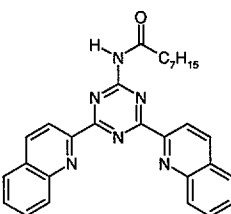
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## Experimental

**Reagents:** The listed oligopyridines and triazines, in Table A8-1, were synthesised at the University of Reading except for Terpy, 98%, which was purchased from Aldrich. The purity of the synthesised ligands were checked by <sup>1</sup>H-NMR, elemental analysis and melting point. *Tert*-butylbenzene (TBB), 99% purity, was used as the diluent in all experiments and was purchased from Acros and 2-bromodecanoic acid (HA), 98% purity, was obtained from Fluka. HPLC-grade acetonitrile from Fischer Scientific, with less than 0.0040% water, was used in the non-aqueous titrations.

**Table A8-1. Ligands studied in this work.**

Ligand	Name/Abbreviation	Ligand	Name/Abbreviation
	2,2'-6',2''-terpyridine <b>Terpy</b>		(4',4''')-di-(4-heptyloxyphenyl)-2,2':6'2'':6''2''':6'''2''''-quinquepyridine <b>Quinque</b>
	4'-tolyl-2,2':6'2''-terpyridine <b>Tolpy</b>		4-octanoyl amino-2,6 di(2-pyridyl) 1,3,5 triazine <b>OADPTZ</b>
	4'-(4-nitrophenyl)-2,2':6'2''-terpyridine <b>Nitrotolpy</b>		4-tetradecanoyl amino-2,6 di(2-pyridyl) 1,3,5 triazine <b>TADPTZ</b>
	4'-(4-dodecyloxyphenyl)-2,2':6'2''-terpyridine <b>Dodoxy</b>		4-tetradecanoyl amino-2,6 di(2-quinoliny) 1,3,5 triazine <b>TADQZ</b>
	(4',4''')-ditolyl-2,2':6'2'':6''2''':6'''2''''-quaterpyridine <b>Quater</b>		4-octanoyl amino-2,6 di(2-quinoliny) 1,3,5 triazine <b>OADQZ</b>

**Procedure:** The solvent mixture of 2-bromodecanoic acid and the extractant (oligopyridine or triazine) in TBB was vigorously shaken with the aqueous phase, containing tracer amounts of  $^{241}\text{Am}$  and  $^{152}\text{Eu}$ , for five minutes at room temperature. After phase disengagement by centrifugation, aliquots of each phase were taken for radiometric analysis. The  $\gamma$ -activities at 59.6 keV and 122 keV, for  $^{241}\text{Am}$  and  $^{152}\text{Eu}$  respectively, were measured using a HPGe detector. The distribution ratio  $D_M$  was the ratio of the radioactivity of aliquots of organic and aqueous phases, with equal volumes.

The basicities were determined by titration in acetonitrile media, using 0.1M  $\text{HClO}_4$  in acetic acid as the titrand /4/. The half-neutralisation potential (HNP) was taken as a value for the basicity after subtraction of the HNP of a imidazole, which was used as an internal reference to be able to adjust for drift of the electrode during the experiment. To facilitate dissolution of the ligands in the titration media, a constant amount of HA was added to the solvent in each experiment. For Quater and Quinque, which are even harder to dissolve, chlorobenzene was also added to the titration media to dissolve the ligands and the ligands were thereafter compared to Terpy in the same media.

## Results and discussion

**Metal extraction:** Extraction studies have been carried out on a number of oligopyridines and triazines in synergy with 2 -bromodecanoic acid (HA) in *tert*-butylbenzene (TBB).

A substitution on the terpyridine was expected to increase the distribution ratios because of an increase in lipophilicity of the ligands, but the distribution ratios for the substituted terpyridines are lower than for the unsubstituted Terpy. Other effects, like the basicity of the ligands, seems to be more important for the metal extraction than lipophilicity. The substituted terpyridines in Figure A8-1, i.e. Tolpy, Dodoxy and Nitrotolpy, show similar nitric acid dependency, distribution ratios and separation factors for americium and europium. The different substituents on the central pyridyl groups doesn't seem to effect the extraction considerably.

