Triazole Diglycolamide Cavitand for lanthanide extraction

M. Wehbie, Guilhem Arrachart, I. Karame, L. Ghannam, S Pellet-Rostaing

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M. Wehbie[a,b], G. Arrachart[a], I. Karamé[b], L. Ghannam[b], and S. Pellet-Rostaing[a*].

[a] *Institut de Chimie Séparative de Marcoule, ICSM, UMR 5257-CEA/CNRS/UM/ENSCM Site de Marcoule, Bât 426, BP 17171, 30207 Bagnols sur Cèze Cedex,* stephane.pellet-rostaing@cea.fr

[b] *Laboratory of Organometallic Catalysis and Coordination Chemistry, Department of Chemistry, Lebanese University, Faculty of Sciences I, Beirut, Lebanon.*

Abstract

Click chemistry, which relies on the efficiency of the copper (I)-catalyzed azide-alkyne cycloaddition, was used to link four diglycolamide (DGA) moieties to a resorcinarene platform leading to a specific tetra-DGA-resorcinarene ligand (c-methylcalix(4)methylresorcinarene-4-triazole-dioctyldiglycolamide denoted CR4-Tz-DODGA). The extraction ability of this ligand was studied in a mixture of toluene / iso-octanol (90/10, v/v) toward rare earth elements (REE) at different nitric acid concentrations, ranging from 1 to 5 M. The results show the efficient extractability of and selectivity towards heavy REEs. The stoichiometry of the extraction was established by the slope analysis method and an extraction mechanism was proposed based on estimates of the thermodynamic parameters. From the extraction behavior of the tetra-DGA-resorcinarene ligand, we present the possibility for the extraction and separation of dysprosium from used permanent magnets.

Keywords: DGA, Resorcinarene, Selective ionic separation, Lanthanide

1. Introduction

Rare earth elements (REEs) comprise the family of lanthanides including scandium and yttrium. Due to their similar chemical properties, REEs are rarely separated from each other.[1] These elements have a wide range of technical applications, and the forecasted average annual demand growth of REEs is stated to increase to more than 8 % every year by 2020.[2] In contrast to increased REE demand, the supply of such materials is currently experiencing a shortage and as an alternative to increased mining operations, recycling can be used to reduce the stress on the rare earth supply.[3] In addition, REEs are significant byproducts of fission reactions as they represent approximately 40% of the fission product mass and include measurable amounts of all lanthanides. The separation of lanthanides from actinides can be a challenging obstacle in effective waste management.[4]

Several methods have been investigated for the recovery of REEs by membrane filtration,[5] solid–liquid separation using chelating organic resins,[6] as well as organic-inorganic materials.[7]

Solvent extraction has long been used for the recovery and the separation of REEs, which is usually accomplished by using phospho-compounds in organic solvents and also in ionic liquid diluents.[9,10] Among many other extractants well-known in the field of metals extraction and nuclear fuel reprocessing, diglycolamides have gained importance within the field since first reported by Stephan and co-workers in 1991. [11,12]

Diglycolamides (DGAs) have favorable characteristics as they are tridentate O-donating ligands, which allows them to form stable complexes with lanthanides and actinides. DGAs consist of C, H, N, and O atoms and can be incinerated completely to form gaseous products after utilization.[13-16] Though several DGA compounds have been studied, the effect of DGA unit preorganization in a macrocyclic platform used in REE extraction has not been examined in detail. The positive effects on the extraction efficiency of ligand preorganization within a platform has been established.[17]

Therefore the advantages preorganization of DGA sites in a calix[4]arene provide have been studied and proven to be far superior to TODGA, with comparable extractions at 100 times lower concentrations and increased efficiency with an increased number of DGA units.[18,19] The number of DGA units and the flexibility provided by spacer lengths is an important parameter in the extraction ability of the ligands. Among different macrocycles, cavitand analogues of C-methylcalix(4)methyl-resorcinarene provides an excellent preorganized platform for the coordination of host systems due to its conformational rigidity, which is assured by the methylene bridge between the hydroxyl groups of two neighboring phenyl rings. Its functionalization can be easily performed making the platform a focus of interest for a wide range of applications, such as being used as host molecules,[20,21] components in liquid crystals,[22] photoresistors,[23] HPLC stationary phases,[24] self-assembled capsules,[25] surfactants, for potential sensor applications,[26] as an antibacterial agent,[27] and with biomolecules.[28]

Click chemistry, developed by Sharpless and co-workers,[29] is widely utilized in various fields, including organic,[30] medicinal,[31] materials,[32] and biological chemistry.[33] Its popularity stems from its simplicity, high conversion, the absence of side product formation, and mild reaction conditions. Therefore, copper-catalyzed azide–alkyne cycloaddition (CuAAC) is one of the most useful reactions for the covalent attachment of appropriate functional groups.

