

Synthesis and characterization of new unsymmetrical diglycolamide extractants for lanthanide ion partitioning: part two – branched alkyl derivatives

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Research Article

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Posted Date: September 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10911434/v1>

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Additional Declarations: No competing interests reported.

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**Synthesis and characterization of new unsymmetrical
diglycolamide extractants for lanthanide ion partitioning:
part two – branched alkyl derivatives**

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Abstract

Six new unsymmetrical diglycolamide (UDGA) ligands have been synthesized and evaluated as new solvent extraction reagents for the partitioning of trivalent lanthanide ions from acidic nitrate media. The distribution of europium (Eu) between aqueous phases of varying nitric acid concentrations and a UDGA organic phase was measured radiometrically. The stoichiometry and conditional extraction constants of the Eu-UDGA complexes present in the organic phase are reported. Luminescence spectroscopy investigations confirmed these same trends and determined relative stability constants and stoichiometry of the complexes in acetonitrile.

Keywords

unsymmetrical diglycolamide, solvent extraction, lanthanide partitioning, nuclear fuel reprocessing, ligand synthesis

Introduction

Diglycolamide (DGA) ligands are diamide analogs of the water-soluble molecule, diglycolic acid, which bind to metal cations through two amidic carbonyl oxygen atoms and a bridging etheric oxygen atom [1]. Organic-soluble diglycolamide compounds were initially developed by Stephan and co-workers in the early 1990s as an alternative to expensive macrocyclic compounds (e.g., cryptands and crown ethers) for the extraction of divalent strontium from several types of aqueous media at varying pH values [2]. In the late 1990s, Sasaki and co-workers synthesized the diglycolamide extractant, *N,N'*-dimethyl-*N,N'*-dihexyldiglycolamide (DMDHDGA, Fig. 1), which efficiently extracted both Eu(III) and Am(III) into a toluene organic phase from an acidic (pH = 3.0) aqueous phase [3, 4].

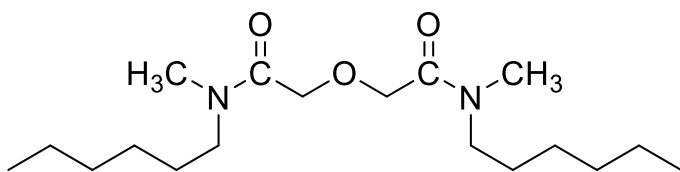


Fig. 1 Structure of *N,N'*-dimethyl-*N,N'*-dihexyldiglycolamide (DMDHDGA)

Sasaki et al. continued in this same vein and synthesized a series of extractants with alkyl chains varying from *n*-propyl to *n*-dodecyl. The *n*-octyl ligand variant, *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, Fig. 2), exhibited good solubility in aliphatic diluents (e.g., 0.1 M TODGA in *n*-dodecane) and quantitatively extracted both actinides and lanthanides from acidic nitrate solutions (e.g., 1 M HNO₃) [5].

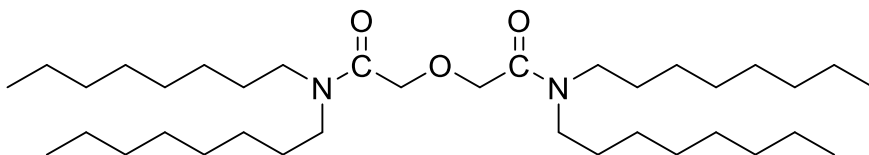


Fig. 2 Structure of *N,N,N',N'*-tetraoctyldiglycolamide (TODGA)

However, the TODGA ligand system does tend toward the formation of a third (heavy organic) phase when pushed to high acidities (e.g., >3 M HNO₃) or high lanthanide cation concentrations (e.g., >14 mM Nd in 1 M HNO₃) [6, 7]. In 2004, Testard et al. theorized that the formation of the third phase was caused by the self-aggregation of the polar TODGA cores into tetrameric reverse micelles [6]. The addition of a phase modifier like tributyl phosphate increases the metal loading capacity of the extractant, but reintroduces phosphorus into the waste stream, which can cause complications [8]. Phosphorus-based extractants or phase modifiers leave behind phosphate residues in the solid waste stream [9]. The diglycolamide ligands contain only carbon, hydrogen, oxygen, and nitrogen, which follows the CHON principle and makes them completely incinerable [10].

In an attempt to combat the phase modifier problem, Ravi and co-workers then synthesized a series of unsymmetrical diglycolamide extractants with longer *n*-dodecyl alkyl chains on one side of the ligand and shorter *n*-octyl chains on the other side. The ligand *N,N*-didodecyl-*N',N'*-dioctyldiglycolamide (D³DODGA, Fig. 3) avoided third phase formation with up to 0.6 M Nd in 3-4 M HNO₃ and a ligand concentration of 0.1 M D³DODGA. As expected, though, D³DODGA also had lower distribution ratios for the extraction of Am(III) and Eu(III) compared to TODGA [11].

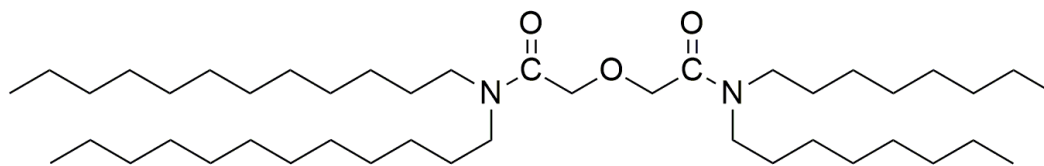


Fig. 3 Structure of *N,N*-didodecyl-*N',N'*-dioctyldiglycolamide (D³DODGA)

Previous work by Tokheim et al. continued to focus on these so-called type 1 unsymmetrical diglycolamides, with the addition of cyclic amides as the hydrophilic moieties. The dioctyl

pyrrolidinyl (DOpyrDGA) and dioctyl piperidinyl (DOpipDGA, Fig. 4) extractants were the most promising ligands for lanthanide metal extraction in the study but still required a 5% 1-octanol phase modifier in the *n*-dodecane diluent phase [12].

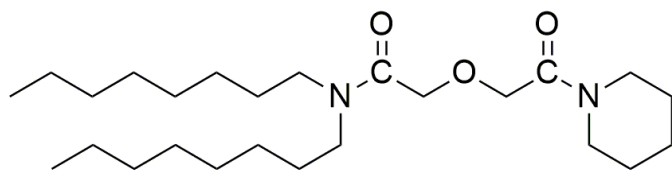


Fig. 4 Structure of *N,N*-dioctyl-*N'*-piperidinyldiglycolamide (DOpipDGA)

Recent work by Kolesar et al. emulated this type 1 UDGA and included six new ligands with the bulkier *n*-dodecyl alkyl chain to improve solubility in the organic diluent. The strongest metal extraction for La, Ce, and Pr was observed with the didodecyl piperidinyl extractant (D³pipDGA, Fig. 5), although this work also utilized the 5% 1-octanol phase modifier in *n*-dodecane [13].

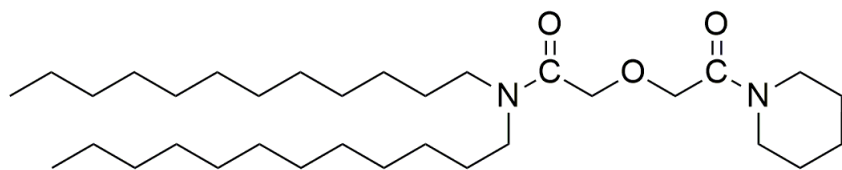


Fig. 5 Structure of *N,N*-didodecyl-*N'*-piperidinyldiglycolamide (D³pipDGA)

The current work focused on a similar polar/nonpolar asymmetry with one end of the molecule being a five- or six-membered ring and the other end being a 2-ethylhexyl or 3,7-dimethyloctyl group. As mentioned above, six straight-chain variants (*n*-hexyl or *n*-octyl) were previously synthesized and were found to quantitatively extract Eu(III) from acidic nitrate media (e.g., 1 M HNO₃). Unfortunately, the three *n*-hexyl derivatives were prone to supramolecular aggregation when in contact with highly acidic nitrate media (e.g., 3 M HNO₃) and formed a problematic third phase [12]. The current work looks at alkyl chains with at least eight carbons with the hope of improved solubility in the organic diluent. The alkyl chains are also branched, which could help eliminate some of the self-aggregation and third phase formation. The branched alkyl group,

2-ethylhexyl, has been used previously to synthesize the symmetrical diglycolamide *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (TEHDGA, Fig. 6), which has slightly lower metal distribution ratios than TODGA [14].

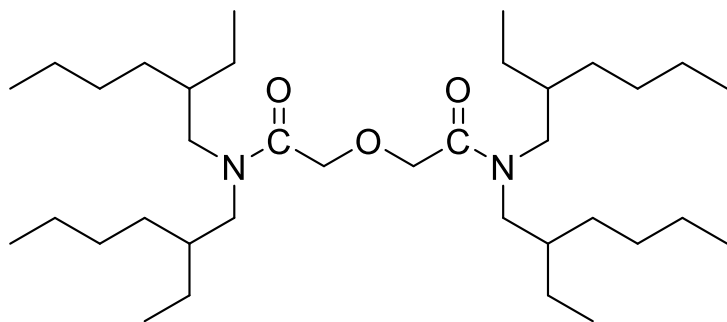


Fig. 6 Structure of *N,N,N',N'*-tetra(2-ethylhexyl)diglycolamide (TEHDGA)

The branched alkyl chains decrease metal extraction but may also decrease extractant aggregation in the organic phase, which could be a necessary tradeoff for a large-scale solvent extraction system. The second branched alkyl group, 3,7-dimethyloctyl, has never been incorporated into a diglycolamide ligand and offers two additional carbon atoms (C_{10} vs. C_8) and shorter branches (methyl vs. ethyl) compared to the 2-ethylhexyl alkyl group. The ensuing article explores the different properties associated with six novel type 1 unsymmetrical diglycolamides. All ligands were synthesized from basic starting materials and characterized using NMR and IR spectroscopy. The purpose of this study was to observe how branched alkyl groups and the number of carbon atoms affect solubility in organic diluents and lanthanide metal extraction. Various solvent extraction experiments were performed to test each new ligand. Luminescence spectroscopy was also utilized to further probe the metal-ligand complexes. The branched alkyl derivatives of this study were also compared to the straight-chain derivatives from previously completed work, part 1 of this endeavor [12].

Experimental

Materials

The diglycolic anhydride starting material was obtained from Alfa Aesar (97%) and used without further purification. Bis(2-ethylhexyl)amine was obtained from Sigma-Aldrich (99%) and distilled out of calcium hydride before use. Bis(3,7-dimethyloctyl)amine was prepared in a separate synthesis from (±)-citronellal (Alfa Aesar, 96%). The cyclic secondary amines (pyrrolidine, piperidine, and morpholine) were all obtained from Sigma-Aldrich (reagent grade) and distilled out of calcium hydride before use. All other synthesis reagents were obtained from Sigma-Aldrich (reagent grade) and used without further purification.