The substituted triazines, TADPTZ and OADPTZ, showed even better extraction than the oligopyridines, although the separation factor is similar to the oligopyridines, see Figure A8-1 and Table A8-2. On the other hand, the quinolinyl derivatives, OADQTZ and TADQTZ, showed almost no contribution to the metal extraction or separation compared to extraction with only HA, see Figure A8-1.

The oligopyridines with four and five pyridyl-groups respectively, Quater and Quinque, both showed larger selectivity for americium over europium than both the substituted terpyridines and the triazines at low nitric acid concentration, Figure A8-2. The number of nitrogens that are coordinated to the metal could be the important factor to achieve good separation of trivalent actinides and lanthanides. However, when the nitric acid concentration is increased the separation factor decreases to a value below the separation factor for the terpyridines, indicating that protonation might hinder the coordination at higher nitric acid concentration.

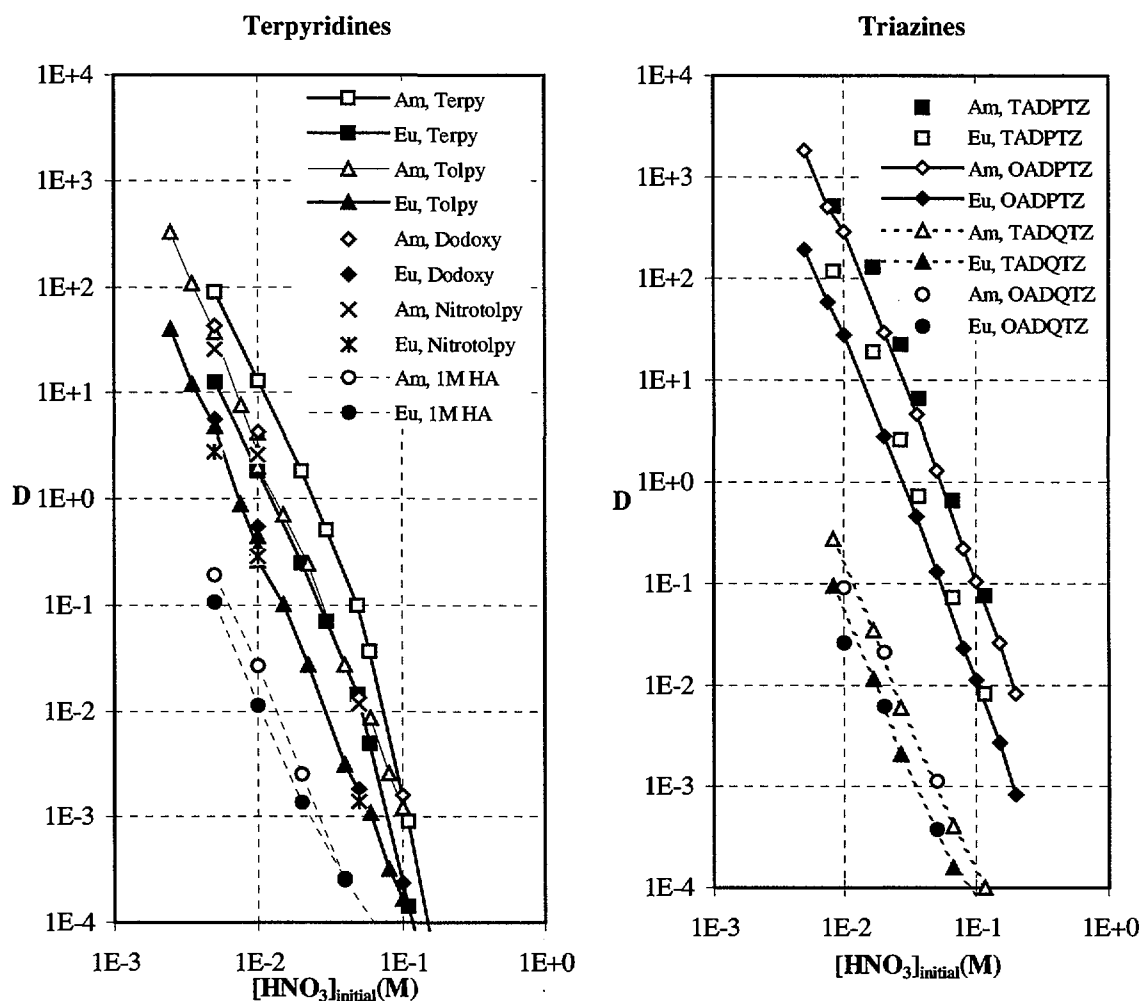
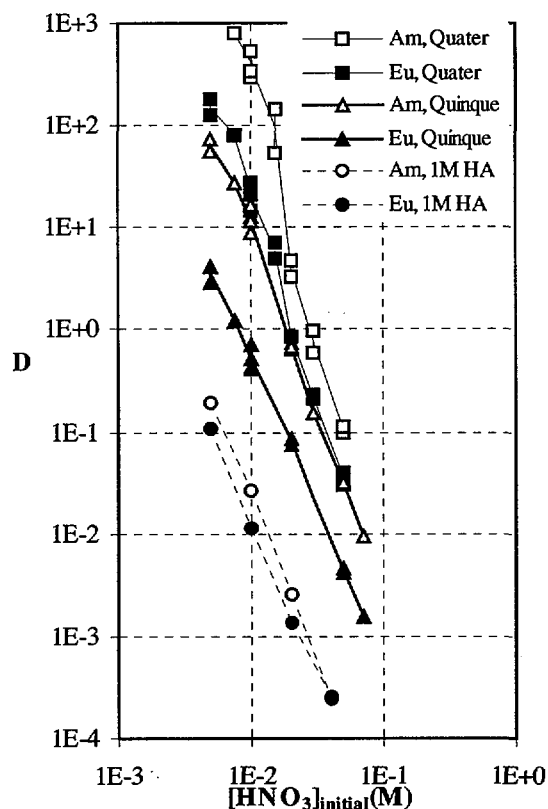