A cavitand containing azide groups was synthesized and engaged in a click reaction with the terminal alkyne of a DGA moiety. The success of the functionalization was monitored by FT-IR, NMR and MS analysis. The performance of the resulting Tetrakis(4-triazolomethyldioctyldiglycolamide)-tetramethyl cavitand (CR4-Tz-DODGA, Figure 1) in solvent extraction experiments was evaluated for REEs under acidic feed conditions. The stoichiometry of the complexes and the extraction mechanism involved are discussed with regards to the extraction of the REEs. Finally, the ligand exhibited highly favorable separation behavior of REEs from a simulated solution of permanent magnets.

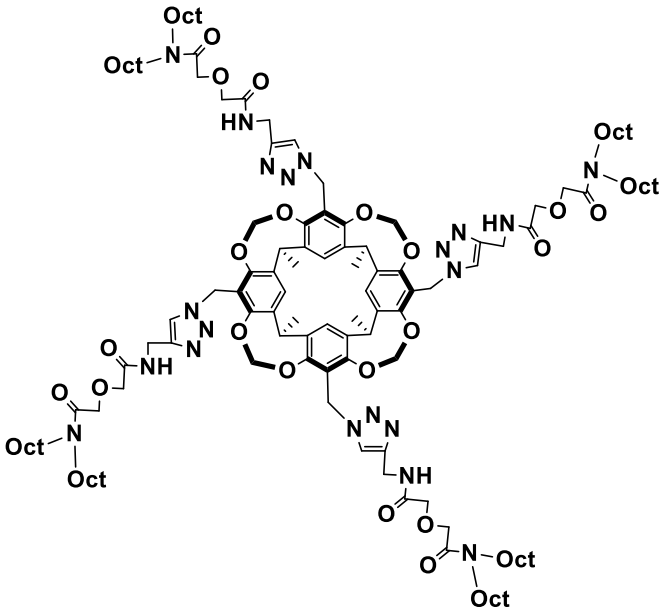


Figure 1: *Structure of CR4-Tz-DODGA*

2. Methods and materials

2.1 Chemicals and analysis

Chemicals (analytically pure) were purchased from Sigma-Aldrich or Alfa Aesar and were used without further purification. Anhydrous solvents were purchased from Acros (AcroSeal®). Reactions were monitored by thin layer chromatography (Merck TLC Silica Gel 60 F254).

Flash chromatography was performed using a combiflash Agilent Intelliflash 971-FP. NMR analyses were performed on a Bruker 400 ultrashield VS spectrometer. Chemical shifts are reported in ppm using the solvent ($CDCl_3$: 7.26 ppm for ^{1}H; 77.16 ppm for ^{13}C) as an internal reference. Metal concentrations were determined using a spectro ARCOS ICPAES spectrometer. Fourier transform infrared (FTIR) measurements were performed on a Perkin Elmer Spectrum 100 instrument in ATR (Attenuated Total Reflection) mode. The measured range was from 400 cm^{-1} to 4000 cm^{-1} with a 4 cm^{-1} beam resolution. Background acquisition was conducted prior to measurement. ESI-MS was performed on a Flexar SQ 300 MS instrument.

2.2 Synthesis

Preparation of Propargyl-DODGA **2**

1.62 g of 2-(2-(dioctylamino)-2-oxoethoxy) acetic acid **1**,[34] (4.54 mmol) and 0.675 g of hydroxyl benzotriazole (4.99 mmol) were poured into 30 ml chloroform at 0 °C. The obtained suspension was stirred for 30 minutes at room temperature, then 0.25 g of propargyl amine

(4.54 mmol) and 1.03 g of dicyclohexylcarbodiimide DCC (4.99 mmol) were added, and the resulting suspension was stirred for two days. After filtration and evaporation of the solvent, the crude product was purified using column chromatography (SiO_2, dichloromethane/methanol 5%), affording compound **2** as a brown dense oil with a yield = 72 %. ^{1}H NMR (400MHz, $CDCl_3$) δ [ppm]: 0.89 (m, 6H, CH_2-C***H*****$_3$**), 1.29 (m, 20H, -NCH_2-C***H***$_2$-CH_3), 1.54 (m, H, J=7.2 Hz, NH-CH_2-C***H***$_2$), 2.21 (t, 1H, J=2.4 Hz, C***H***), 3.1 (t, 2H, 7.6 Hz, N-C***H***$_2$-heptyl), 3.23 (t, 2H, 7.6 Hz, N-C***H*****$_2$**-heptyl), 4.09 (d, 2H, J=2.8 Hz, N-C***H***$_2$) 4.1 (s, 2H, CO-C***H*****$_2$**-CO), 4.25 (s, 2H, CO-C***H*****$_2$**-CO), 8.2(s, 1H, N***H***-C=O). ^{13}C NMR (400MHz, $CDCl_3$) δ [ppm]:14.1, 22.6, 26.9, 27.0, 27.6 (NH-***C***H_2), 28.5, 28.9, 29.2, 29.2, 29.3, 29.4, 31.7, 31.8, 46.2, 46.8 (-***C***H_2-), 71.2(≡***C***H), 69.6 & 71.8 (-***C***H_2O-), 79.5(-***C***≡), 168.1, 169.4 (***C***=O).

