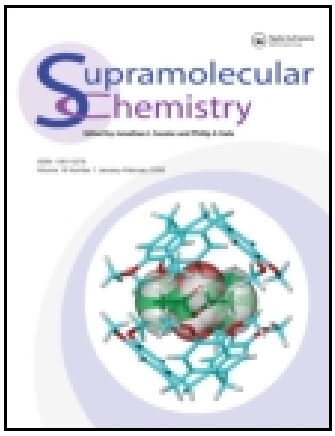

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Synthesis and Am/Eu extraction of novel TODGA derivatives†

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Various ligands with structural modifications of the *N,N,N′,N′*-tetraoctyl-3-oxapentanediamide (TODGA) skeleton were synthesised in good yields. These modifications include (1) the increase in chain length from one carbon to two carbons between the central ether oxygen atom and the amide moieties, (2) the addition of substituents on the carbon between the central oxygen atom and the amide moieties on one and both sides of the central oxygen, (3) the replacement of the central oxygen by a (substituted) nitrogen atom and (4) synthesis of a rigidified glycolamide. The effect of the structural modifications on their extraction behaviours toward Am(III) and Eu(III) at various nitric acid concentrations was studied. In most of the cases, the extraction does not exceed that of TODGA in the entire acidity range of 0.001–4 mol/l HNO_3. The extraction behaviour of monomethyl–TODGA derivative **10a** resembles that of TODGA at high nitric acid concentrations. However, at lower acidities, its *D* values are much lower, which is beneficial for possible back-extraction steps. The aza-tripodal ligands **18a,b** show reverse extraction properties compared to TODGA as far as the pH influence is concerned: at pH 2, the D_{Am} values are 49.9 and 3.1, the D_{Eu} values are 5.9 and 0.2, and the $S_{Am/Eu}$ values are 8 and 11, respectively.

Keywords: TODGA derivatives; extraction; Eu(III) and Am(III)

Introduction

During the generation of nuclear energy in nuclear power plants, a large amount of spent nuclear fuel containing radioactive by-products is produced. The amount of radioactive nuclear waste and its radiotoxicity can be reduced by the partitioning and transmutation strategy (*1*). In this strategy, the long-lived radionuclides, mainly plutonium, and the minor actinides (Am, Cm and Np) are recovered and converted to short-lived or stable isotopes by irradiation in a dedicated reactor. Plutonium, the main contributor to radiotoxicity, can already be recovered today by the plutonium uranium extraction (PUREX) process, which with some modifications can also recover neptunium (advanced PUREX). In order to achieve a significant reduction in the radiotoxicity of spent fuel, americium and curium should also be removed from the highly active raffinate of the PUREX process. The chemical similarity of trivalent actinides (An) and lanthanides (Ln) combined with the unfavourable mass ratio necessitates very demanding and complex process steps. Processes developed over the last 20 years are predominantly based on the combined extraction of actinides and lanthanides from the PUREX raffinate followed by their subsequent group separation (*2*). Different types of ligands for the separation of actinides and lanthanides have been developed as described in recent reviews (*3*, *4*, *5*).

Various processes for co-extraction of An and Ln were developed in recent years, like the trans uranium extraction (TRUEX) (*6*) (based on carbamoylmethyl phosphine oxides [CMPO]), trialkylphosphine oxides (TRPO) (*7*) (based on TRPO), di(isodecylphosphoric acid) [DIDPA] (*8*) (based on diisodecyl phosphoric acid) and diamide extraction (DIAMEX) (*9*) (based on diamide extraction) processes.

During the 1980s, the family of malonamides was developed for the extraction of actinides from PUREX raffinates (*10*). Structural optimisations ultimately led to the DIAMEX reference compound *N,N′*-dimethyl-*N,N′*-dioctylhexylethoxy malonamide (*9*, *11*).

In the early 1990s, Stephan et al. (*12*) reported on the extraction of different metal ions using multidentate ligands such as diglycolamides (DGA). The DGA substance class with an ether group between both amide functions resembles the malonamides. During the late 1990s, Sasaki and Choppin (*13*, *14*) recognised that these ligands are particularly suitable for extracting actinides from acidic waste solutions. Extensive extraction studies have been performed with this

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†Dedicated to the memory of Dmitry Rudkevich.

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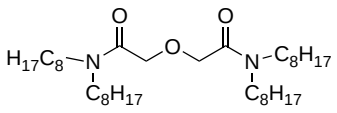


Chart 1.

very promising substance class (*15*). The change from a bidentate ligand (e.g. malonamide) to a tridentate DGA significantly increased the affinity not only for trivalent actinides but also for the lanthanides. Different DGAs have been synthesised, and *N,N,N′,N′*-tetraoctyl-3-oxapentanediamide (TODGA, Chart 1) was found to have the best properties in terms of extraction, solubility in aliphatic solvents and stability. However, TODGA has a tendency to form a third phase in aliphatic solvents such as *n*-dodecane, particularly at high metal and nitric acid concentrations (*16*, *17*).

In general, the DGAs have drawn attention as very effective ionophores for the complexation of f-elements (*18*). TODGA has been preorganised on various tripodal platforms (*19–21*) and as bis(DGA) (*22*).

Except for the replacement of the central oxygen atom by sulphur (*17*), to the best of our knowledge, the effect of structural modifications of TODGA on the extraction behaviour has not yet been studied. In the case of malonamides, small changes in the substitution pattern on the central carbon atom positively influenced the extraction ability (*23*). Herein, we describe the synthesis of different types of TODGA derivatives, among which the replacement of the central oxygen atom for NR groups, and their extraction properties for americium(III) and europium(III), simulating the extraction of actinides(III) and lanthanide-s(III) from nitric acid solutions.