Figure A8-1. Extraction of americium and europium with 0.02M oligopyridine or triazine and 1M 2-bromodecanoic acid (HA) in *tert*-butylbenzene compared to extraction with only 1M HA.

Table A8-2. Extraction data with 0.02M oligopyridine and 1M HA in TBB at 0.01M HNO<sub>3</sub>, Average  $\Delta$ HNP measured in acetonitrile, addition of 0.25mmol HA.  $\Delta$ HNP = HNP<sub>ligand<sup>-</sup></sub> - HNP<sub>imidazole</sub> (\* interpolated values).

Ligand	$\Delta$ HNP(mV)	D <sub>Am</sub>	SF (D <sub>Am</sub> /D <sub>Eu</sub> )
Dodoxy	127	4.2	7.7
Tolpy	138	2.8	8.3
Terpy	165	13	7.2
Nitrotolpy	187	2.6	9.0
TADPTZ	187	359	7.5*
OADPTZ	190	287	10
OADQTZ	215	0.09	3.5
TADQTZ	232	0.16	3.0*



**Figure A8-2.** Extraction of americium and europium by 0.02M of Quater or Quinque and 1M 2-bromodecanoic acid in tert-butylbenzene from different initial nitric acid concentrations.

**Basicity:** The basicity of the ligands are assumed to be related to the metal extraction due to competition between protons and metal ions for the binding sites in the molecules, when extracted from acidic media. The basicity was therefore measured for the different ligands, using non-aqueous titration in acetonitrile media. The potential at the half-neutralisation volume (HNP) was used as a measure for the basicity, adjusted with HNP for an internal reference.

The titrations of the different ligands showed lower basicity, higher  $\Delta$ HNP, for Terpy compared to the substituted terpyridines, Dodoxy and Tolpy, as seen in Table A8-2. The metal extraction is highest for Terpy compared to the other terpyridines which is consistent with the assumption that low basicity gives high metal extraction. However, Nitrotolpy showed the lowest basicity of the terpyridines but also the lowest metal extraction. Low solubility of this ligand in the organic phase might cause the lower extraction. By adding extra lipophilic groups, to increase the solubility, the extraction might increase.