Preparation of cavitand **3**

Cavitand **3** was prepared as described by Cram *et al*, and identified by comparison of its ^{1}H NMR spectrum with literature values.[35] **3** was obtained as dark yellow powder (yield 88 %). ^{1}H NMR (400 MHz, DMSO) δ [ppm]: 1.70 (d, 12 H, C***H***$_3$CH), 2.00 (s, 12 H, ArC***H***$_3$)**,** 4.46 (q.4H, CH_3C***H***), 7.41 (s, 4 H, Ar***H***), 8.70 (s, 8 H, ArO***H***). m/z: 543 [$(M-H)^+$].

Preparation of cavitand **4**

Cavitand **4** was prepared by adapting a procedure described in the literature by using dichloromethane instead of bromochloromethane.[27] **4** was obtained as a white powder (yield 84 %) and the ^{1}H NMR spectrum was in agreement with the previously reported spectrum in the literature.[35],[36], ^{1}H NMR (400MHz, $CDCl_3$) δ [ppm]: 1.73 (d, 12 H, C***H***$_3$CH), 2.00 (s, 12 H, ArC***H***$_3$), 4.29 (d, 4 H, inner of OC***H***$_2$O), 5.20 (q, 4 H, CH_3C***H***), 5.92 (d, 4 H, outer of OC***H***$_2$O), 7.14 (s, 4 H, Ar***H***).

Preparation of cavitand **5**

Cavitand **5** was prepared using a procedure described by Moran *et al.* **5** was obtained as a white powder (yield 90 %). ^{1}H NMR (400MHz, $CDCl_3$) δ [ppm]: 1.75 (d, 12H, J=7.4 Hz, CHC***H***$_3$), 4.42 (s, 8 H, C***H***$_2$Br), 4.57 (d, 4 H, J = 7.0Hz, inner OC***H***$_2$O), 5.02 (q, 4 H, J=7.4 Hz, C***H***), 6.04 (d, 4 H, J=7.0 Hz, outer OC***H***$_2$O), 7.26 (s, 4 H, Ar***H***).

Preparation of cavitand **6**

In a round bottomed flask, cavitand **5** (2 g, 2.4 mmol) was dissolved in 60 ml of acetone. Sodium azide (2 g, 30.76 mmol) was added to the solution. The mixture was stirred under reflux for 4 h. The mixture was filtered over Celite and washed with acetone. The collected solution was evaporated using a rotary evaporator and the residue was purified using column chromatography (SiO_2, ethyl acetate /cyclohexane, 65/35). Cavitand **6** was obtained as a white powder (yield 85 %). ^{1}H NMR (400MHz, $CDCl_3$) δ [ppm]: 1.75 (d, 12H, *J*=7.4 Hz, CHC***H***$_3$), 4.3 (s, 8 H, C***H***$_2N_3$), 4.42 (d, 4 H, *J*=7.0Hz, inner OC***H***$_2$O), 5.0 (q, 4 H, *J*=7.4 Hz, CH_3C***H***), 6.0 (d, 4 H, *J*=7.0 Hz, outer OC***H***$_2$O), 7.3 (s,4 H, Ar***H***); ^{13}C-NMR ($CDCl_3$, 400MHz), δ [ppm]: 153.3 (Ar-Cq), 139.1 (Ar-Cq), 122.2 (Ar-Cq), 120.3 (Ar-H), 99.7 (Ar-CH_2-Ar), 45.1 (Ar-CH_2-N3), 31.2 (Ar-CH-Ar), 16.1 (CH3). (m/z): 835 [$(M+Na)^+$]; FT-IR (ATR crystal): ν (cm^{-1}) 2090 (ν_{as} -N_3).