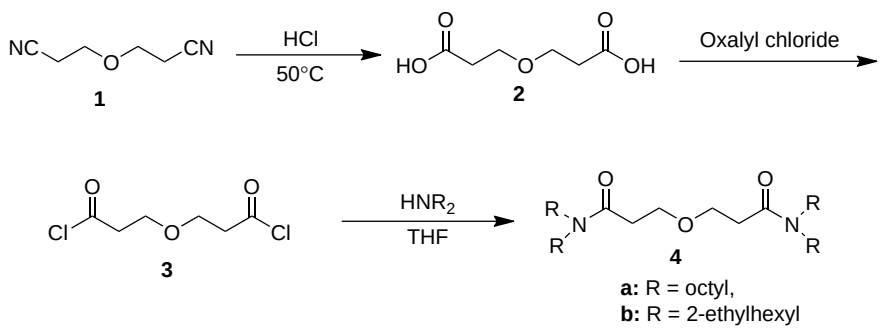
Results and discussion

Synthesis

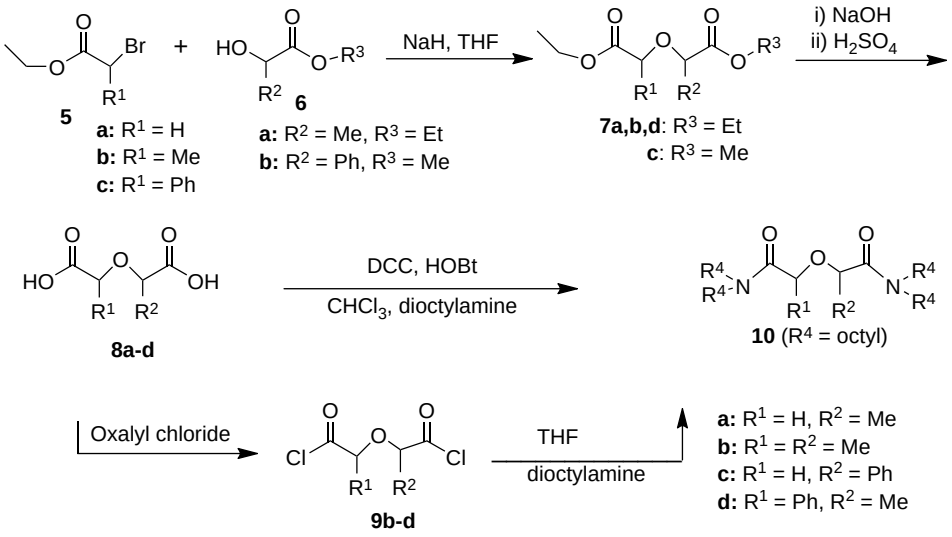
First, we prepared 3,3′-oxybis(*N,N*-alkylpropanamides) **4a,b** (Scheme 1), in which compared to TODGA the chain length between the central oxygen atom and amide moieties is enlarged. Commercially available 2-cyanoethyl ether **(1)** was converted to 3,3′-oxydipropanoic acid **(2)** according to a slightly modified literature procedure (*24*); in our hands, a longer reaction time (48 h instead of 24 h at 50°C) was needed to have full conversion. In literature (*25*), dicarboxylic acid dichloride **3** has been prepared by reaction of dicarboxylic acid **2** with thionyl chloride. However, oxalyl chloride appeared to be a more suitable reagent due to its lower boiling point giving rise to an easier workup procedure. Subsequent reaction of diacid dichloride **3** with an appropriate dialkylamine afforded the target compounds **4a** and **4b** in 78 and 62% yield, respectively. The characterisation of **4a,b** followed from its spectral data. The ^{1}H NMR spectra show a clear shift of the $CH_2C(O)$ triplet at 3.10 ppm in **3** to about 2.58 ppm in **4a,b**.

The synthesis of a series of TODGA derivatives **10a–d** having one or two substituents at the carbon atoms next to the central oxygen atom is summarised in Scheme 2. α-Bromoesters **5a–c** and α-hydroxyesters **6a,b** were coupled in the presence of NaH in tetrahydrofuran (THF) to give the diesters **7a–d** in good yields. Saponification of the ester groups in **7a–d** with NaOH in methanol afforded the dicarboxylic acids **8a–d**. The TODGA derivatives **10a–d** were prepared both by reaction of dicarboxylic acids **8a–d** with dioctylamine in the presence of dicyclohexylcarbodiimide (DCC) and 1-hydroxybenzotriazole (HOBT) and via the diacid dichlorides **9b–d** obtained by the treatment of **8a–d** with oxalyl chloride. The DCC coupling method gave rise to higher yields (70–76%) and less side products. The formation of the TODGA derivatives **10a–d** was confirmed by the NMR data; the ESI mass spectra exhibit distinct M + H peaks.

The basicity of the central oxygen atom plays an important role in the extraction of metal ions with different nitric acid concentrations (*18e*). The introduction of methyl and phenyl groups in TODGA derivatives will influence the basicity of the central oxygen atom. However, also steric interactions between these groups may play a role in the extraction. To study this effect, the rigidified tetrahydrofuran TODGA derivative **14** was synthesised (Scheme 3). Starting from the commercially available furan-2,5-dicarboxylic acid



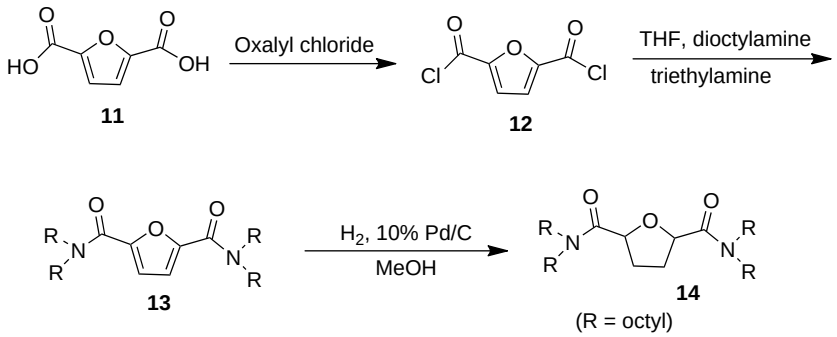
Scheme 1. Synthesis of TODGA derivatives with extended chain.



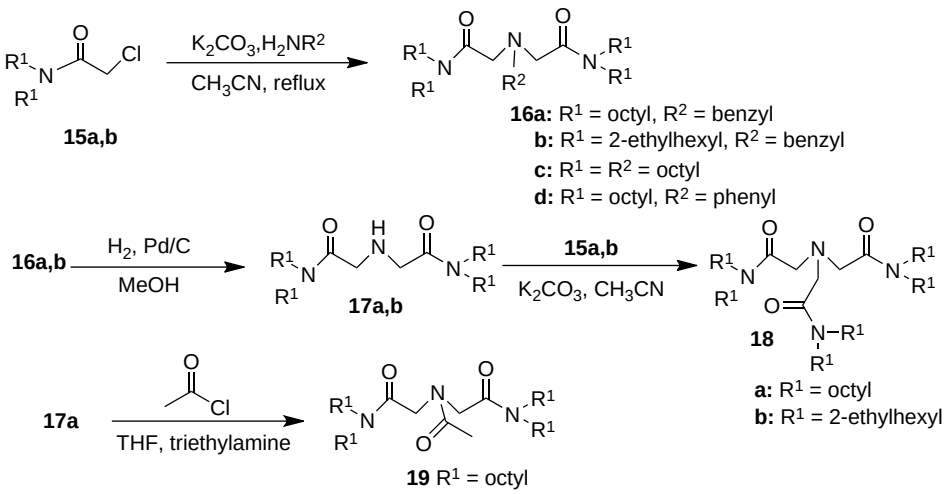
Scheme 2. Synthesis of substituted diglycolamides.