All nitric acid solutions were titrated with sodium hydroxide to determine accurate concentrations using a Mettler Toledo DL50 titrator. The radiotracer europium-152/154 was produced by neutron activation of Eu_2O_3 (Arris International Corp., 99.999%) in the 1 MW Teaching Research Isotopes General Atomics (TRIGA) nuclear reactor at the Washington State University Nuclear Science Center (WSUNSC). A cold europium nitrate stock solution was prepared by the addition of concentrated nitric acid to Eu_2O_3 .

Organic diluents *n*-octane, 1-octanol, *n*-dodecane, and acetonitrile were obtained from Acros Organics (99%), Sigma-Aldrich (99%), Alfa Aesar (99%), and Fisher Scientific (HPLC grade), respectively, and used without further purification. Synthesized unsymmetrical diglycolamide ligands were purified by Kugelrohr distillation (Büchi) or flash chromatography (Teledyne Isco CombiFlash®) and were characterized using infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and high-resolution mass spectrometry (HRMS). The symmetrical diglycolamide *N,N,N',N'*-tetraoctyldiglycolamide (TODGA, >99% purity) was

generously donated by Dr. Yuji Sasaki from the Japan Atomic Energy Research Institute in Tokai, Ibaraki, Japan.

Synthesis of UDGA extractants

The secondary amine, bis(3,7-dimethyloctyl)amine, was prepared in a separate synthesis through the reductive amination and hydrogenation of citronellal with hydrogen and ammonia in the presence of platinum and rhodium catalysts. The reaction details are shown in Fig. 7.

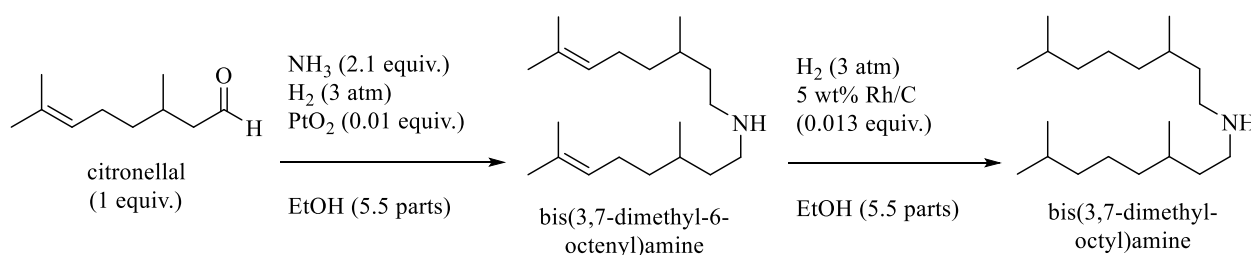


Fig. 7 Reductive amination (step 1) and hydrogenation (step 2) of citronellal

The amidation of diglycolic anhydride and methylation of diglycolamic acid (Fig. 8) were adapted from previous works by Ramirez et al. and Stodola, respectively [15, 16].

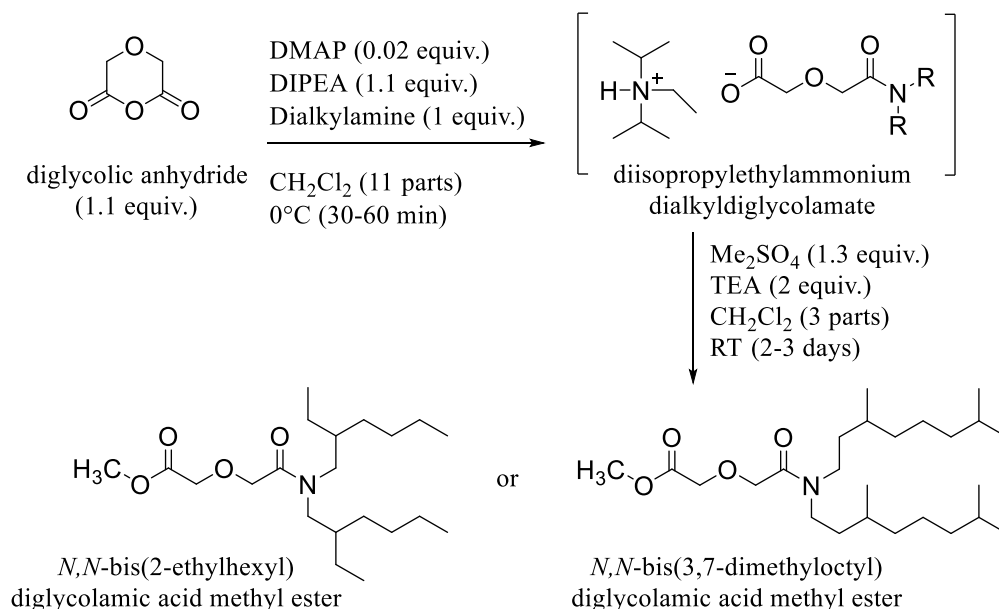


Fig. 8 Amidation of diglycolic anhydride with bis(2-ethylhexyl)amine or bis(3,7-dimethyloctyl)amine (step 1) followed by the methylation of the dialkyl diglycolamate salt with dimethyl sulfate (step 2) [R = 2-ethylhexyl or 3,7-dimethyloctyl]

The amidation of the diglycolamic acid methyl ester (Fig. 9) was adapted from a review on amide bond formation by Montalbetti and Falque [17]. All steps were performed under ambient atmospheric conditions.

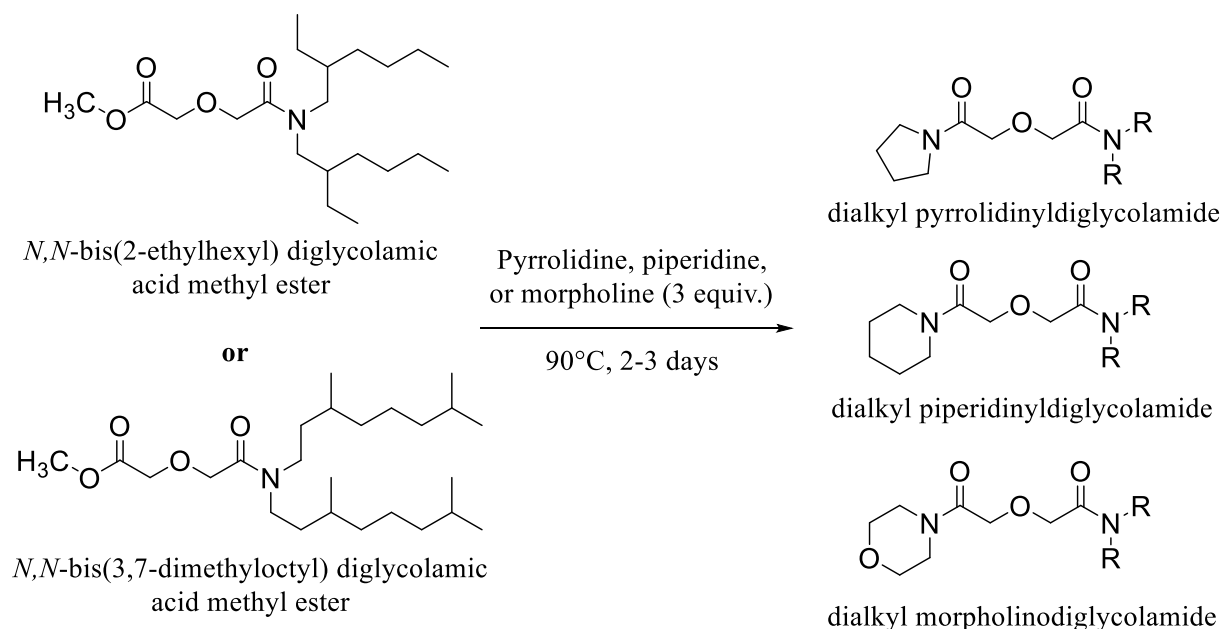


Fig. 9 Amidation of dialkyl diglycolamic acid methyl esters with three different cyclic secondary amines (pyrrolidine, piperidine, and morpholine) [R = 2-ethylhexyl or 3,7-dimethyloctyl]

The structures of the six newly synthesized unsymmetrical diglycolamides are shown in Fig. 10.

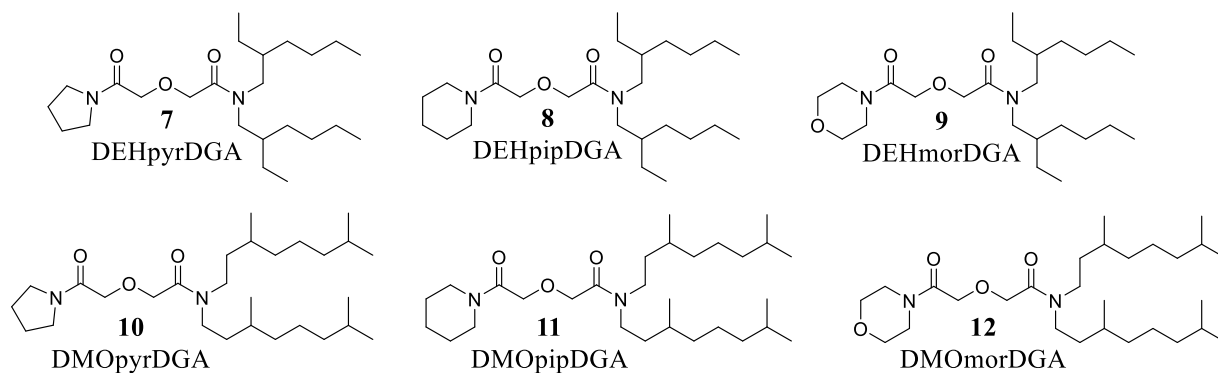


Fig. 10 Structures of newly synthesized unsymmetrical diglycolamides (7-12) with acronyms provided (DEH = bis(2-ethylhexyl), DMO = bis(3,7-dimethyloctyl), pyr = pyrrolidinyl, pip = piperidinyl, mor = morpholino, DGA = diglycolamide)

Ligands **7-12** were fully characterized using ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and high-resolution mass spectrometry. Data for ligand DEHpyrDGA(7) are shown below (data for ligands **8-12** can be found in supplementary material):

DEHpyrDGA(7): ^1H -NMR (300 MHz, CDCl_3 , δ): 4.38 (s, 2H), 4.29 (s, 2H), 3.49 (t, $J = 6.8$ Hz, 2H), 3.41 (t, $J = 6.7$ Hz, 2H), 3.28 (m, 2H), 3.10 (d, $J = 7.5$ Hz, 2H), 1.94 (p, $J = 6.4$ Hz, 2H), 1.85 (p, $J = 6.2$ Hz, 2H), 1.67 (m, 1H), 1.57 (m, 1H), 1.25 (br m, 16H), 0.87 (br m, 12H). ^{13}C -NMR (151 MHz, CDCl_3 , δ): 169.60, 167.73, 69.86, 69.41, 50.24, 48.09, 45.97, 45.67, 38.08, 36.82, 30.69, 30.63, 28.97, 28.96, 28.84, 28.83, 26.32, 24.04, 23.97, 23.93, 23.21, 23.14, 14.20, 14.15, 11.09, 10.78, 10.77. IR (NaCl, film) ν_{max} (cm^{-1}): 2959 (s, CH, aliphatic), 2929 (s, CH, aliphatic), 2871 (s, CH, aliphatic), 2859 (s, CH, aliphatic), 1654 (s, C=O), 1455 (m, C-N), 1422 (m, C-N), 1123 (m, C-O). HRMS-MALDI TOF/TOF (m/z): $[\text{M} + \text{H}]^+(\text{calc.}) = 411.35874$; $[\text{M} + \text{H}]^+(\text{exp.}) = 411.35913$. Overall yield = 78%.