Preparation of cavitand **7**

Azide **6** (1 eq, 0.2 g, 0.246 mmol) was dissolved in a mixture of THF/H_2O (2:1 v/v 5 ml). **2** (4 eq, 0.388 g, 0.984 mmol), $CuSO_4.5H_2O$ (0.4 eq, 0.025 g, 0.098 mmol) and sodium ascorbate (0.8 eq, 0.039 g, 0.197 mmol) were added to the solution. The resulting mixture was stirred at 50° C for 24 h, then THF was evaporated and the resulting precipitate was dissolved in 30 ml DCM and washed 3 times with 30 ml of 25% Ammonia. The organic layer was dried over anhydrous Na_2SO_4. The solvent was evaporated and the crude product was purified using flash chromatography (SiO_2, dichloromethane/methanol 5%) to afford the pure product (yield 65 %). ^{1}H NMR (400MHz, $CDCl_3$) δ [ppm]: 0.88 (t, 24H, J= 6.4 Hz, CH_2-CH_3), 1.29 (m, 80H, -CH_2-(CH_2)$_{40}$-CH_3), 1.54 (p, 16H, J=7.2 Hz, NH-CH_2-CH_2), 1.77 (d, 12H, J=7.2 Hz, CHCH_3), 3.1 (t, 8H, 7.2 Hz, N-CH_2-heptyl), 3.33 (t, 8H, 7.2 Hz, N-CH_2-heptyl), 4.1 (s, 8H, CO-CH_2-O), 4.24 (s, 8H, O-CH_2-CO), 4.15 (m, 4 H, inner OCH_2O), 4.55 (s, 4H, Tz-CH_2-NH), 4.98 (q, 4 H, J=7.4 Hz, CH-CH_3), 5.27 (s, 4H, Ar-CH_2-Tz), 5.82 (m, 4 H, J=6.8 Hz, outer OCH_2O), 7.2 (s, 4 H, ArH), 7.6 (s, 4H TzCH), 8.09 (s, 4H, NH); ^{13}C NMR (400MHz, $CDCl_3$) δ [ppm]: 14.1, 16.2, 22.6, 26.9, 27.1, 27.7, 28.9, 29.2, 29.3, 29.4, 31.2, 31.8, 31.8, 34.6 (Ar-*C*H-CH_3), 44.0, 46.2, 46.8, 69.5, 71.5, 99.7 (O-*C*H_2-O), 120.8 (Ar-*C*H), 122.8 (Tz*C*H), 129.7, 138.9, 144.7 (Tz*C*), 153.4, 168.1(*C*O-N), 169.7 (*C*O-N); (m/z): 2413 [(M+Na)$^+$]; FT-IR (ATR crystal): ν (cm^{-1}) 1643 (νC=O).

2.3 Extraction experiments

Rare earth element (REE) stock solutions were prepared at the desired acidity from 1000 mg·L^{-1} ICP standard (in 1% HNO_3) of lanthanum, europium and ytterbium. A synthetic solution mimicking the leaching of magnets was prepared from 1000 mg·L^{-1} ICP standard (in 1% HNO_3) of neodymium, dysprosium, iron and boron. The desired concentrations were prepared by dilution using ultrapure water (MilliQ, Millipore, >18 MΩ cm^{-1}) and the acidity was adjusted with nitric acid.

Organic solutions of CR4-Tz-DODGA at varying concentrations were prepared in a mixture of toluene / iso-octanol (90/10 v/v). Iso-octanol was used as a phase modifier. Turbid solutions were obtained when solutions without the phase modifier were mixed with > 2 M nitric acid.