(11), there are two ways for the synthesis of **14**, viz. reduction of the furan ring as the first or the final step. Although the reduction of the ring in **11** has been described (*26*), we were not able to drive the reaction to completion, and consequently we encountered separation problems. Therefore, the second approach was followed. Furan 2,5-dicarboxylic acid **(11)** was converted into the corresponding dichloride **12** using oxalyl chloride in THF instead of thionyl chloride as described in literature (*27*). Subsequent reaction of **12** with dioctylamine gave *N,N,N′,N′*-tetraoctylfuran-2,5-dicarboxamide **(13)** in 50% yield (over two steps), which was reduced at 10 bar H_2 using 10% Pd/C as catalyst in methanol to give the target compound **14** in quantitative yield. The ^{1}H NMR spectrum of **13** exhibits a characteristic singlet for the furan ring at 6.92 ppm. However, upon reduction, the ^{1}H NMR spectrum of **14** shows the hydrogens of the tetrahydrofuran ring as multiplets at 1.96–2.11, 2.41–2.51 and 4.53–4.62 ppm (2H each) indicating the formation of diastereoisomers.

To replace the central oxygen atom in TODGA by nitrogen, the approach depicted in Scheme 4 was employed. Since nitrogen is trivalent, three ligating groups can be introduced to it. *N,N*-Dialkyl-2-chloroacetamides **(15a,b)** were reacted with various amines in refluxing acetonitrile to get **16a–d** containing different groups on nitrogen. The benzyl group of **16a,b** was removed by hydrogenolysis in the presence of 10% Pd/C as a catalyst to give **17a,b**, which upon further treatment with acetyl chloride (in the case of **17a**) gave **19,** and with **15a,b** afforded the tripodal ligands **18a,b**. In the ^{1}H NMR spectra, the characteristic singlet of **15a,b** at 4.03 ppm was shifted to 3.50–3.55 ppm in **16a,b** and to 4.22 ppm in the case of **16d** along with the appearance of peaks in the aromatic region. The formation of **17a,b** from **16a,b** was proven by the complete disappearance of the aromatic hydrogen atoms. The introduction of the third ligating site in **18a,b** was among others confirmed by the ESI mass spectra. In the case of **19**, a characteristic singlet appeared



Scheme 3. Synthesis of a rigidified diglycolamide.



Scheme 4. Synthesis of TODGA derivaties with a central nitrogen atom.

in the ^{1}H NMR spectrum at 2.03 ppm indicating the introduction of the acetyl moiety.

Extraction

All the synthesised ligands were tested using liquid–liquid extraction, and the extractabilities of the various ligands for Am(III) and Eu(III) are expressed by the distribution ratios, D_{Am} and D_{Eu}. The distribution ratios of Am and Eu are plotted as a function of the initial nitric acid concentration. The separation factor $SF_{Am/Eu}$ is the ratio of the distribution ratios, D_{Am}/D_{Eu}, and describes the selectivity of Am over Eu.

Since TODGA shows a slightly higher affinity towards trivalent lanthanides comparing to trivalent actinides, no significant increase of the separation factor between these two element groups was expected for the synthesised TODGA derivatives. However, the ligands containing a central nitrogen atom within their structure show a significant selectivity for americium as described later.

Extraction of Am(III) and Eu(III) with ligands containing oxygen as a central atom

The nature of the structure plays an important role on the extractability of the ligands. DGA contain three oxygen atoms that can easily capture the metal ions and act as tridentate ligands. From the literature (*15*, *16*), it is well known that the number of the DGA coordinated to trivalent actinides is estimated to be between three and four for Am(III) and Cm(III) by slope analysis. The synthesised ligands **4a,b** also contain three oxygens. However, they do not extract neither Am nor Eu from nitric acid solutions. The distribution ratios D_{Am} and D_{Eu} are below 0.01 in the

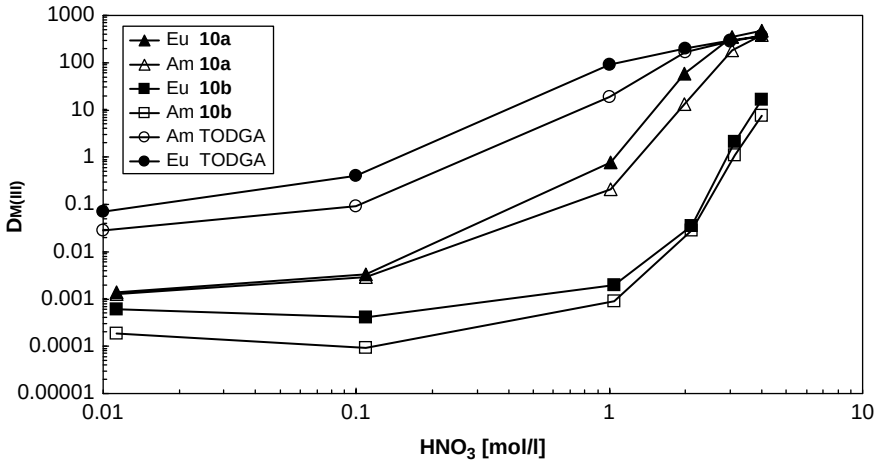


Figure 1. Nitric acid dependency for the extraction of ^{241}Am and ^{152}Eu by TODGA, **10a** and **10b**. Organic phase: 0.1 mol/l of ligand in TPH. Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu, mixing time: 15 min; $T = 22°C \pm 1°C$.

entire acidity range of 0.001–4 mol/l HNO_3. It seems that an effective metal complexation is not possible due to the increased length of the aliphatic chain between the two amide groups (compared to TODGA) making the distance between the coordinating moieties too large.

In Figure 1, the extraction results of **10a** and **10b** are compared with those of TODGA. It is observed that with increasing nitric acid concentration of the aqueous phase, the extraction of Am and Eu increases. It has been reported that the TODGA molecules aggregate in the organic phase when the aqueous phase acidity is low (*18e*). From the neutral character of the DGA and the strong D_M dependence on the HNO_3 concentration, it is assumed that the new ligands act as solvating extractants. The metals are extracted as neutral species (e.g. $Am(NO_3)_3L_n$, where L is the DGA and n is the number of L's). Ligand **10a** extracts Am and Eu more efficiently than **10b**, not as good as TODGA. The order of extractability is TODGA > **10a** > **10b**. Only at high nitric acid concentrations of 3 and 4 mol/l, the distribution ratios for **10a** are as high (over 100) as for TODGA. The differences in the extraction strength are attributed to the addition of one or two methyl groups, which decreases the flexibility of the molecule. In principle, one or two methyl groups will make the central oxygen atom more basic. Apparently, due to sterical constraints, this does not result in better extraction properties compared to TODGA.

Ligands **10c** and **10d** do not extract Am and Eu as efficiently as TODGA (Figure 2). The addition of one phenyl group to the carbon atom between the central oxygen and the carbonyl of the carboxamide group decreases the extraction properties of the ligand **(10c)**, although after adding a phenyl group on one side and a methyl group on the other side **(10d),** the distribution ratios do not change significantly compared to **10c** (Figure 2). The dominant influence of the phenyl group is clear. Both sterically and probably electronically, it has a negative influence on the extraction behaviour.