Liquid-liquid solvent extraction

All solvent extraction experiments were conducted at room temperature ($22 \pm 1^\circ\text{C}$) unless otherwise indicated. All organic solutions were prepared by mass of both the ligand and the diluent. The mixed organic diluent (e.g., 5.0% v/v 1-octanol in *n*-dodecane) was made in large batches to maintain consistency in the diluent makeup. The organic phase (2000 μL) was pre-equilibrated with a metal-free aqueous phase (2000 μL) for 30 minutes in a 4 mL screw-cap glass vial using a Fisher ScientificTM Analog Vortex Mixer on level 9 (ca. 2850 rpm). This equilibration procedure was adequate to bring the biphasic system to thermodynamic equilibrium. The samples were then

centrifuged for 5 minutes to achieve complete phase separation. Three aliquots (500 μ L) of fresh aqueous phase were pipetted into three different 2 mL glass, screw-cap vials. Three aliquots (500 μ L) of the pre-equilibrated organic phase were taken and transferred to the same 2 mL screw-cap glass vials. For radiotracer experiments, a 5.0 μ L aliquot of radioactive europium-152/154 was spiked into each 2 mL vial containing both phases. The spiked phases were then contacted for at least 30 minutes using a Vortex mixer. The samples were centrifuged again to separate the two phases completely prior to sampling. A 200 μ L sample was taken from the organic phase of each vial and deposited in a capped polyethylene tube for gamma counting. A second 200 μ L sample was then taken from the aqueous phase and deposited in a polyethylene tube for gamma counting. The plastic gamma tube samples were then counted on a Packard COBRA II gamma counter. The counts per minute (cpm) in each phase represent the partitioning of the europium metal from the aqueous phase into the organic phase. The distribution ratio (D_{Eu}) was determined by the relationship in Eq. 1.

$$D_{\text{Eu}} = \frac{[\text{Eu}]_{\text{org}}}{[\text{Eu}]_{\text{aq}}} = \frac{\text{cpm (organic phase)}}{\text{cpm (aqueous phase)}} \quad (1)$$

The uncertainty associated with each distribution ratio was a combination of the standard deviation of three data points and the propagated counting error. The vast majority of reported distribution ratios have less than 10% uncertainty.

Luminescence spectroscopy

All luminescence spectroscopy titrations were performed at room temperature ($22 \pm 1^\circ\text{C}$). Both the titrand and titrant were dissolved in acetonitrile to allow for mutual solubility of both the free metal and the UDGA ligand in a single phase. The titrand for these experiments was a solution of 0.5 mM $\text{Eu}(\text{NO}_3)_3$ in 0.3 mM HNO_3 /0.2 M H_2O /99.7% MeCN. The same titrand solution was used

for each of the seven titrations (ligands **7-12** and TODGA). The titrant solution was created fresh for each experiment entirely by mass for each component (purified UDGA or TODGA ligand, MeCN ($d = 0.781 \text{ g}\cdot\text{cm}^{-3}$), 0.096 M HNO_3 ($d = 1.004 \text{ g}\cdot\text{cm}^{-3}$)). The ligand concentrations varied from 5 to 6 mM UDGA in $0.3 \text{ mM HNO}_3/0.2 \text{ M H}_2\text{O}/99.7\% \text{ MeCN}$. The titrand ($1000 \mu\text{L}$ of $0.5 \text{ mM Eu(NO}_3)_3$ in $0.3 \text{ mM HNO}_3/0.2 \text{ M H}_2\text{O}/99.7\% \text{ MeCN}$) was pipetted into an open top, 1.4 mL Spectrocell Semi-Micro Fluorimeter FUV cell (quartz) with a PTFE lid and five polished windows (path length = $4 \times 10 \text{ mm}$, spectral range = $170\text{-}2200 \text{ nm}$). The titrant was added in $10.0 \mu\text{L}$ aliquots using a $5\text{-}50 \mu\text{L}$ Finnpiptette®. The solution was equilibrated for 1 minute before the emission spectrum was acquired. A lifetime measurement was taken of the original titrand and after the final $10.0 \mu\text{L}$ aliquot addition. The number of $10.0 \mu\text{L}$ aliquots needed to reach the end of the titration (defined as a 5:1 ligand-to-metal ratio in solution) was determined by the concentration of the titrant solution.

Luminescence spectroscopy emission experiments were performed using a HORIBA Jobin Yvon FluoroMax®-4 spectrofluorometer. The excitation source for the emission experiments was an ozone-free, continuous output 150 W xenon lamp with an excitation wavelength range of $220\text{-}600 \text{ nm}$. An excitation wavelength of 393 nm (excitation slit width = 3 nm) was used to excite the $4f$ electrons in the Eu^{3+} cation. The excitation source was coupled to a Czerny-Turner monochromator with 1200 grooves/mm gratings [18]. A second monochromator was set up at a 90° angle from the excitation source to avoid reflected light and collimate the emission. The emission slit width was set to 1 nm . Emission spectra were obtained using the FluorEssence™ software (HORIBA Scientific, version 3.5 for Windows®). The emission spectra were recorded in the range of $550\text{-}650 \text{ nm}$ at increments of 0.25 nm and an integration time of 1 second.

Results and Discussion

Liquid-liquid solvent extraction

Ligand solubility

All ligands were found to be highly soluble in the aliphatic diluents *n*-octane and *n*-dodecane. Exact solubility limits for each ligand were not determined due to the limited amount of synthesized material but a known range of solubility goes from 35 to 43 g UDGA per liter of *n*-octane and *n*-dodecane. The ligand solubility decreased drastically, however, when the organic solvent was put in contact with an aqueous phase containing nitric acid and Eu(III). A solubility experiment was performed with ligand **11** ((*N,N*-bis(3,7-dimethyloctyl)-*N'*-piperidinyl diglycolamide, DMOpipDGA) with 10.0 mM Eu(III) in 1.004 M HNO₃ contacted with 0.0114 M DMOpipDGA in *n*-octane. This resulted in the formation of a cloudy third phase, which does not allow for efficient phase separation. A second sample of 0.0109 M DMOpipDGA in 5.0% v/v 1-octanol/*n*-octane was contacted with an identical aqueous phase and remained clear and biphasic. A mixture of 5.0% v/v 1-octanol/*n*-dodecane was chosen as the preferred diluent for the solvent extraction experiments in this study.

Equilibration Time

The unsymmetrical diglycolamide (UDGA) ligand **10** (*N,N*-bis(3,7-dimethyloctyl)-*N'*-pyrrolidinyl diglycolamide, DMOPyrDGA) was used to determine the contact time required to reach thermodynamic equilibrium. This experiment monitored the distribution ratio (D_{Eu}) with increasing equilibration time (Fig. 11).

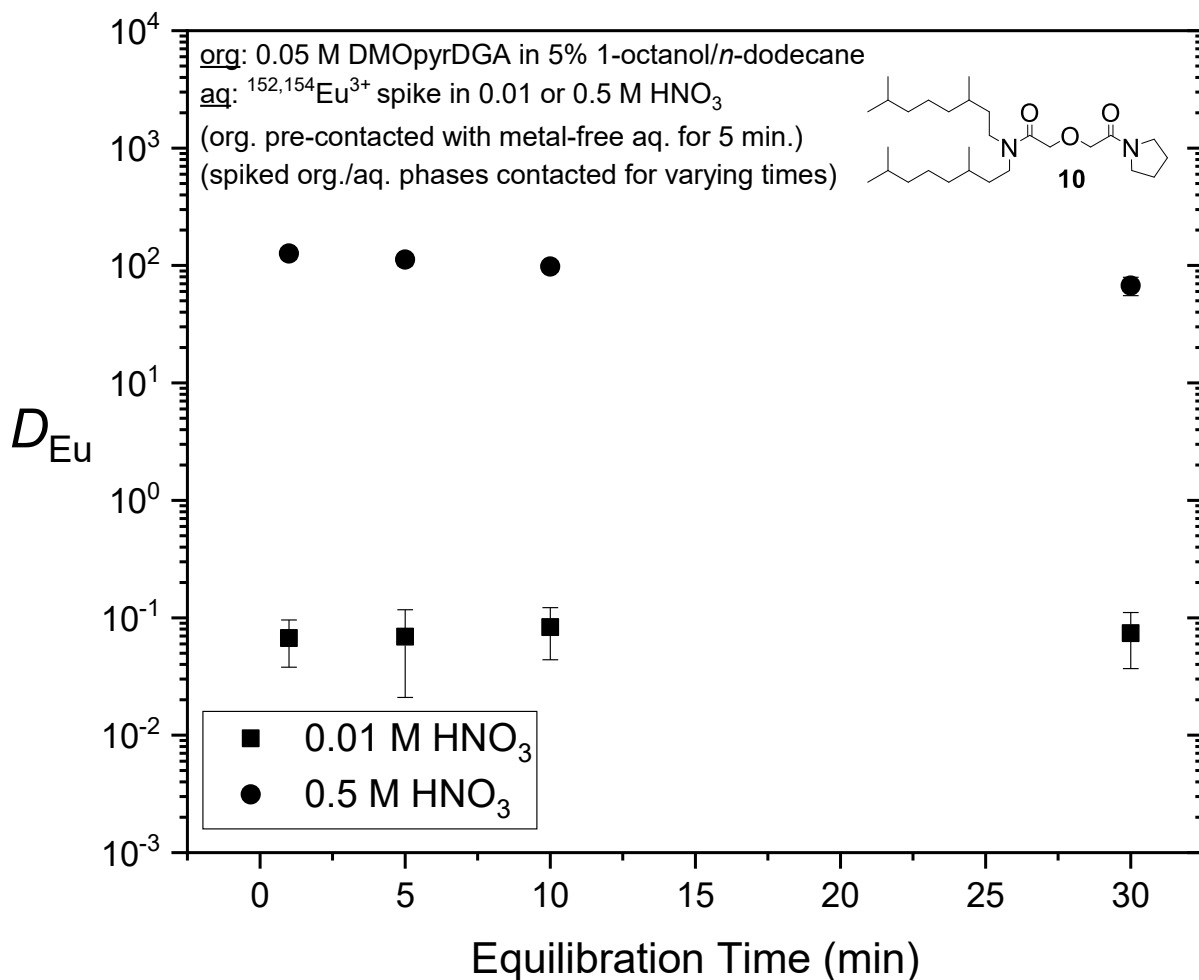


Fig. 11 The extraction of Eu(III) from 0.01 and 0.5 M HNO_3 by *N,N*-bis(3,7-dimethyloctyl)-*N'*-pyrrolidinyldiglycolamide (DMOpyrDGA) with varying equilibration times. Organic phases were pre-equilibrated with metal-free aqueous phase for 5 minutes. These new unsymmetrical diglycolamide (UDGA) ligands have compact, cyclic amides on one end and less steric bulk around the binding pocket, compared to TODGA. It was expected that the required equilibration times would be shorter than those used for TODGA (e.g., 20-minute equilibration time for Ln(III))[19]. The results in Fig. 11 support this assertion. The distribution ratios (D_{Eu}) for metal extraction from both 0.01 M and 0.5 M nitric acid quickly came to

equilibrium and levelled off after only one minute of equilibration on a Vortex mixer. All solvent extraction experiments henceforth use a 30-minute contact time unless otherwise stated.