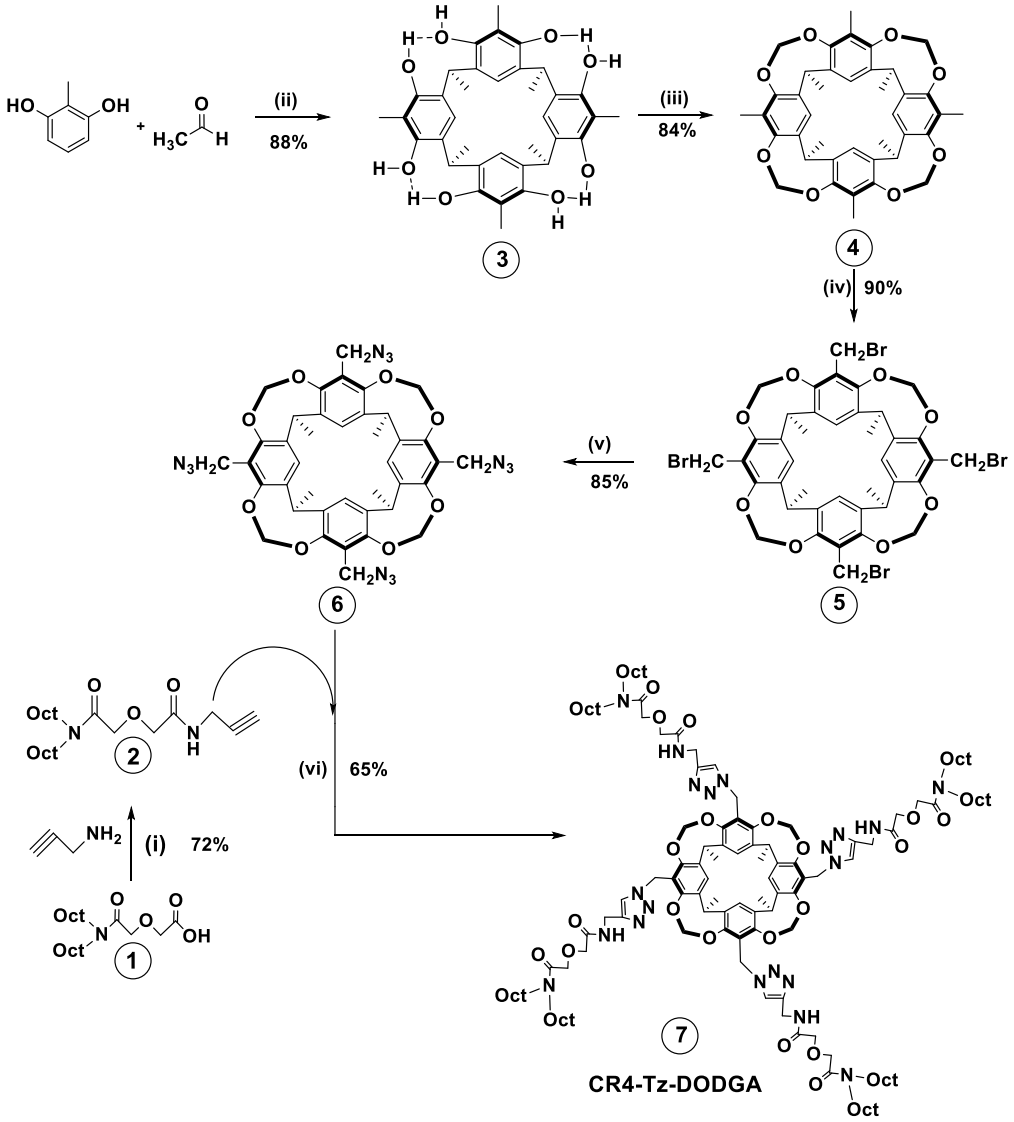
Organic phases were pre-equilibrated with an aqueous phase at the same acidity as the extraction step without REE cations. The pre-equilibrated organic phases were then mixed with an equal volume of an aqueous acidic stock solution of REEs in a thermostated shaker (Infor-ht® ecotron) at 25°C for one hour at 400 rpm. Phases were separated after centrifugation at 4000 rpm for 30 minutes (sigma 3-16 PK). After centrifugation, the separated aqueous phases were subjected to ICP-AES analysis to determine the distribution ratio (D_M), which is the ratio of the total concentration of metal M in the organic phase to the total concentration of the same metal in the aqueous phase, i.e., $D_M = [M_{org}]/[M_{aq}]$. The suitability of the extractant is also associated with the separation factors $SF_{M1/M2}$ that is the ratio of the distribution ratios D_{M1} and D_{M2} ($SF_{M1/M2} = D_{M1}/D_{M2}$), and finally describes the selectivity for M1 over M2. The experiments were carried out in duplicate

with a precision of ± 5%. The full set of solvent extraction data of the lanthanide cations (La^{3+}, Eu^{3+}, and Yb^{3+}) are summarized in Table S1 in the supporting information.

3. Results and discussion

3.1 Synthesis and characterizations of CR4-Tz-DODGA

CR4-Tz-DODGA was synthesized via a general synthetic route in six steps according to scheme 1. The "clickable DGA" (**2**) was prepared by amide coupling of propargylamine with DODGA **1** using DCC as the coupling agent in the presence of HOBt.[34]



Scheme 1: *Synthetic route for CR4-Tz-DODGA*
(i) DCC + HOBT/$CHCl_3$ (ii) H_2O-EtOH/HCl, 80°C; (iii)CH_2Cl_2/K_2CO_3/DMF-70°C; (iv) NBS-Benzoyl peroxide/CCl_4 reflux; (v) NaN_3/Acetone, 60°C; (vi) $CuSO_4$,5H_2O, sodium ascorbate/THF-H_2O.