By the introduction of a tetrahydrofuran ring into the centre of the molecule **(14),** the extraction of Am and Eu was decreased compared to TODGA (Figure 3). In the case of a furan ring (ligand **13**), extraction of neither Am nor Eu was detected. In the latter case, the character of the oxygen atom in the aromatic furan ring is completely different compared to that in TODGA being less basic (*28*), explaining the lack of extraction. Surprisingly, the extraction behaviour of tetrahydrofuran **14** is better than that of dimethyl-TODGA **10b**, despite the lower concentration and the rigidification of the ligand.

From the different studied DGA analogues, ligand **10a** shows the best features with respect to further process of optimisation studies. As already discussed, **10a** shows a high extraction capability towards actinides and lanthanides at high nitric acid concentration, and the respective $D_{Am,Eu}$ values are comparable with those obtained for TODGA. Upon decreasing nitric acid concentration, however, the distribution ratios decrease much faster than for TODGA. At 0.1 mol/l nitric acid, the distribution ratios are approximately two orders of magnitude lower than for TODGA. This is favourable considering the conditions of the partitioning of high-level radioactive waste, since it facilitates the back-extraction step, i.e. the strip solution can have a higher acidity or fewer back-extraction stages are necessary to achieve a complete reversible process. The results of a recently performed counter current test, fully described in Refs (*29*) and (*30*), show that, during a TODGA-based actinide partitioning process, the complete stripping of actinides and lanthanides from a loaded organic phase was achieved with diluted nitric acid (0.01 mol/l) using a rather large number of stripping stages (e.g. 12). Within this process, it was shown that TODGA also extracts nitric acid, which will be stripped back into the aqueous phase, thereby decreasing the stripping

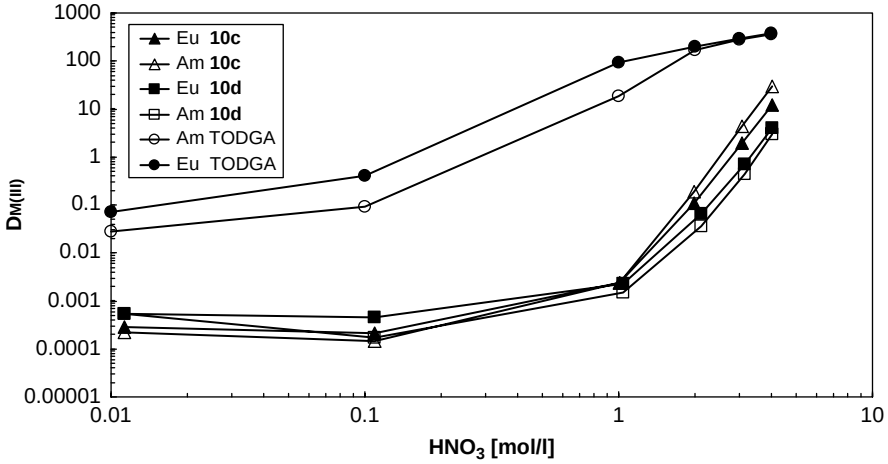


Figure 2. Nitric acid dependency for the extraction of ^{241}Am and ^{152}Eu by TODGA, **10c** and **10d**. Organic phase: 0.1 mol/l of ligand in TPH. Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu, mixing time: 15 min; $T = 22°C \pm 1°C$.

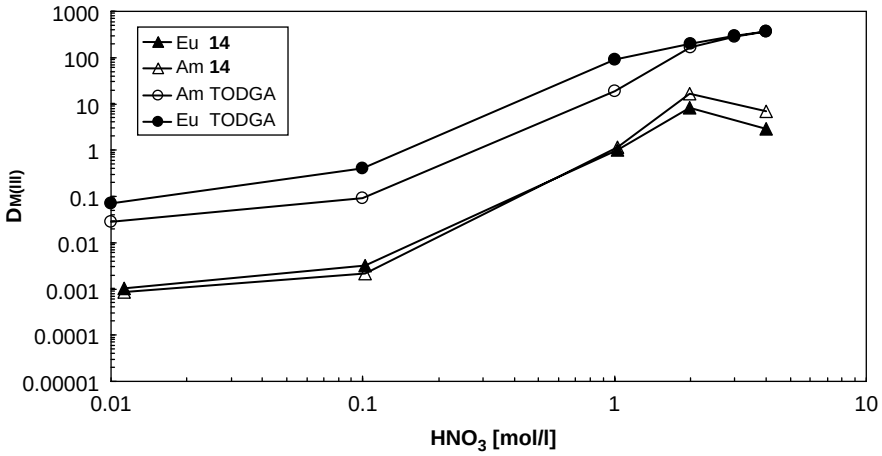


Figure 3. Nitric acid dependency for the extraction of ^{241}Am and ^{152}Eu by TODGA and **14**. Organic phase: 0.1 mol/l of TODGA or 0.08 mol/l of **14** in TPH. Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu, mixing time: 15 min TODGA (60 min ligand **14**); $T = 22°C \pm 1°C$.

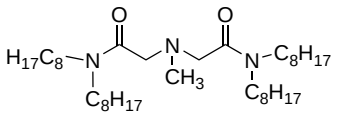
efficiency. So it can be supposed that this effect is not as important for **10a** as extracting molecule, since stripping is not so sensitive to an acidity change.

Extraction of Am(III) and Eu(III) with ligands containing nitrogen as a central atom

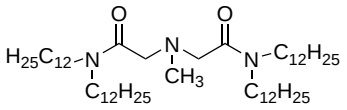
Several new ligands were synthesised composed of three donor atoms, namely two carbonyl oxygens and one nitrogen in the ether position of the central frame. Due to the softness of the nitrogen, it is expected that, beside the extractability, probably also a discrimination between the trivalent actinides and lanthanides can be achieved. The extraction studies, however, reveal that the ligands **16a,c,d, 17a** and **19** do not show any significant extraction of Am and Eu in the region between 0.01 and 4 mol/l nitric acid. The distribution ratios for Am and Eu were below 0.1 for **16a,b** and **17a** and even below 0.01 for **16d** and **19**. Similar ligands (Chart 2), where the nitrogen atom is bearing a methyl group, have already been studied by Sasaki et al. (*31*) for the extraction of technetium(VII), rhenium(VII), palladium(II) and plutonium(IV).

In these cases, the extraction of oxometallates was observed, and the results of slope analyses (log D vs. log [ligand]) indicate the species extracted to be 1:1 metal–ligand complexes. They found that the extraction of the oxometallates decreases with increasing nitric acid concentration. Tc(VII) and Re(VII) have remarkably high D values in the range between 0.1 and 1 mol/l nitric acid. The extraction of actinides was also studied using MIDOA (see Chart 2). For Pu(IV), the D values increase up to a maximum at 3 mol/l nitric acid with D_{Pu} of about 100. The decrease at higher acidities was attributed to competition with nitric acid. The neptunium extraction as Np(V) was low ($D_{Np} < 0.1$), and the extraction of Am(III) was very low ($D_{Am} < 0.01$) in the entire nitric acid concentration range of 0.1–6 mol/l. This is in agreement with our observations.