Nitric acid dependence

Examining the metal extraction from a broad range of nitric acid concentrations is important for the overall evaluation of the newly synthesized unsymmetrical diglycolamides. The relative partitioning of metal cations (e.g., Eu^{3+}) into an organic phase containing solvating extractants is greatly affected by the concentration of nitric acid (or nitrate ion) in the aqueous phase. At low concentrations of HNO_3 (e.g., 0.01 M), solvating extractants lack sufficient NO_3^- counter anions to drive the extraction of trivalent metal cations, which are strongly solvated by water molecules. At high concentrations of HNO_3 (e.g., 1 M), there is a large excess of available NO_3^- anion to drive the phase transfer reaction of the neutral metal-ligand complex and the metal cations are more weakly hydrated due to the decrease in available water (salting-out effect) [20]. Nitric acid dependence experiments were performed for ligands **7-9** and are shown in Fig. 12.

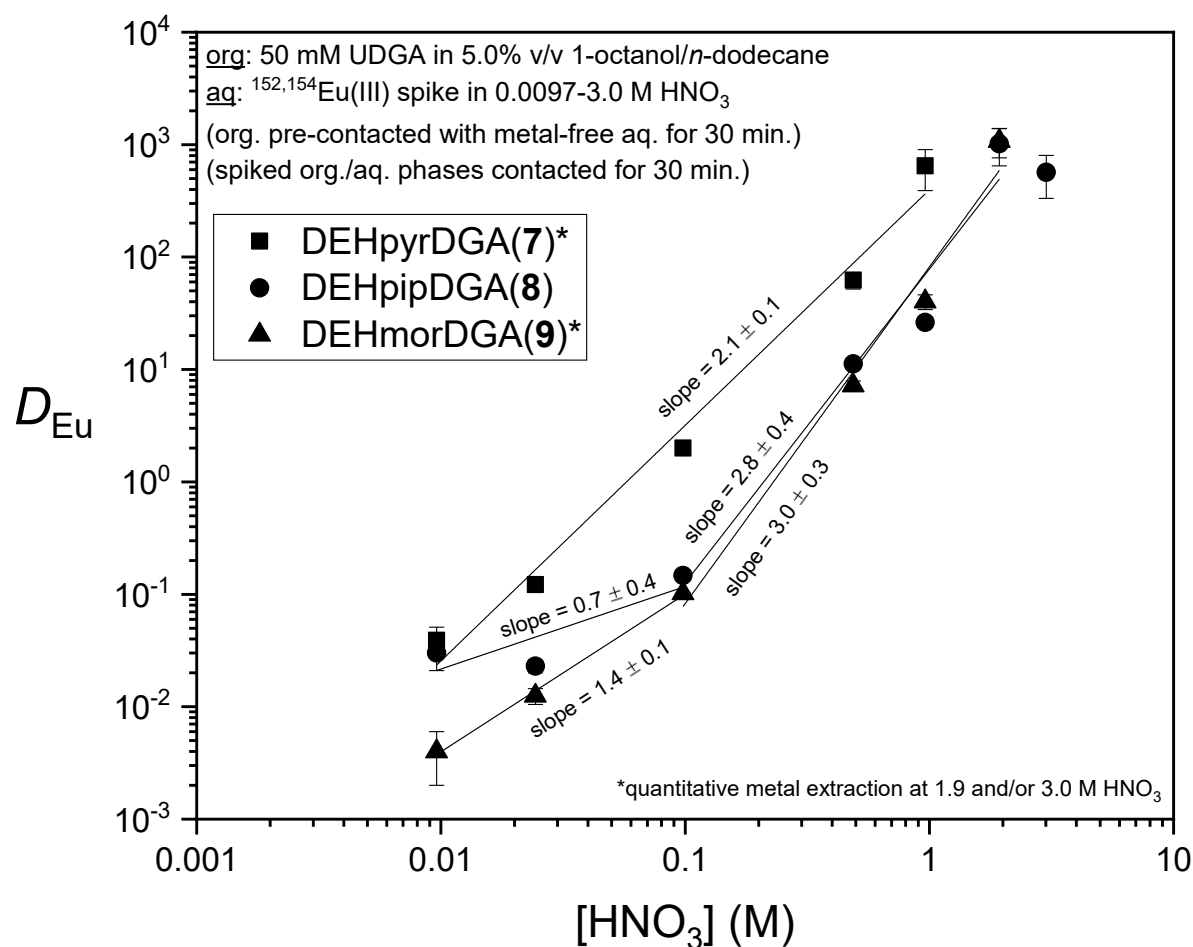
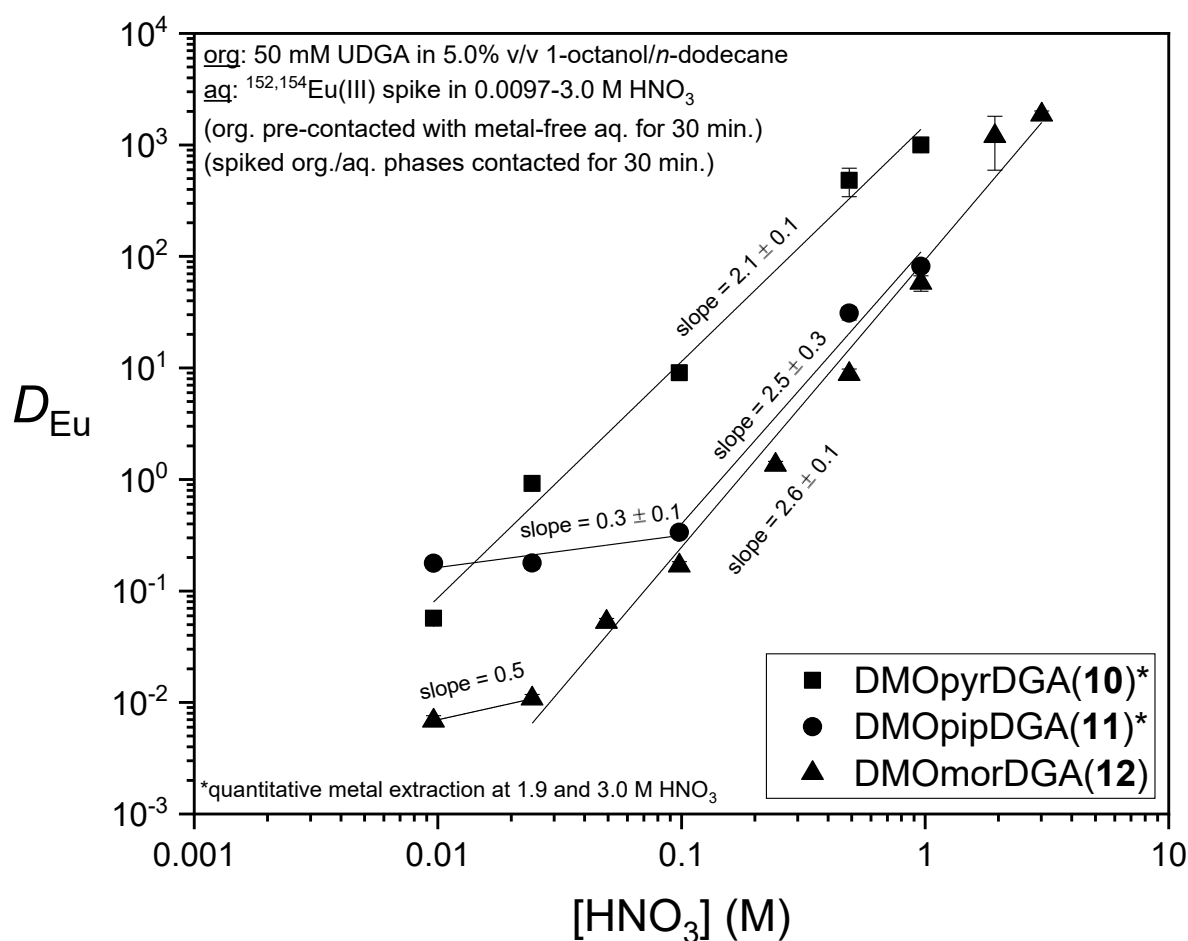


Fig. 12 The extraction of $^{152,154}\text{Eu(III)}$ by the bis(2-ethylhexyl) derivatives (7-9) from varying concentrations of nitric acid. Lines and slopes were added to illuminate data trends. The asterisk (*) signifies quantitative metal extraction at 1.9 and/or 3.0 M HNO_3 . The bis(2-ethylhexyl) derivatives (7-9) all favor the retention of the metal ($D_{\text{Eu}} \leq 0.04$) in the aqueous phase at 0.01 M nitric acid. DEHmorDGA(9) achieves even lower metal extraction ($D_{\text{Eu}} = 0.004 \pm 0.002$) at 0.01 M HNO_3 which could be favorable for the eventual metal stripping in a separations process. All three bis(2-ethylhexyl) derivatives favor the extraction of the metal ($D_{\text{Eu}} \geq 25$) into the organic phase at 1 M nitric acid. DEHpyrDGA(7) achieves quantitative metal extraction ($D_{\text{Eu}} = 900 \pm 200$) at 1 M HNO_3 which is crucial to reduce the total number of extraction steps in an industrial process. The increased metal extraction by DEHpyrDGA(7) could be

279 attributed to the smaller five-membered pyrrolidinyl ring compared to the larger six-membered
 280 piperidinyl and morpholino ring structures. DEHpipDGA(8) and DEHmorDGA(9) behave
 281 similarly throughout the range of acidity with the exception of the order of magnitude difference
 282 at 0.01 M HNO₃. The DEH derivatives can quantitatively extract Eu(III) ($D_{\text{Eu}} > 100$) at high acidity
 283 ($[\text{HNO}_3] \geq 2 \text{ M}$) while only DEHmorDGA(9) inhibits Eu(III) extraction ($D_{\text{Eu}} < 0.01$) at low acidity
 284 ($[\text{HNO}_3] \leq 0.025 \text{ M}$). The morpholino derivative has more limited solubility in the diluent,
 285 however, which prevents more concentrated ligand solutions that are necessary for extracting
 286 metals under more realistic process conditions. Nitric acid dependence experiments were also
 287 performed for ligands **10-12** and are shown in Fig. 13.