The selective and efficient introduction of azido groups to an appropriate position on the cavitand was performed in three steps. Cavitands **4** and **5** were prepared according to procedures previously described in the literature.[35,36] Derivative **6**, having azido groups,

was prepared by nucleophilic substitution of cavitand **5** using NaN_3 in acetone. The 'Click' linkage of DGA derivative **2** was efficiently accomplished with azido-containing resorcinarene under Cu(I)-catalyzed conditions using $CuSO_4.5H_2O$/sodium ascorbate as the catalyst. ^{1}H-NMR spectra of cavitands **6** and **7** are in accordance with their structures.

The success in the functionalization of the resorcinarene by the DGA unit was monitored by FT-IR, ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{1}H COSY, and ^{1}H-^{13}C HSQC in addition to high resolution mass spectroscopy (see Figures S1 –S5 in the supporting information). The disappearance of the azide stretching vibration at 2090 cm^{-1} could be observed in the IR spectrum, which indicates the complete conversion of the N_3 groups into the triazole functionalities, and the formation of new stretching bands at 1644 cm^{-1}, corresponding to the amide groups of the DGA side arms, was observed (Figure 2).

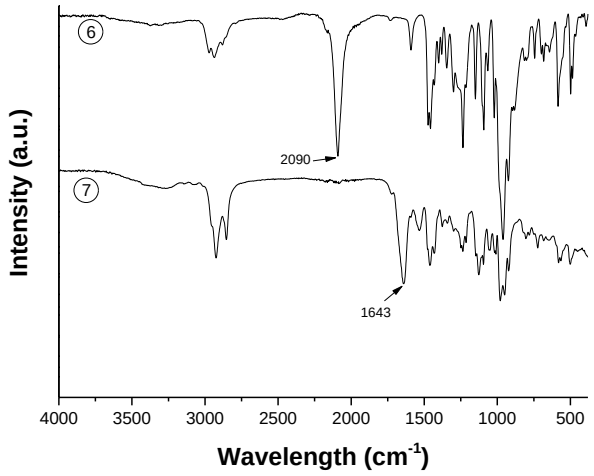


Figure 2: *FT-IR spectra: cavitands **6** and **7**.*

Isolation of the final product was further confirmed by a resonance signal at 7.63 ppm in the ^{1}H-NMR spectrum (Figure 3a) and two resonance signals at 122.8 and 144.7 ppm in ^{13}C-NMR spectrum (Figure 3b), characteristic of 1,4-disubstituted 1,2,3-triazoles. In addition, the DGA side arms were identified by the two resonance signals of the methylene groups at 68.8 and 69.1 ppm, and two other signals at 168.14 and 169.74 ppm in the ^{13}C-NMR spectrum, corresponding to the amide carbonyl groups.

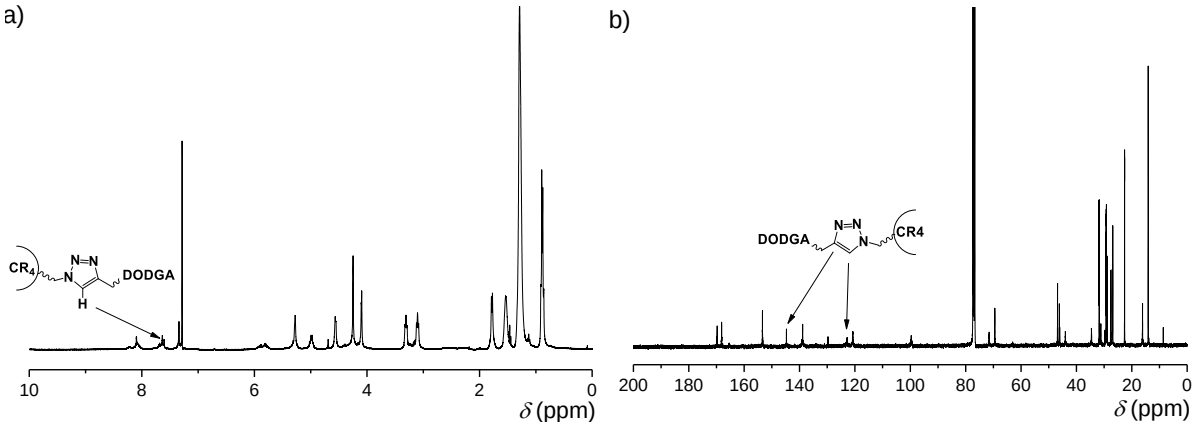


Figure 3: *a) ^{1}H and b) ^{13}C NMR spectra of Cavitand **7** with characteristic signals to the 1,4-disubstituted 1,2,3-triazoles*

3.2. Application in ionic separation

Solvent extraction was carried out using a CR4-Tz-DODGA solution in a mixture of toluene and iso-octanol (9/1, v/v). The extraction profile was established for La, and Eu as light rare earth elements (LREE) and Yb as a heavy rare earth element (HREE). The metal to ligand ratios (M : L) were varied from (1 : 0.33) up to (1 : 5). At a (1 : 3) ratio, which is a very weak ratio with respect to what has been used for similar platforms,[16] we obtained very interesting results and the ligand was able to extract approximately 97 % of Yb with a distribution coefficient of 31 (Table 1).