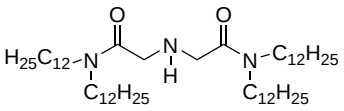
Ligands **18a** and **18b** differ from the above-studied N-bearing ligands, because they contain a third amide function at the central N atom. They showed reverse extraction properties compared to TODGA: both ligands extract Am and Eu more efficiently at low nitric acid concentrations (Figure 4). Moreover, they show a higher affinity towards Am over Eu with separation factors



MIDOA



MIDDA



IDDA

Chart 2.

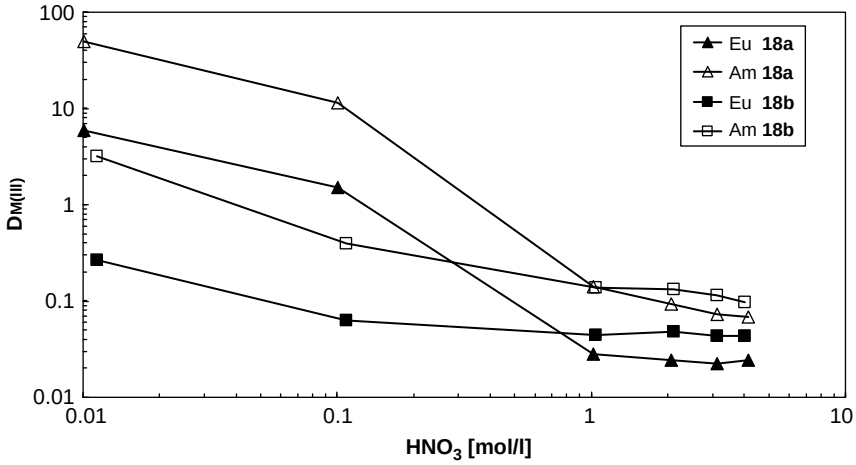


Figure 4. Nitric acid dependency for the extraction of ^{241}Am and ^{152}Eu by **18a** and **18b**. Organic phase: 0.1 mol/l of the ligand in TPH. Aqueous phase: variable concentration of nitric acid, tracers: ^{241}Am, ^{152}Eu, mixing time: 15 min; $T = 22°C \pm 1°C$.

$SF_{Am/Eu}$ of 8 and 11 at 0.01 mol/l nitric acid for **18a** and **18b**, respectively. This type of ligands also act as tridentate chelating ligands, but not by coordination of the metal by the two carbonyl oxygens and the central *N* atom (vide supra), but instead by the additional oxygen of the third amide moiety. Since the *D* values decrease with increasing acidity, it is assumed that the ligands (L) are protonated at the central *N* atom, and the extraction of actinides (M^{3+}) can be explained by ion-pair extraction. This is only a hypothesis and needs to be studied very carefully by the well-known slope analysis.

Conclusion

Different types of structurally modified TODGA derivatives have been prepared. The extraction behaviour of monomethyl–TODGA derivative **10a** resembles that of the parent TODGA at high nitric acid concentrations. However, at 0.1 mol/l nitric acid, the *D* values are about two orders of magnitude lower compared to TODGA, which is potentially useful for back-extraction processes. The aza-tripodal ligands **18a,b**, in which probably three amide groups are involved in the complexation, exhibit a reverse complexation behaviour compared to TODGA as far as the pH influence is concerned. At 0.01 mol/l nitric acid, interesting *D* and $SF_{Am/Eu}$ values are obtained.

Experimental

General

All moisture-sensitive reactions were carried out under an argon atmosphere. The solvents and all reagents were obtained from commercial sources and used without further purification. Solvents were dried according to standard procedures and stored over molecular sieves. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity INOVA (300 MHz) spectrometer. ^{1}H NMR chemical shift values (300 MHz) are reported as δ using the residual solvent signal as an internal standard ($CDCl_3$, δ 7.257). ^{13}C NMR chemical shift values (75 MHz) are reported as δ using the residual solvent signal as an internal standard ($CDCl_3$, δ 77.0). All NMR spectra were recorded in $CDCl_3$. Electrospray ionisation (positive mode) mass spectra were recorded on a WATERS LCT mass spectrometer. High-resolution mass spectra were obtained with a JOEL T100CS AccuTOF mass spectrometer at the Radboud University at Nijmegen. Elemental analyses were performed using a Flash 200 CHN analyzer of Thermo Scientific/Interscience. Analytical TLC was performed using Merck-prepared plates (silica gel 60 F-254 on aluminium). Column chromatography was carried out on Merck silica gel 60 (230–400 mesh).

General procedure for the preparation of 3,3′-oxybis(N,N-dialkylpropanamides) (4a,b)

To a solution of a dialkylamine (1 mmol) and triethylamine (0.11 g, 1.1 mmol) in freshly distilled THF (25 ml) was added a solution of 3,3′-oxydipropanoyl chloride **3** (*25*) (0.1 g, 0.5 mmol) in THF (5 ml) at room temperature. The reaction mixture was stirred at room temperature overnight. When the reaction mixture was filtered, the solvent was evaporated under reduced pressure. The residue was dissolved in ethyl acetate (50 ml), and the resulting solution was successively washed with 5% HCl solution (3 × 50 ml) and with water (3 × 50 ml). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to afford the pure products as oils.

3,3′-Oxybis(N,N-dioctylpropanamide) (4a)

Yield 78%; ^{1}H NMR: δ 0.83–0.90 (m, 12H), 1.18–1.36 (m, 40H), 1.48–1.54 (m, 8H), 2.58 (t, 4H, $J = 6.9$ Hz), 3.75 (t,

4H, $J = 6.9$ Hz), 3.17–3.21 (m, 4H), 3.22 (t, 4H, $J = 6.9$ Hz); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.1, 45.4, 66.1, 169.8; ESI-MS *m/z*: 609.6 $[M + H]^+$; HRMS (ESI) calcd for $C_{38}H_{77}N_2O_3$: 609.5934, found: 609.5915 $[M + H]^+$.

3,3′-Oxybis(N,N-bis(2-ethylhexyl)propanamide) (4b)

Yield 62%; ^{1}H NMR: δ 0.81–0.92 (m, 24H), 1.09–1.40 (m, 32H), 1.47–1.72 (m, 4H), 2.60 (t, 4H, $J = 7.2$ Hz), 3.76 (t, 4H, $J = 7.2$ Hz), 3.12 (d, 2H, $J = 7.5$ Hz), 3.24–3.27 (m, 2H); ^{13}C NMR: δ 11.4, 14.2, 23.1, 23.9, 29.2, 33.9, 37.1, 50.8, 67.1, 170.9; ESI-MS *m/z*: 609.6 $[M + H]^+$ and 627.6 $[M + H_2O]^+$; HRMS (ESI) calcd for $C_{38}H_{77}N_2O_3$: 609.5934, found: 609.5914 $[M + H]^+$.