289 **Fig. 13** The extraction of $^{152,154}\text{Eu(III)}$ by the bis(3,7-dimethyloctyl) derivatives (**10-12**) from
290 varying concentrations of nitric acid. Lines and slopes were added to illuminate data trends. The
291 asterisk (*) signifies quantitative metal extraction at 1.9 and 3.0 M HNO_3

292 The bis(3,7-dimethyloctyl) derivatives (**10-12**) all favor the retention of the metal ($D_{\text{Eu}} \leq 0.2$) in
293 the aqueous phase at 0.01 M nitric acid. DMOmorDGA(**12**) achieves more than an order of
294 magnitude lower metal extraction ($D_{\text{Eu}} = 0.007 \pm 0.001$) at 0.01 M HNO_3 which matches the trend
295 between the bis(2-ethylhexyl) derivatives. DMOPyrDGA(**10**) generally has higher metal
296 extraction than the other two DMO derivatives and has a more linear nitric acid dependence
297 throughout the entire range. DMOPipDGA(**11**) and DMOmorDGA(**12**) have small ranges of
298 nearly constant metal extraction at low acidity ($[\text{HNO}_3] \leq 0.025 \text{ M}$), which could be a useful
299 attribute for ease of pH adjustment on a large scale. All three DMO derivatives quantitatively
300 extract Eu(III) at high acidity ($[\text{HNO}_3] \geq 1 \text{ M}$) although DMOPyrDGA(**10**) achieves this feat at
301 the slightly lower acidity of 0.5 M HNO_3 . The morpholino derivative, DMOmorDGA(**12**), is the
302 most promising candidate using these experimental data due to the much lower distribution ratios
303 at 0.01 M HNO_3 than the other two candidates but this ligand was also found to have limited
304 solubility in the diluent, which would restrict its use under more realistic process conditions. The
305 two groups of DEH(**7-9**) and DMO(**10-12**) follow similar trends overall with the DMO derivatives
306 having slightly higher distribution ratios for Eu(III) than are seen in the DEH samples. Previous
307 work by Sasaki et al. has shown symmetrical 2-ethylhexyl derivatives to have decreased metal
308 extraction compared to straight C_8 chains but there have been no results reported with the doubly
309 branched 3,7-dimethyloctyl groups in the existing literature[14]. The more favorable extraction of
310 the DMO derivatives could stem from the small methyl branches off the alkyl chain as opposed to
311 the larger ethyl branches of the DEH derivatives. Further nitric acid dependence experiments with

the piperidinyll and pyrrolidinyl derivatives are necessary before the best candidates can be singled out for larger scale production.

Metal-ligand complex stoichiometry

The UDGA ligands **7-12** synthesized in this work are organic-soluble extractants and so do not form crystals readily. Thus, an alternative method for determining ligand-to-metal ratios was necessary. Further solvent extraction experiments offer a representation of the coordination complex in a realistic organic phase (e.g., 5.0% v/v 1-octanol/*n*-dodecane). The simplified extraction of Eu(III) by a UDGA is represented by the reaction shown in Eq. 2. The extraction of water and nitric acid has been neglected in this representation. The overlined species are in the organic phase.



The conditional extraction equilibrium constant for this extraction reaction can then be written as Eq. 3,

$$K_{\text{ex}} = \frac{[\overline{\text{Eu}(\text{UDGA})_n(\text{NO}_3)_m}]}{[\text{Eu}^{3+}][\text{NO}_3^-]^m[\overline{\text{UDGA}}]^n} \quad (3)$$

Absent the effects of nitric acid extraction, the $\text{Eu}^{3+}:\text{NO}_3^-$ stoichiometry should be 1:3 to satisfy the requirements of electroneutrality in the extractant phase, hence m should ideally be three. The idealized distribution ratio expression for Eu(III) can be expressed as Eq. 4,

$$D_{\text{Eu}} = \frac{[\overline{\text{Eu}(\text{UDGA})_n(\text{NO}_3)_m}]}{[\text{Eu}^{3+}]} \quad (4)$$

Substituting Eq. 4 into Eq. 3 and converting to the logarithmic form gives Eq. 5,

$$\log(D_{\text{Eu}}) = n \cdot \log[\overline{\text{UDGA}}] + \log K_{\text{ex}} + m \cdot \log[\text{NO}_3^-] \quad (5)$$

332 At a constant aqueous nitrate concentration of 1 M, the last term in Eq. 5 becomes zero. Eq. 5 can
333 then be represented by the equation for a straight line ($y = mx + b$) where $y = \log(D_{\text{Eu}})$, $m = n$ (the
334 average number of extractant molecules associated with each metal center), $x = \log[\overline{\text{UDGA}}]$, and
335 $b = \log K_{\text{ex}}$. This mathematical relationship can help to obtain both the ligand-to-metal ratio (n) in
336 the organic phase and the conditional extraction equilibrium constant ($\log K_{\text{ex}}$).

337 A series of solvent extraction experiments were run in which the concentration of UDGA ligand
338 was varied while the concentration of HNO_3 was held constant at 1 M. The metal partitioning was
339 measured radiometrically by introducing a $^{152,154}\text{Eu(III)}$ spike (10^{-5} M total Eu^{3+}) into the biphasic
340 system and measuring the counts per minute (cpm) in each separated phase. The mixed diluent
341 5.0% v/v 1-octanol/*n*-dodecane was used throughout to prevent third phase formation and allow
342 for clean phase disengagement. The concentration range for each UDGA ligand varied depending
343 on metal extraction strength (e.g., 5.0, 10.0, 20.0, and 40.0 mM DEHpyrDGA) and used at least
344 four triplicate data points for the linear fitting in OriginPro®. Every triplicate data point was
345 plotted individually instead of plotting y-axis $\pm$ error to avoid any weighting of data points.
346 Distribution ratios (D_{Eu}) were multiplied by a factor of 3.49 to account for the nitrate complexation
347 in the aqueous phase. This factor nitrate complexation factor was previously determined by
348 Andersson et al. [21]. The concentration of UDGA ligand was plotted versus the Eu(III)
349 distribution ratios on a logarithmic scale to utilize Eq. 5. An example of the graphed data for
350 DEHpyrDGA is shown in Fig. 14 (see supplementary material for graphs of the other ligands **8-**
351 **12** and TODGA).

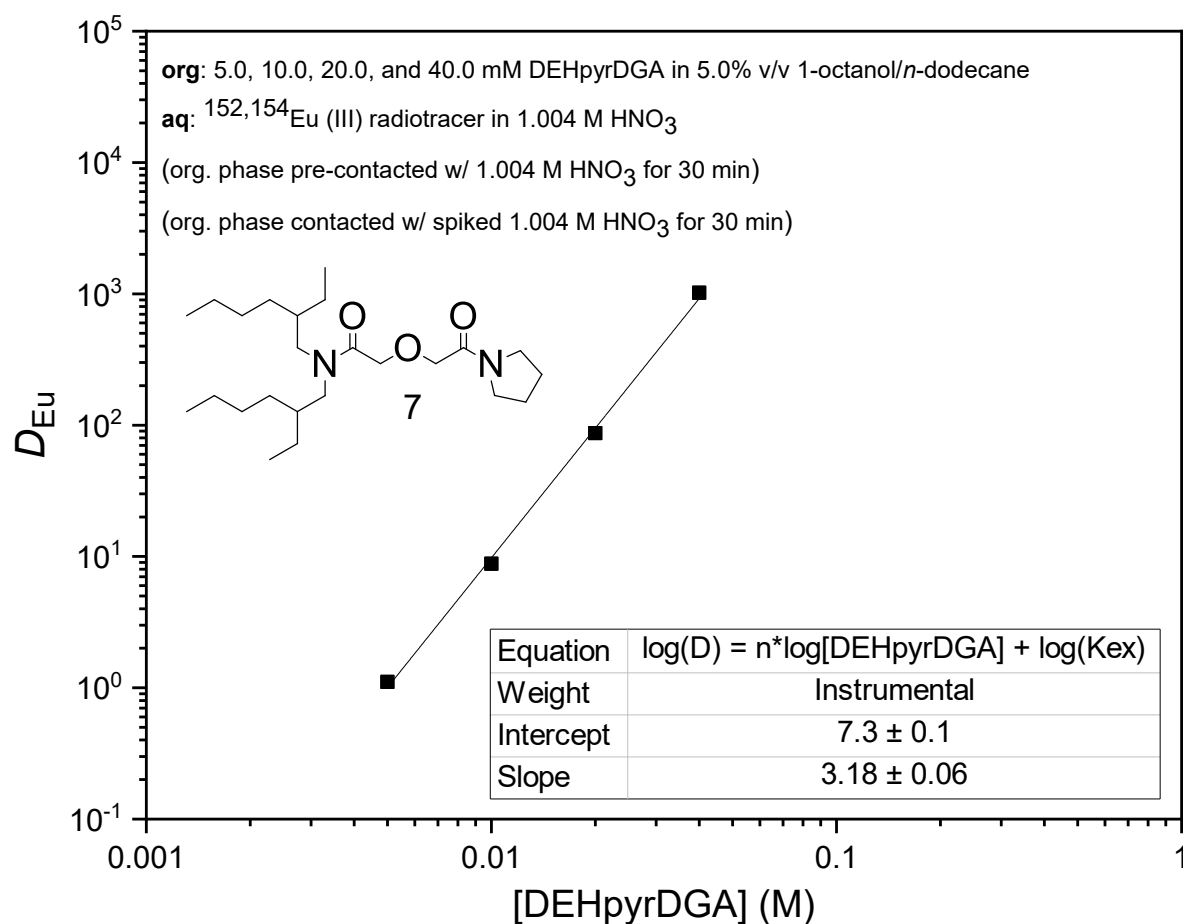


Fig. 14 The partitioning of Eu(III) metal between 1.004 M HNO_3 and varying [DEHpyrDGA] in 5.0% v/v 1-octanol/*n*-dodecane

The slope (n) of the linear fit in Fig. 14 is 3.18 ± 0.06 , which represents a reasonable ligand to metal center ratio for this diluent when compared with previous studies by Sasaki et al. [22]. Sasaki and co-workers found that the number of ligands associated with a single Eu(III) metal center increased with decreasing diluent dielectric constant (e.g. 2.48:1 for 1-octanol and 4.10:1 for *n*-dodecane).

The nitrate corrected distribution ratios are given in Table 1 along with the calculated conditional extraction equilibrium constants ($\log K_{\text{ex}}$) and metal-ligand complex stoichiometry (n) for unsymmetrical diglycolamide ligands (7-11) and TODGA with Eu(III).

Table 1. Nitrate corrected distribution ratios (D_{Eu}) for radiotracer $^{152,154}\text{Eu}(\text{III})$ in 1.004 M HNO_3 at varying concentrations (range = 2.5 – 100 mM) of unsymmetrical diglycolamide ligands (**7-12**) and TODGA in 5.0% v/v 1-octanol/*n*-dodecane are given. A linear fit was applied to the plot of $\log[\text{DGA}]$ vs. $\log[D_{\text{Eu}}]$ to determine the conditional extraction equilibrium constants ($\log K_{\text{ex}}$) and metal-ligand complex stoichiometry (n) for unsymmetrical diglycolamide ligands (**7-12**) and TODGA (**TO**). Reported confidence interval is $\pm 1 \sigma$.