Table 1: *Extraction equilibrium constants for La(III), Eu(III), and Yb(III) at 298 K.*

		[Ligand] mM					**Av. $Log_{(Kex)}$**
		0.33	1.00	2.00	3.00	5.00	
La	D	<0.01	0.01	0.52	0.10	0.33	
	$Log_{(Kex)}$	3.08	3.17	3.25	3.19	3.27	3.19
Eu	D	0.02	0.17	0.57	1.44	4.92	
	$Log_{(Kex)}$	4.50	4.52	4.48	4.53	4.60	4.53
Yb	D	0.37	3.40	12.21	31.22	140.2	
	$Log_{(Kex)}$ at β=0.1	4.79	4.75	4.40	4.35	4.47	4.55
	$Log_{(Kex)}$ at β=0.25	5.44	5.40	5.06	5.00	5.12	5.21

Organic phase: 1-5 mM CR4-Tz-DODGA in toluene / iso-octanol (90/10 v/v);
Aqueous phase: 1 mM $Ln(NO_3)_3$ in 5 M HNO_3.

3.2.1. Effect of nitric acid concentration

Figure 3 represents the distribution coefficients and the selectivity results obtained for the extraction of La^{3+}, Eu^{3+}, and Yb^{3+} with 1 mM CR4-Tz-DODGA while varying the concentration of nitric acid from 1 to 5 M. The presented data clearly shows the dependence of the distribution values and the selectivity factors on the concentration of the feed nitric acid. The results are in good agreement with the behavior observed in liquid-liquid extraction systems using neutral ligands (solvating agents). Generally, an increase in the feed nitric acid concentration leads to an increase in the distribution ratio values,[37] this is also the case in our study. The extraction of REEs increased with an increase in the nitric acid concentration up to 5 M (Figure 4). At the above conditions, efficient extraction of LREEs where not observed, while extraction of HREE was favored at higher HNO_3 concentration, indicating the possibility of selective extraction of HREE. By increasing the ligand concentration at 5 mM, it was possible to perform a mutual separation of REEs with an extraction efficiency value24% for La, 83% for Eu and 99% for Yb (see supporting information Table S1).

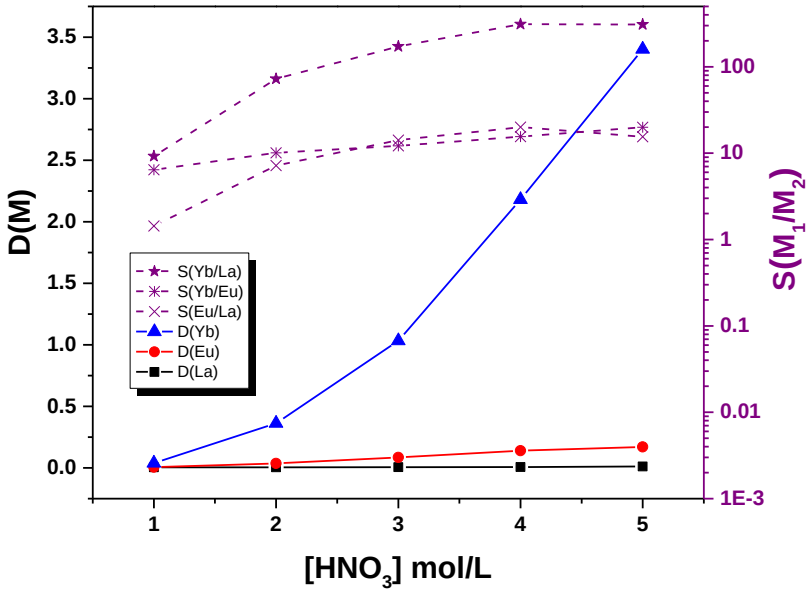


Figure 4: *Effect of nitric acid concentration on the Distribution ratios and the selectivity factors of La(III), Eu(III), and Yb(III); Organic phase: 1 mM CR4-Tz-DODGA in toluene / iso-octanol (90/10 v/v); Aqueous phase: 1 mM $Ln(NO_3)_3$ in 1 – 5 M HNO_3.*

However, an increase in the concentration of nitric acid from 1 to 5 M resulted in an increase of up to 20 and 300 times for the separation factors $SF_{(Yb/Eu)}$ and $SF_{(Yb/La)}$, respectively. The trend in extraction performance seems to be related to the charge density of the metal ion, showing a higher selectivity for the heavy rare earth elements (HREEs). This indicates that the rigidity of the macrocycle has a dramatic influence on the selectivity and complexation of metal ions, which largely depends on the ionic radius of the metal.