General procedure for the preparation of diesters 7a–d

To a solution of the commercially available α-bromopropanoates **5a–c** (1 mmol) and α-hydroxyesters **6a,b** (1 mmol) in THF (25 ml) was added sodium hydride (60% in oil, 0.04 g, 1.1 mmol) portion-wise at 0°C. The reaction mixture was slowly brought to room temperature within a period of 1 h, whereupon it was refluxed for 1 h. The mixture was filtered, and the solvent was evaporated. The residue was dissolved in chloroform (50 ml), and the resulting solution was successively washed with 10% HCl (3×50 ml), saturated $NaHCO_3$ solution (3×50 ml) and water (50 ml). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure, and the residue was purified by chromatography (SiO_2, CH_2Cl_2).

***Ethyl 2-(2-ethoxy-2-oxoethoxy)propanoate (7a)* (*32*)**

Yield 84%; ^{1}H NMR: δ 1.25 (t, 6H, $J = 6.0$ Hz), 1.44 (d, 3H, $J = 6.0$ Hz), 4.00–4.27 (m, 7H); ^{13}C NMR: δ 14.3, 18.5, 61.2, 66.9, 75.2, 170.1, 172.8; ESI-MS *m/z*: 205.1 $[M + H]^+$.

***Diethyl 2,2′-oxydipropanoate (7b)* (*32*)**

Yield 84%; ^{1}H NMR: δ 1.28 (t, 6H, $J = 6.0$ Hz), 1.46 (d, 6H, $J = 6.0$ Hz), 4.09 (q, 2H, $J = 6.0$ Hz), 4.20 (q, 4H, $J = 6.0$ Hz); ^{13}C NMR: δ 14.3, 18.5, 61.3, 80.5, 173.0; ESI-MS *m/z*: 219.1 $[M + H]^+$.

Methyl 2-(2-ethoxy-2-oxoethoxy)-2-phenylacetate (7c)

Yield 74%; ^{1}H NMR: δ 1.27 (t, 3H, $J = 6.0$ Hz), 3.72 (s, 3H) 4.14 (s, 2H), 4.21 (q, 2H, $J = 6.0$ Hz), 5.18 (s, 1H), 7.32–7.47 (m, 5H); ^{13}C NMR: δ 14.3, 52.6, 61.2, 66.1, 80.5, 126.8, 128.8, 135.5, 170.0, 170.8; ESI-MS *m/z*: 253.0 $[M + H]^+$.

Ethyl 2-(2-methoxy-2-oxo-1-phenylethoxy)propanoate (7d)

Yield 45%; ^{1}H NMR: δ 1.21 (t, 3H, $J = 6.0$ Hz), 1.25 (t, 3H, $J = 6.0$ Hz), 1.44 (d, 1.5H, $J = 6.0$ Hz), 1.52 (d, 1.5H, $J = 6.0$ Hz), 3.95 (q, 0.5H, $J = 6.0$ Hz), 4.18 (m, 4.5H), 5.06 (s, 1H), 7.31–7.50 (m, 5H); ^{13}C NMR: δ 14.3, 18.6, 61.4, 67.3, 80.5, 126.7, 128.9,135.5, 170.6, 170.8; ESI-MS *m/z*: 281.1 $[M + H]^+$.

General procedure for the preparation of dicarboxylic acids 8a–d

To a solution of diesters **7a–d** in methanol (30 ml) was slowly added NaOH (0.70 g) at 0°C. The mixture was allowed to come to room temperature and was stirred overnight. The solvent was evaporated under reduced pressure. The white powder was dissolved in a minimum amount of water and was acidified with sulphuric acid. The solution was then extracted with diethyl ether (3×50 ml). The extract was concentrated under reduced pressure to give the dicarboxylic acids **8a–d**, which were used without further purification.

General procedure for the preparation of substituted DGA's 10a–d

A mixture of dicarboxylic acids **8a–d** (1 mmol), dioctylamine (0.48 g, 2 mmol), triethylamine (0.21 g, 2 mmol), DCC (0.41 g, 2 mmol) and HOBT (0.27 g, 2 mmol) in chloroform (60 ml) was stirred overnight at room temperature. The solvent was evaporated, and the resulting solid was dissolved in *n*-hexane (25 ml). After filtration, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2:MeOH = 98:2).

2-(2-(Dioctylamino)-2-oxoethoxy)-N,N-dioctylpropanamide (10a)

Yield 76%; ^{1}H NMR: δ 0.83–0.92 (m, 12H), 1.18–1.35 (m, 40H), 1.40 (d, 3H, $J = 6.0$ Hz) 1.44–1.58 (m, 8H), 3.15–3.44 (m, 8H), 3.90 (d, 1H, $J = 12.0$ Hz), 4.28 (d, 1H, $J = 12.0$ Hz), 4.55 (q, 1H, $J = 6.0$ Hz); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 46.1, 46.8, 67.2, 71.9, 168.1, 171.2; ESI-MS *m/z*: 595.4 $[M + H]^+$ and 613.5 $[M + H_2O]^+$; HRMS (ESI) calcd for $C_{37}H_{75}N_2O_3$: 595.5778, found: 595.5792 $[M + H]^+$.

2,2′-Oxybis(N,N-dioctylpropanamide) (10b)

Yield 72%; ^{1}H NMR: δ 0.83–0.92 (m, 12H), 1.18–1.36 (m, 40H), 1.45–1.55 (m, 8H), 3.03–3.24 (m, 6H), 3.41–3.51 (m, 2H), 1.40 (d, 6H, $J = 6.6$ Hz), 4.22 (q, 3H, $J = 6.6$ Hz); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0,

52.5, 74.5, 169.1; ESI-MS *m/z*: 609.5 $[M + H]^+$; HRMS (ESI) calcd for $C_{38}H_{77}N_2O_3$: 609.5934, found: 609.5930 $[M + H]^+$.

*2-(2-(Dioctylamino)-2-oxoethoxy)-*N,N*-dioctyl-2-phenylacetamide (10c)*

Yield 70%; ^{1}H NMR: δ 0.85–0.92 (m, 12H), 1.18–1.36 (m, 40H), 1.44–1.58 (m, 8H) 2.99–3.48 (m, 8H), 4.15 (d, 1H, $J = 15.0$ Hz), 4.30 (d, 1H, $J = 15.0$ Hz), 5.30 (s, 1H), 7.30–7.37 (m, 3H), 7.47 (s, 2H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 46.2, 48.2, 67.5, 80.0, 128.5, 129.0, 136.5, 168.5, 169.5, 171.5; ESI-MS *m/z*: 657.8 $[M + H]^+$; HRMS (ESI) calcd for $C_{42}H_{77}N_2O_3$: 657.5934, found: 657.5937 $[M + H]^+$.