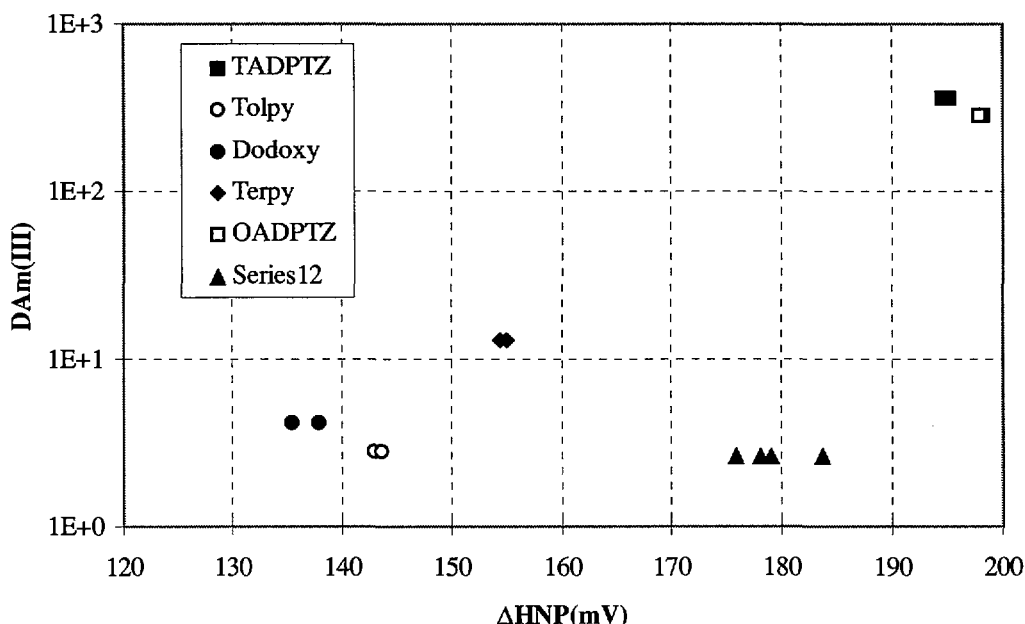
The substituted triazines showed even lower basicity compared to the substituted oligopyridines, see Table A8-2. The di-pyridyltriazines, TADPTZ and OADPTZ, also showed better metal extraction, but the quinolinyl derivatives, TADQ TZ and OADQ TZ, showed the lowest metal extraction of all studied ligands. The metal extraction seen in Figure A8-1 is mainly due to HA in this system. Molecular modelling shows that there is steric hindrance in the molecule and this might make a coordination difficult and therefore decrease the extraction.

The separation factor doesn't seem to change much when basicity changes. The best separation factors were achieved by Quater and Quinque at low nitric acid concentration and their basicity was shown to be even higher than Terpy, see Table A8-3. The number of nitrogens that coordinate to the metal during the extraction might be more important for the separation, as mentioned earlier.

**Table A8-3. Extraction data with 0.02M oligopyridine and 1M HA in TBB. Average  $\Delta$ HNP measured in 60% acetonitrile / 40% chlorobenzene with addition of 1mmol HA,  $\Delta$ HNP =  $HNP_{\text{ligand}} - HNP_{\text{imidazole}}$  (\* interpolated values).**

Name	$\Delta$ HNP(mV)	$D_{Am}$	SF ( $D_{Am}/D_{Eu}$ )
Terpy	127	13	7.2
Quater	112	390	19
Quinque	100	12	22

The relation between metal extraction and basicity is seen in Figure A8-3 where  $D_{Am(III)}$  at 0.01M  $HNO_3$  is plotted versus the  $\Delta$ HNP for the different ligands. The quinolinyl derivatives were excluded in this graph since they don't contribute to the extraction compared to HA alone. Nitrotolpy is also a bit out of range, but solubility problems with this ligand is probably effecting the metal extraction, as discussed earlier.



**Figure A8-3. Extraction of Am(III) at 0.01M  $HNO_3$  with 0.02M of the ligand, 1M HA in tert-butylbenzene plotted versus basicity (HNP) in acetonitrile.**

## References

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