Ligand	$^{152,154}\text{Eu}(\text{III})$ Distribution Ratios				Linear Fit Results	
	$[\text{DGA}]_1$	$[\text{DGA}]_2$	$[\text{DGA}]_3$	$[\text{DGA}]_4$	y-intercept ($\log K_{\text{ex}}$)	slope (n)
7	1.11 ± 0.04	8.8 ± 0.3	87 ± 2	1000 ± 100	7.3 ± 0.1	3.18 ± 0.06
8	0.65 ± 0.02	59 ± 3	400 ± 60	1100 ± 200	6.34 ± 0.03	3.26 ± 0.02
9	0.026 ± 0.002	0.14 ± 0.01	1.06 ± 0.04	19 ± 1	5.5 ± 0.6	3.2 ± 0.3
10	0.56 ± 0.01	13.7 ± 0.03	76 ± 2	600 ± 70	8.2 ± 0.4	3.2 ± 0.2
11	7.8 ± 0.3	630 ± 30	3500 ± 700	8000 ± 1000	7.2 ± 0.1	3.13 ± 0.06
12	0.055 ± 0.007	0.38 ± 0.02	third phase	third phase	-	-
TO	0.327 ± 0.009	2.5 ± 0.1	19.2 ± 0.4	141 ± 7	6.26 ± 0.02	2.93 ± 0.01

The ligand to metal ratios (n) for the Eu-UDGA complexes fall in between the Sasaki et al. literature values for Eu-TODGA (4.10 ± 0.05 in *n*-dodecane and 2.48 ± 0.07 in 1-octanol)[22]. The combination of both diluents brings the ligand-to-metal ratio to an average of about 3:1. An experiment was run using TODGA in 5.0% v/v 1-octanol/*n*-dodecane to confirm these results and the 3:1 stoichiometry was verified. The conditional extraction equilibrium constants ($\log K_{\text{ex}}$) also agree with the general trend of extraction strength between ligands seen in other solvent extraction experiments: decreasing in strength from pyrrolidinyl to piperidinyl to morpholino derivatives. Interestingly, the dimethyloctyl pyrrolidinyl ligand (**10**) has an extraction equilibrium constant nearly an order of magnitude larger than the 2-ethylhexyl pyrrolidinyl ligand (**7**) which may suggest a benefit of the shorter methyl branches. The same trend is seen in the increased order of

380 magnitude extraction strength of the dimethyloctyl piperidinylligand (**11**) compared to the
 381 2-ethylhexyl piperidinylligand (**8**). The dimethyloctyl morpholino ligand (**12**) displayed a third
 382 phase at the higher ligand concentrations, so no $\log K_{\text{ex}}$ or metal:ligand ratio was determined. The
 383 morpholino ligands had increased issues with third phase formation throughout all the solvent
 384 extraction studies, which could be due to the extra etheric oxygen on the amidic ring attracting
 385 polar molecules like water and nitric acid into the nonpolar organic phase. Fig. 15 shows a similar
 386 trend in the extraction of Eu(III) from 1.004 M HNO_3 by ligands **7-12** and TODGA in 5.0% v/v
 387 1-octanol/*n*-dodecane.

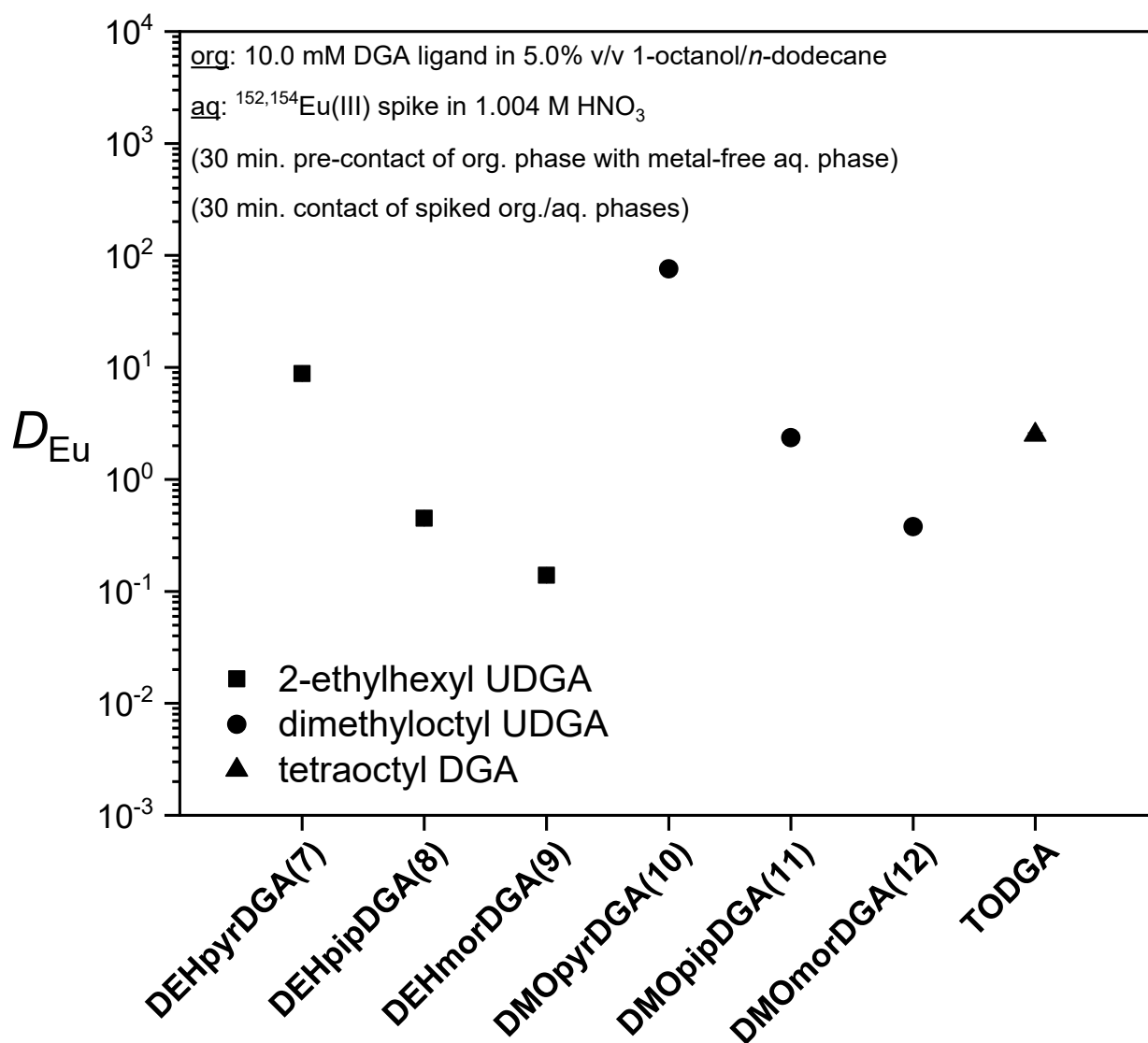


Fig. 15 The nitrate-corrected distribution ratios (D_{Eu}) for radiotracer $^{152,154}\text{Eu}(\text{III})$ between a 10.0 mM diglycolamide (ligands **7-12** and TODGA) in 5.0% v/v 1-octanol/*n*-dodecane organic phase and a 1.004 M HNO_3 aqueous phase

The two pyrrolidinyl derivatives (**7** and **10**) have the highest $^{152,154}\text{Eu}(\text{III})$ distribution ratios of all seven ligands and DMOpyrDGA(**10**) exhibits nearly quantitative metal extraction under the test conditions. Europium extraction decreases from pyrrolidinyl to piperidinyl to morpholino rings, which likely correlates with an increase in steric hindrance around the metal binding site. The orientation of the 5-membered pyrrolidinyl ring is only slightly staggered while the 6-membered piperidinyl and morpholino rings adopt a chair configuration. This puts the third atom on the piperidinyl or morpholino ring out-of-plane with the amide (assuming that the chair configuration is the lowest energy orientation in the 6-membered rings), which causes the metal binding site to be more sterically hindered than the mostly in-plane (5-membered) pyrrolidinyl ring. The 6-membered morpholino ring ($-\text{NC}_4\text{H}_8\text{O}$) replaces the methylene group ($-\text{CH}_2-$) in the piperidinyl ring with an oxygen atom, which should be less sterically hindered and lead to an increase in metal complexation strength (assuming that it can adopt a suitable configuration). The opposite trend occurs in the data, however, and there is a small decrease in metal extraction from the piperidinyl (**8** and **11**) to the morpholino (**9** and **12**) derivatives.

It is possible that the morpholino ligands are weaker because they extract greater stoichiometric amounts of nitric acid, which can in principle compete for the binding site with $\text{Eu}(\text{NO}_3)_3$. The Lewis base oxygen atom in the morpholino ring could interact with the proton in a nitric acid molecule, leading to an increase in nitric acid extraction. This would lead to a decrease in free ligand concentration and could suppress metal distribution ratios. Based on a steric bulk argument, TODGA should be a much weaker extractant than the more compact unsymmetrical

diglycolamides. The two, long straight-chain alkyl groups (C₈) on both sides of the TODGA molecule may serve to decrease nitric acid extraction while not completely blocking metal complexation. Further experiments to determine nitric acid extraction are necessary for better interpretation of metal partitioning results between the various ligands.

Luminescence spectroscopy

A solution of Eu(III) nitrate in the polar organic solvent acetonitrile (MeCN) was titrated with the unsymmetrical diglycolamides (also dissolved in MeCN) and spectral changes were monitored using luminescence spectroscopy. Changes in the hypersensitive peak around 615 nm and the magnetic dipole peak at 592 nm represented changes in the metal-ligand complex speciation. In each ligand system, the titrations were run until the ligand-to-metal ratio was greater than five or to the point at which there were no additional spectral changes. The spectra from a representative titration with DMOMorDGA(**12**) and Eu(III) are shown in Fig. 16 (see supplementary material for spectra of the other five UDGA ligands and TODGA).