*2-(2-(Dioctylamino)-2-oxo-1-phenylethoxy)-*N,N*-dioctylpropanamide (10d)*

Yield 74%; ^{1}H NMR: δ 0.85–0.92 (m, 12H), 1.17–1.34 (m, 40H), 1.37 (d, 1.5H, $J = 6.6$ Hz), 1.44 (d, 1.5H, $J = 6.6$ Hz), 1.44–1.58 (m, 8H), 2.90–3.50 (m, 8H), 4.27 (q, 0.5H, $J = 6.6$ Hz), 4.51 (q, 0.5H, $J = 6.6$ Hz), 5.11 (s, 0.5H), 5.22 (s, 0.5H), 7.30–7.48 (m, 5H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 47.5, 71.9, 79.2, 127.9, 129.1, 137.2, 169.5, 171.5; ESI-MS *m/z*: 671.7 $[M + H]^+$; HRMS (ESI) calcd for $C_{43}H_{79}N_2O_3$: 671.6091, found: 671.6091 $[M + H]^+$.

N,N,N′,N′-*Tetraoctylfuran-2,5-dicarboxamide (13)*

To a solution of furan-2,5-dicarboxylic acid **11** (0.4 g, 2.56 mmol) in THF (25 ml) was added oxalyl chloride (0.64 g, 5.1 mmol). The reaction mixture was refluxed overnight. The solvent and the excess of oxalyl chloride were evaporated under reduced pressure. The obtained furan-2,5-dicarbonyl dichloride **12** was directly reacted with dioctylamine (1.54 g, 6.4 mmol) in THF (30 ml) using triethylamine (0.71 g, 7 mmol) as a base. The reaction mixture was stirred at room temperature overnight. The solvent was evaporated, and the residue was dissolved in dichloromethane (50 ml). The resulting solution was washed with 5% HCl solution (3 × 50 ml) and with water (3 × 50 ml). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography (SiO_2, CH_2Cl_2:MeOH = 97:3) to afford **13** as an oil. Yield 50%; ^{1}H NMR: δ 0.85–0.92 (m, 12H), 1.18–1.35 (m, 40H), 1.54–1.58 (m, 8H), 3.39–3.56 (m, 8H), 6.92 (s, 2H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 46.8, 140.2, 154.9, 169.9; ESI-MS *m/z*: 603.6 $[M + H]^+$; HRMS (ESI) calcd for $C_{38}H_{71}N_2O_3$: 603.5465, found: 603.5463 $[M + H]^+$.

N,N,N′,N′-*Tetraoctyltetrahydrofuran-2,5-dicarboxamide (14)*

A solution of **13** (0.69 g, 1.16 mmol) in methanol (30 ml) in the presence of 10% Pd/C (0.25 g) was kept under 8 bar H_2 in an autoclave overnight. After removal of the catalyst by filtration, the solvent was evaporated under reduced pressure to afford **14** as an oil in quantitative yield. ^{1}H NMR: δ 0.85–0.94 (m, 12H), 1.16–1.36 (m, 40H), 1.44–1.64 (m, 8H), 3.15–3.32 (m, 6H), 3.42–3.55 (m, 2H), 1.96–2.11 (m, 2H), 2.41–2.51 (m, 2H), 4.53–4.62 (m, 2H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 46.4, 47.0, 78.1, 169.5; ESI-MS *m/z*: 607.6 $[M + H]^+$; HRMS (ESI) calcd for $C_{38}H_{75}N_2O_3$: 607.5778, found: 607.5754 $[M + H]^+$.

*General procedure for the preparation of 2,2′-(alkylazanediyl)bis(*N,N*-dialkylacetamides) 16a–d*

A mixture of 2-chloro-*N,N*-dialkylacetamides **15a,b** (*33*) (6.2 mmol), alkylamine/arylamine (3.1 mmol), K_2CO_3 (1.2 g, 9 mmol) and KI (0.25 g) in acetonitrile (30 ml) was refluxed overnight. The acetonitrile was evaporated, and the residue was dissolved in ethyl acetate (50 ml). The resulting solution was washed with dil. HCl (3 × 50 ml) and with water (3 × 50 ml). The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography (SiO_2).

*2,2′-(Benzylazanediyl)bis(*N,N*-dioctylacetamide) (16a)*

Eluent: CH_2Cl_2:EtOAc = 7:3; oil; yield 78%; ^{1}H NMR: δ 0.85–0.92 (m, 12H), 1.17–1.34 (m, 40H), 1.47–1.55 (m, 8H), 3.10 (t, 4H, $J = 7.5$ Hz), 3.22 (t, 4H, $J = 7.5$ Hz), 3.50 (s, 4H), 3.84 (s, 2H), 7.20–7.42 (m, 5H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 46.3, 55.0, 59.4, 127.7, 128.8, 130.2, 167.9; ESI-MS *m/z*: 670.6 $[M + H]^+$; HRMS (ESI) calcd for $C_{43}H_{80}N_3O_2$: 670.6251, found: 670.6216 $[M + H]^+$.

*2,2′-(Benzylazanediyl)bis(*N,N*-bis(2-ethylhexyl)acetamide) (16b)*

Eluent: CH_2Cl_2:EtOAc = 7:3; oil; yield 70%; ^{1}H NMR: δ 0.81–0.92 (m, 24H), 1.09–1.40 (m, 32H), 1.47–1.75 (m, 4H), 3.10 (d, 2H, $J = 7.5$ Hz), 3.18–3.35 (m, 2H), 3.55 (s, 4H), 3.89 (s, 2H), 7.20–7.42 (m, 5H); ^{13}C NMR: δ 11.4, 14.2, 23.1, 23.9, 29.3, 34.0, 46.3, 55.0, 59.4, 127.7, 128.8, 130.2, 167.9; ESI-MS *m/z*: 670.6 $[M + H]^+$; HRMS (ESI) calcd for $C_{43}H_{80}N_3O_2$: 670.6251, found: 670.6226 $[M + H]^+$.

*2,2′-(Octylazanediyl)bis(*N,N*-dioctylacetamide) (16c)*

Eluent: CH_2Cl_2:EtOAc = 7:3; oil; yield 75%; ^{1}H NMR: δ 0.85–0.92 (m, 15H), 1.17–1.34 (m, 50H), 1.47–1.55 (m, 10H), 2.67–2.73 (m, 2H), 3.22 (t, 8H, $J = 6.9$ Hz), 3.48–

3.56 (m, 4H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 46.5, 49.1, 56.2; ESI-MS *m/z*: 692.6 $[M + H]^+$; HRMS (ESI) calcd for $C_{44}H_{90}N_3O_2$: 692.7033, found: 692.7000 $[M + H]^+$.

*2,2′-(Phenylazanediyl)bis(*N,N*-dioctylacetamide) (16d)*

Eluent: CH_2Cl_2; yield 65%; mp 46–48°C; ^{1}H NMR: δ 0.85–0.92 (m, 12H), 1.17–1.34 (m, 40H), 1.47–1.54 (m, 8H), 3.22 (t, 4H, $J = 7.5$ Hz), 3.36 (t, 4H, $J = 7.5$ Hz), 4.22 (s, 4H), 6.42 (d, 2H, $J = 7.8$ Hz), 6.64 (t, 1H, $J = 7.2$ Hz), 7.14 (t, 2H, $J = 8.0$ Hz); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.6, 29.4, 32.0, 46.5, 47.6, 53.9, 117.8, 112.5, 129.3, 149.0, 169.6; ESI-MS *m/z*: 656.8 $[M + H]^+$. Elem. Anal. calcd for $C_{42}H_{77}N_3O_2$: C, 76.89; H, 11.83; N, 6.40. Found: C, 76.88; H, 11.86; N, 6.37; HRMS (ESI) calcd for $C_{42}H_{78}N_3O_2$: 656.6094, found: 656.6069 $[M + H]^+$.