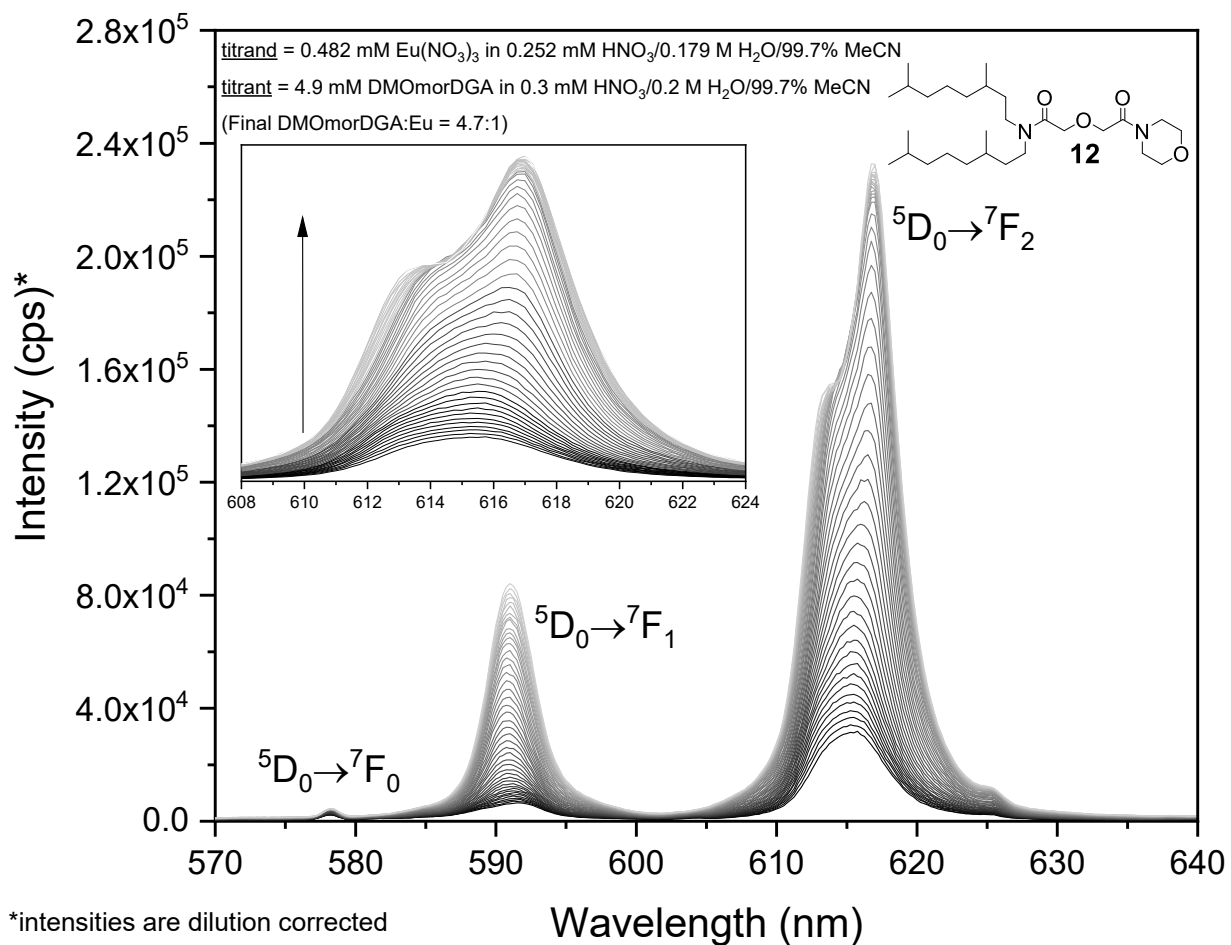
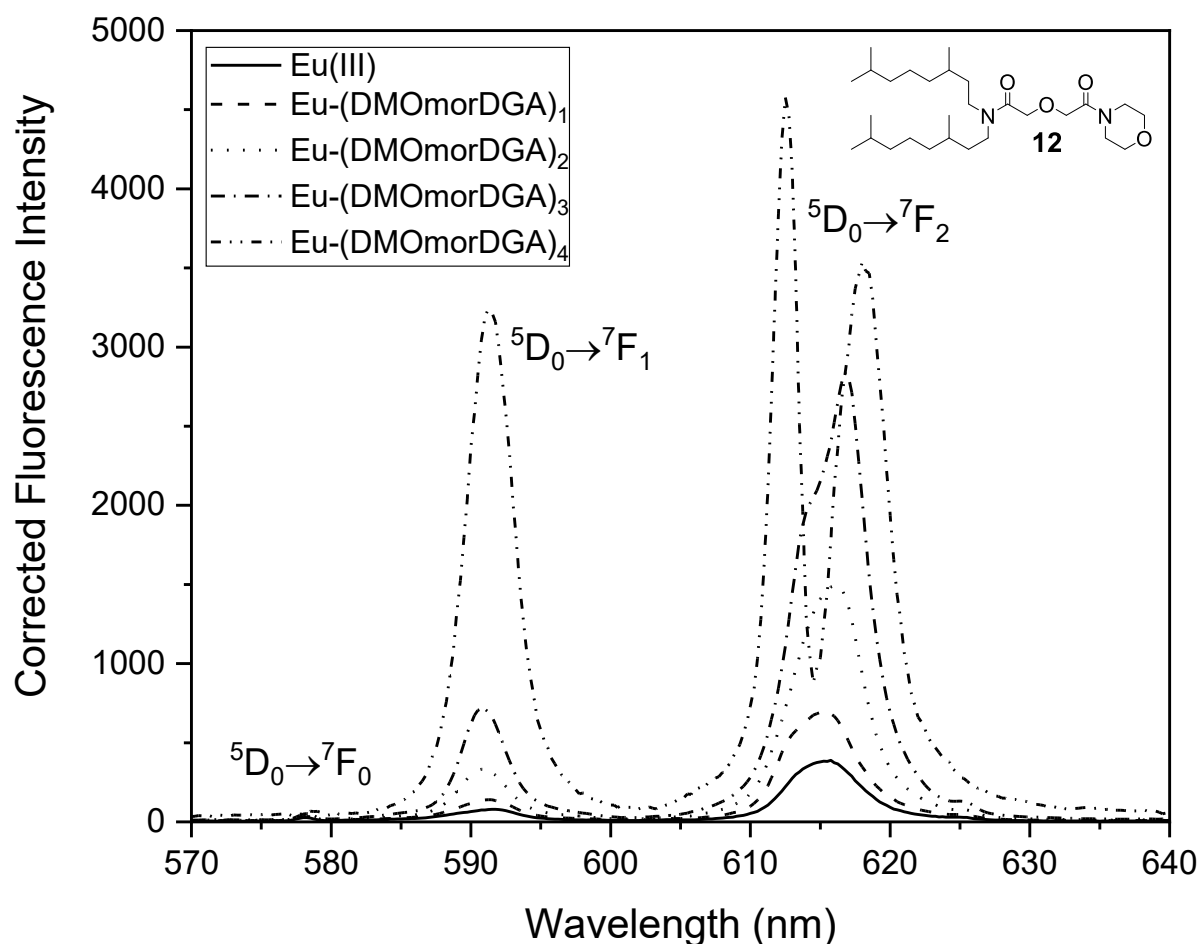


Fig. 16 Emission spectra of Eu(III) with increasing concentration of the ligand *N,N*-bis(3,7-dimethyloctyl)-*N'*-morpholinodiglycolamide (DMOMorDGA). Inset of 608-624 nm included to show the peak splitting toward the end of the titration (black line = beginning; light gray line = end)

In each ligand system, most of the spectral changes occur at the hypersensitive peak (ca. 615 nm), which eventually splits into two peaks at ca. 613 and 617 nm (see inset in Fig. 16). The magnetic dipole transition peak at 592 nm remains at the same wavelength throughout the titration but does steadily increase in magnitude until levelling off at the end of the titration. The relatively weak electric dipole transition at 578 nm experiences a small redshift to 578.5 nm during the titration but the peak intensity was too small for data fitting purposes. Corrected fluorescence intensity spectra were generated by the HypSpec fitting program for each metal-ligand species and Eu(III).

438 The spectra for the 1:1 through 1:4 Eu(III) complexes with DMOmorDGA are shown in Fig. 17.
 439 Similar spectra were resolved for each system that converged on an internally consistent model.



440
 441 **Fig. 17** Corrected fluorescence intensity spectra for Eu(III)-DMOmorDGA complexes in
 442 0.3 mM HNO₃/0.2 M H₂O/99.7% MeCN

443 The corrected fluorescence intensity spectra show the changes in both peak intensity and
 444 wavelength. The magnetic dipole peak at 592 nm exhibits a subtle blue-shift to 591 nm from
 445 Eu(III) to Eu-DMOmorDGA and a red-shift back to 592 nm between Eu-(DMOmorDGA)₃ and
 446 Eu-(DMOmorDGA)₄. The intensity of the 592 nm peak also increases exponentially from the
 447 beginning to the end of the titration. The largest spectral changes occur at the hypersensitive peak
 448 around 615 nm where the development of a second blue-shifted peak adds a shoulder to the 1:1,

1:2, and 1:3 complexes. The blue-shifted peak (613 nm) is almost resolved from the red-shifted peak (617 nm) in the 1:4 complex spectrum and the relative intensity of the 613 nm peak becomes greater than the 617 nm peak with the formation of the terminal complex, Eu-(DMOmorDGA)₄. HypSpec was used to obtain conditional stability constants (β_{MHL}) for the four metal-ligand species using non-linear least-squares regression analysis [23] The equilibrium expressions for each β_{MHL} are shown in Eqs. 6-9. Nitrate concentrations were held constant during each titration and have been omitted from the equilibria. Any protonated (H) species have also been omitted since these titrations all took place in the organic solvent, acetonitrile, which would preclude cationic species.

$$\beta_{101} = [\text{Eu}(\text{UDGA})]/[\text{Eu}][\text{UDGA}] \quad (6)$$

$$\beta_{102} = [\text{Eu}(\text{UDGA})_2]/[\text{Eu}][\text{UDGA}]^2 \quad (7)$$

$$\beta_{103} = [\text{Eu}(\text{UDGA})_3]/[\text{Eu}][\text{UDGA}]^3 \quad (8)$$

$$\beta_{104} = [\text{Eu}(\text{UDGA})_4]/[\text{Eu}][\text{UDGA}]^4 \quad (9)$$

The β_{MHL} values are exceedingly large, so a logarithmic operator was applied to give more meaningful numerical results. Each model was first tested starting with the 1:1 metal-ligand complex ($\log \beta_{101}$) and new fits were attempted after the addition of each new species (e.g., $\log \beta_{102}$, $\log \beta_{103}$, and $\log \beta_{104}$). Varying sets of stability constants were calculated for the two, three, and four species systems but the four species system was finally accepted as the most accurate due to known experimental metal-ligand ratios and factor analysis within HypSpec. Most of the full data sets did not successfully converge on stability constant values immediately without some alteration. Series of data points were graphed near important wavelengths (e.g., 592 nm, 613 nm, and 617 nm) and observed for discontinuities or aberrations in the curve. The data sets were then truncated (usually near the 1:4 metal-ligand ratio) and the model was re-tested. This process

was repeated until stability constants converged with reasonable values and low error ($\leq 3\%$). The quality of the fit was tested by entering much lower initial values (e.g., $\log \beta_{101} = 4$) and confirming the convergence to the same higher value (e.g., $\log \beta_{101}$ (DMOmorDGA) = 7.49 ± 0.06). The titrations and data fitting routines were repeated for all six unsymmetrical diglycolamide ligands and TODGA. The conditional stability constants are reported in Table 2. The uncertainties in the conditional stability constants ($\log \beta_{\text{MHL}}$) were calculated in HypSpec and reported at $\pm 2\sigma$.