*General procedure for the preparation of 2,2′-azanediylbis(*N,N*-dialkylacetamides) 17a,b*

A mixture of **16a,b** (1.5 mmol) and 10% Pd/C (0.25 g) in ethanol (40 ml) was kept under H_2 atmosphere overnight. After removal of the catalyst by filtration, the solvent was evaporated under reduced pressure to afford **17a,b** as oils in quantitative yield.

*2,2′-Azanediylbis(*N,N*-dioctylacetamide) (17a)*

^{1}H NMR: δ 0.85–0.92 (m, 12H), 1.17–1.34 (m, 40H), 1.47–1.54 (m, 8H), 2.62–2.82 (bs, 1H), 3.10 (t, 4H, $J = 5.6$ Hz), 3.22 (t, 4H, $J = 5.6$ Hz), 3.50 (s, 4H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.6, 29.5, 32.1, 42.6, 172.5; ESI-MS *m/z*: 580.5 $[M + H]^+$; HRMS (ESI) calcd for $C_{36}H_{74}N_3O_2$: 580.5781, found: 580.5759 $[M + H]^+$.

*2,2′-Azanediylbis(*N,N*-bis(2-ethylhexyl)acetamide) (17b)*

^{1}H NMR: δ 0.81–0.92 (m, 24H), 1.09–1.40 (m, 32H), 1.47–1.75 (m, 4H), 3.10 (d, 2H, $J = 7.5$ Hz), 3.18–3.35 (m, 2H), 3.59 (s, 4H); ^{13}C NMR: δ 11.4, 14.2, 23.1, 23.9, 29.3, 34.0, 42.6, 171.9; ESI-MS *m/z*: 580.5 $[M + H]^+$; HRMS (ESI) calcd for $C_{36}H_{74}N_3O_2$: 580.5781, found: 580.5759 $[M + H]^+$.

*General procedure for the preparation of nitrilotris(*N,N*-dialkylacetamides) 18a,b*

A mixture of **17a,b** (1 mmol), 2-chloro-*N,N*-dialkylacetamides **15a,b** (1 mmol), K_2CO_3 (0.41 g, 3 mmol) and KI (0.25 g) in acetonitrile (30 ml) was refluxed overnight. The acetonitrile was evaporated, and the residue was dissolved in ethyl acetate (50 ml). The resulting solution was washed with 5% HCl (3 × 50 ml) and water (3 × 50 ml), dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by chromatography (SiO_2, CH_2Cl_2:EtOAc = 7:3) to afford pure **18a,b** as oils.

*2,2′,2″-Nitrilotris(*N,N*-dioctylacetamide) (18a)*

Yield 75%; ^{1}H NMR: δ 0.83–0.91 (m, 18H), 1.11–1.36 (m, 60H), 1.36–1.57 (m, 12H), 3.15–3.31 (m, 12H), 3.62 (s, 6H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 46.5, 52.5, 169.2; ESI-MS *m/z*: 862.0 $[M + H]^+$ and 884.0 $[M + Na]^+$; HRMS (ESI) calcd for $C_{54}H_{109}N_4O_3$: 861.8500, found: 861.8509 $[M + H]^+$.

*2,2′,2″-Nitrilotris(*N,N*-bis(2-ethylhexyl)acetamide) (18b)*

Yield 70%; ^{1}H NMR: δ 0.81–0.92 (m, 36H), 1.09–1.40 (m, 48H), 1.47–1.75 (m, 6H), 3.01–3.38 (m, 12H), 3.72 (s, 6H); ^{13}C NMR: δ 11.4, 14.2, 23.1, 23.9, 29.3, 34.0, 37.4, 52.6, 169.3; ESI-MS *m/z*: 862.0 $[M + H]^+$; HRMS (ESI) calcd for $C_{54}H_{109}N_4O_3$: 861.8500, found: 861.8527 $[M + H]^+$.

*2,2′-(Acetylazanediyl)bis(*N,N*-dioctylacetamide) (19)*

To a solution of **17a** (1.15 g, 2 mmol) in freshly distilled THF (25 ml), containing triethylamine (0.22 g, 2.1 mmol) as a base, was added dropwise a solution of acetyl chloride (0.15 g, 2 mmol) in THF (5 ml). The reaction mixture was stirred at room temperature overnight. Subsequently, the reaction mixture was filtered, and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (50 ml). The resulting solution was washed with a saturated $NaHCO_3$ solution (3 × 50 ml) and with water (3 × 50 ml), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography (SiO_2, CH_2Cl_2:EtOAc = 7:3) to give pure **19** as an oil. Yield 89%; ^{1}H NMR: δ 0.81–0.92 (m, 12H), 1.09–1.39 (m, 40H), 1.36–1.56 (m, 8H), 2.03 (s, 3H), 3.10–3.32 (m, 8H), 4.26 (s, 4H); ^{13}C NMR: δ 14.3, 22.8, 27.2, 28.7, 29.3, 32.0, 48.2, 56.3, 171.5, 173.5; ESI-MS *m/z*: 622.7 $[M + H]^+$; HRMS (ESI) calcd for $C_{38}H_{76}N_3O_3$: 622.5887, found: 622.5907 $[M + H]^+$.

Extraction procedure

All the ligands were dissolved in total petroleum hydrocarbons (TPH) to a preferable concentration of 0.1 mol/l. Only ligand **14** was tested at a concentration of 0.08 mol/l due to a lack of the ligand. The obtained organic solvent was contacted with nitric acid of variable concentrations (0.01–4 mol/l) containing traces of Am(III) and Eu(III). Nitric acid solutions were prepared by diluting concentrated nitric acid (Merck KGa,

Darmstadt, Germany) with Ultra pure water. The acidity was checked by titration with NaOH.

The batch extraction experiments were performed in 2 ml glass vials. Organic and aqueous phases (500 μl) were spiked with 10 μl of radiotracer (^{241}Am, ^{152}Eu, approx. 25 KBq/ml) and shaken by a vortex mixer for 15 min until equilibrium (in the case of **14,** the mixing time was 60 min). Separation of the phases by centrifugation was followed by sampling of 200 μl of each phase for analysis using high-purity germanium spectrometer system obtained from EG&G Ortec, München, Germany, and equipped with the gamma vision software. The γ-lines at 59.5 and 121.8 keV were examined for ^{241}Am and ^{152}Eu, respectively. The distribution ratio D was measured as the ratio between the radioactivity of an isotope in the organic and the aqueous phases. Distribution ratios between 0.1 and 100 exhibit a maximum error of ± 5%. The error may be up to ± 20% for smaller and larger values.

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