Table 2. Conditional stability constants ($\log \beta_{\text{MHL}}$) for Eu(III)-UDGA and Eu(III)-TODGA complexes in 0.3 mM HNO₃/0.2 M H₂O/99.7% MeCN

Ligand	$\log \beta_{101}$	$\log \beta_{102}$	$\log \beta_{103}$	$\log \beta_{104}$
DEHpyrDGA(7)	8.9 ± 0.2	15.9 ± 0.3	21.9 ± 0.4	24.5 ± 0.4
DEHpipDGA(8)	7.89 ± 0.08	14.7 ± 0.1	19.8 ± 0.1	23.2 ± 0.2
DEHmorDGA(9)	7.5 ± 0.1	14.0 ± 0.1	19.3 ± 0.1	21.8 ± 0.2
DMOpyrDGA(10)	7.9 ± 0.1	14.8 ± 0.2	20.5 ± 0.3	24.8 ± 0.3
DMOpipDGA(11)	7.66 ± 0.04	13.7 ± 0.1	18.7 ± 0.1	22.5 ± 0.1
DMOmorDGA(12)	7.49 ± 0.06	13.7 ± 0.1	18.6 ± 0.1	21.1 ± 0.2
TODGA	6.28 ± 0.02	11.69 ± 0.02	17.03 ± 0.02	21.55 ± 0.02

Error reported is $\pm 2\sigma$

The less bulky europium-unsymmetrical diglycolamide 1:4 complexes (in acetonitrile) are generally stronger than the 1:4 Eu-TODGA complex with the exception of DEHmorDGA(**9**) and DMOmorDGA(**12**) which have values that nearly match TODGA. These data support the idea that a decrease in steric crowding around the binding site (e.g., pyrrolidine ring instead of *n*-octyl chain) can increase metal-ligand complex stability. The decrease in complex stability for the morpholino derivatives could be caused by a decrease in ligand basicity due to the presence of an oxygen atom

486 in the ring. The same overall trend in complex stability was seen in earlier experiments using
487 liquid-liquid solvent extraction ($\log K_{\text{ex}}$ values, see Table 1) wherein the pyrrolidinyll and
488 piperidinyll UDGA ligands were found to be stronger Eu(III) extractants than TODGA while the
489 morpholino UDGA ligands were found to be slightly weaker. A direct comparison of the Eu(III)
490 luminescence spectroscopy data ($\log \beta_3$) with the radiotracer $^{152,154}\text{Eu(III)}$ solvent extraction data
491 ($\log K_{\text{ex}}$) is illustrated graphically in Fig. 18. The solvent extraction data determined the extracted
492 Eu-UDGA complex to be 1:3 on average, so the corresponding 1:3 complex stability constant ($\log$
493 β_3) was used as a comparison.

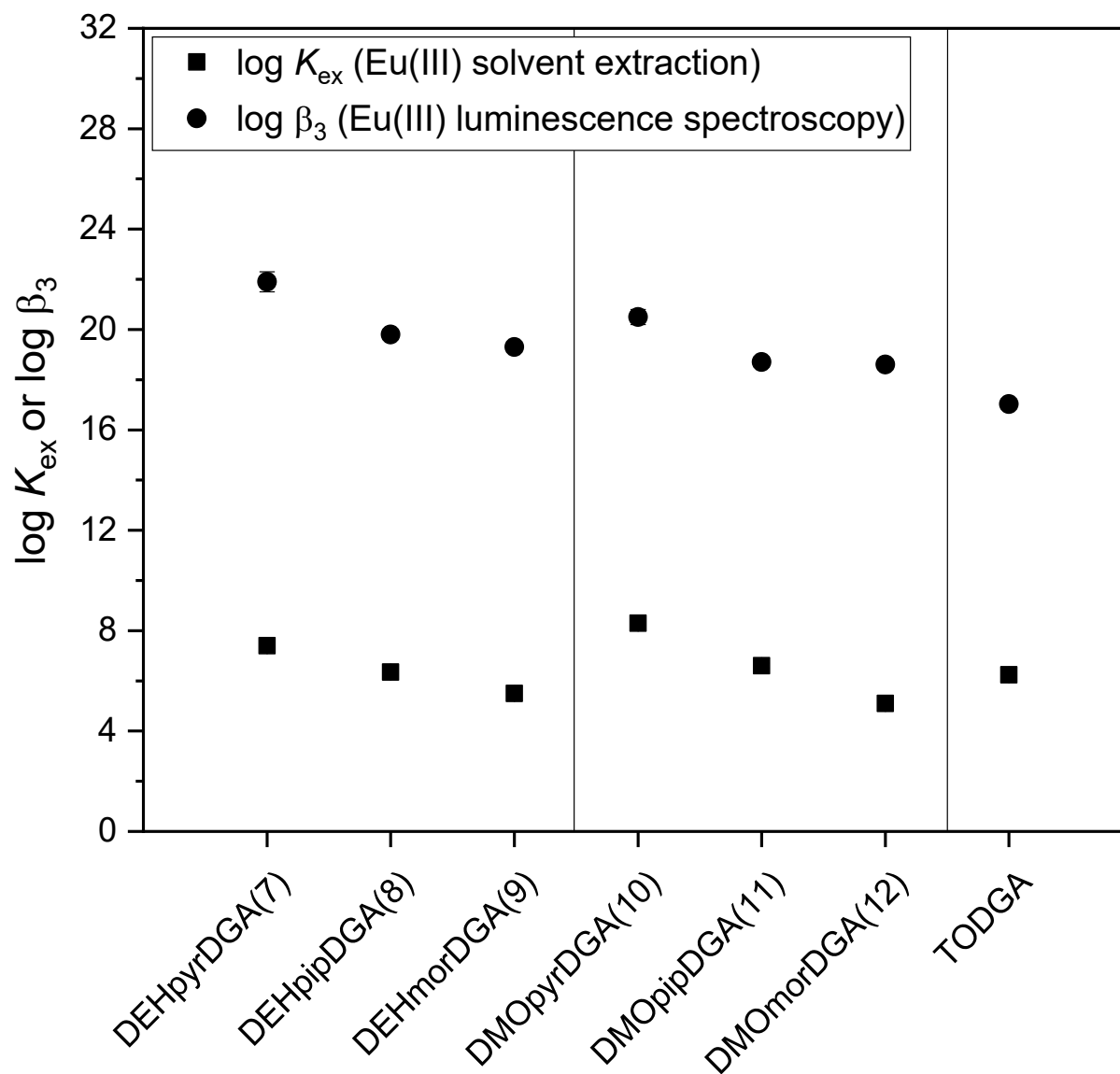


Fig. 18 Comparison of $\log K_{\text{ex}}$ values (obtained from previous radiotracer $^{152,154}\text{Eu(III)}$ solvent extraction ligand dependence data in Table 1) and $\log \beta_3$ values (obtained from Eu(III) luminescence spectroscopy titrations in Table 2) for the unsymmetrical diglycolamides (7-12) and TODGA

The general trend for the $\log K_{\text{ex}}$ and $\log \beta_3$ values is similar except for a relative decrease in metal-ligand complex stability for the two morpholino ligands (9 and 12) in solvent extraction results. As previously mentioned, it is possible that the morpholino ligands extract large amounts

of nitric acid in a biphasic solvent extraction system, which decreases the free ligand available for Eu(III) metal extraction. This effect would be minimal in the monophasic acetonitrile solvent where the concentration of nitric acid is less than the Eu(III) metal available. The relationship between the $\log K_{\text{ex}}$ and $\log \beta_3$ values is mostly qualitative, however, since the solvent conditions between the experiments vary greatly (5.0% v/v 1-octanol/*n*-dodecane in contact with 0.985 M HNO₃ versus 0.3 mM HNO₃/0.2 M H₂O/99.7% MeCN). The solvation of the Eu³⁺ cation changes greatly between the acidic aqueous environment in solvent extraction experiments and the predominantly acetonitrile (99.7% volume) environment in the luminescence spectroscopy titrations. The weaker MeCN ligands (compared to H₂O) are more easily displaced by the UDGA ligands, which leads to much larger values for the 1:3 conditional stability constants ($\log \beta_3$) compared to the $\log K_{\text{ex}}$ values.

Conclusions

Six new unsymmetrical diglycolamides were synthesized using a three-step organic synthesis. The trivalent lanthanide metal extraction behavior of the unsymmetrical diglycolamides (**7-12**) was studied using radiotracer ^{152,154}Eu(III). DMOpyrDGA(**10**) in 5.0% v/v 1-octanol/*n*-octane was contacted via Vortex mixing with Eu(NO₃)₃ in 0.985 M HNO₃ for varying amounts of time and was found to reach equilibrium in one minute. The conditional metal extraction equilibrium constants ($\log K_{\text{ex}}$) were determined using a ligand dependence slope analysis experiment and the pyrrolidinyl (**7** and **10**) UDGA ligands were found to be ten and nearly one hundred times stronger, respectively, than the symmetrical diglycolamide, TODGA. The even larger bis(3,7-dimethyloctyl) piperidinyl (**11**) UDGA ligand was also found to have a ten times greater extraction strength than TODGA, which makes it the third candidate for ligand development

moving forward. The bis(2-ethylhexyl) piperidinyl (**8**) UDGA ligand displayed comparable extraction strength to TODGA, while both morpholino ligand (**9** and **12**) were much weaker extractants than TODGA and tended towards third phase formation. The same slope analysis solvent extraction experiments also determined the metal-ligand complex stoichiometry (in 5.0% v/v 1-octanol/*n*-dodecane) to be approximately 1:3 for the UDGA ligands and TODGA. The change in Eu(III) extraction with varying concentrations of HNO₃ was determined radiometrically and compared across the ligand series. The pyrrolidinyl derivatives (**7** and **10**) dissolved in 5.0% v/v 1-octanol/*n*-dodecane were the strongest extractants for Eu(III) at high acidity and had a linear dependence between metal distribution ratios and nitric acid concentration (slope = 2.1 ± 0.1). The morpholino derivatives (**9** and **12**) were the weakest extractants for Eu(III) at low acidity, which is desirable for an efficient metal stripping step in an industrial scale solvent extraction process. The morpholino derivatives were also prone to third phase formation, however, which excludes them from further study. The piperidinyl derivatives (**8** and **11**) exhibit extraction properties in between the pyrrolidinyl and morpholino derivatives but have the advantage of improved solubility in aliphatic diluents (e.g., *n*-dodecane). Overall, the best extractant candidate was DMOpyrDGA(**10**) because of the combination of metal extraction at high acidity, metal stripping at low acidity, and improved solubility in the diluent. Longer alkyl chains (C₁₂ or C₁₄) coupled with the compact pyrrolidine ring may further improve ligand solubility in *n*-dodecane while maintaining fast extraction kinetics and high metal-ligand complex stability. Previous work from part 1 of this same study found that the smaller dihexyl (C₆) alkyl chains (ligands **1-3**) were too short to maintain organic phase solubility with Eu(III) extracted. The dioctyl (C₈) derivatives (**4-6**) performed better than the dihexyl ligands but the morpholino ligand (**6**) struggled with weak metal extraction and competing nitric acid extraction. The dioctyl pyrrolidinyl ligand (**4**) had the

highest distribution ratios for Eu(III), while the dioctyl piperidinylligand (**5**) fell in between the other two analogues.

Luminescence spectroscopy titrations were performed and resulted in the formation of 1:1 through 1:4 metal-ligand complexes for all six UDGA ligands and TODGA in the polar organic solvent acetonitrile. Conditional stability constants were calculated by fitting the spectral data in HypSpec [23] DMOpyrDGA(**10**) formed the strongest 1:4 complex with Eu(III) ($\log \beta_4 = 24.8 \pm 0.3$) while DMOmorDGA(**12**) formed the weakest 1:4 complex with Eu(III) ($\log \beta_4 = 21.1 \pm 0.2$). With the exception of DMOmorDGA(**12**), all of the UDGA ligands formed stronger complexes with Eu(III) in acetonitrile. TODGA remains the best of the diglycolamide extractants, however, due to its relatively high solubility in *n*-dodecane and its high metal distribution ratios at 1 M nitric acid [14].

Acknowledgements

This research was supported by a grant from the United States Department of Energy – Nuclear Energy University Programs.

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