3.2.2. Effect of extractant concentration

CR4-Tz-DODGA is considered to be a neutral complex extractant which forms complexes with the trivalent lanthanides through a mechanism which can be described using the following equation.[16]

$$M^{3+} + 3NO_3^- + n\bar{L} \overset{K_{ex}}{\rightleftharpoons} \overline{M(NO_3)_3.L_n} \qquad (1)$$

In this equation, M represents the REEs, L represents the neutral extractant (CR4-Tz-DODGA), and $\overline{M(NO_3)_3.L_n}$ represents the metal–extractant complex in the organic phase. An overbar refers to a species in the organic phase and the absence of an overbar denotes an aqueous species.

Given that REEs extraction occurs primarily by a solvation mechanism, the metal M must be neutralized by NO_3^-. Acid extraction by the neutral compound was considered negligible.[38]

To determine the stoichiometry of complexation n, the distribution ratios for the metal extraction at constant acidity were plotted as a function of extractant concentrations. The equilibrium concentration of extractant equals approximately its initial concentration, while in our calculations we considered the concentration of the ligand at equilibrium, $[L]_{free}$, to obtain more accurate results. The D values increased with increased ligand concentrations, which indicates that the CR4-Tz-DODGA is directly participating in complex formation.

The slope analysis method (Figure 5) was used to confirm the ratio of the ligand to the metal, straight lines with slopes of 2.13, 1.99 and 2.12 were found for Yb(III) and Eu(III) and La(III), respectively. This result suggests that the metal : ligand extraction complex stoichiometry for Ln (III) is 1 : 2, which is consistent with the solvent extraction studies reported in the literature.[16],[39],

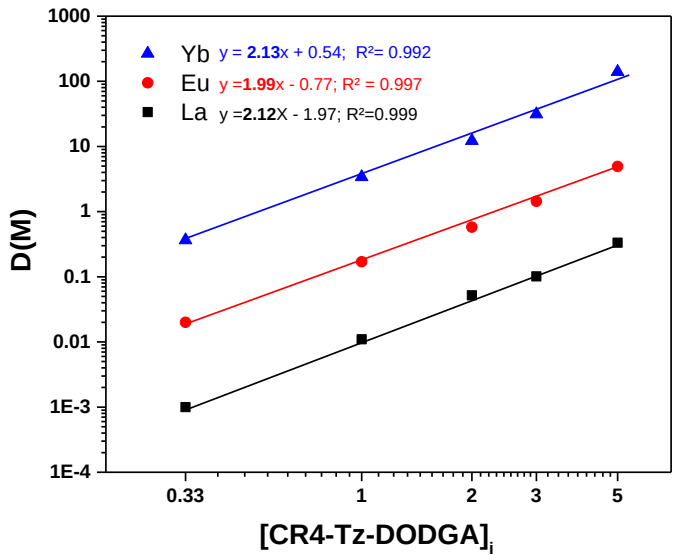


Figure 5: *Effect of the extractant concentration on the distribution ratios of Ln(III); Organic phase: 0.33-5 mM CR4-Tz-DODGA in toluene / iso-octanol (90/10 v/v); Aqueous phase: 1 mM $Ln(NO_3)_3$ 5M in HNO_3.*

Therefore the extraction constant, K_{ex}, can be represented as:

$$K_{ex} = \frac{\overline{[M(NO_3)_3.L_2]}}{[M^{3+}] \times [NO_3^-]^3 \times \overline{[L]^2_{free}}} \quad (2)$$

The distribution constant is represented in terms of the stability constant, β_i, for nitrate complexes of M(III) as described in the following equation:

$$D_M = \frac{\overline{[M(NO_3)_3.L_2]}}{[M^{3+}]\,(1 + \sum \beta_i\,[NO_3^-]^i)} \quad (3)$$

By substituting the value of $\overline{[M(NO_3)_3.L_n]}/[M^{3+}]$ from eq (3) into equation (2) the constant of extraction can be expressed as:

$$K_{ex} = \frac{D_M\,(1 + \sum \beta_i\,[NO_3^-]^i)}{[NO_3^-]^3 \times \overline{[L]^2_{free}}} \quad (4)$$

The β_i values for the NO_3^- complexation of La(III), and Eu(III) were obtained from the literature as (β_1 = 1.29, β_2 =0.36 for La) and (β_1 = 1.86, β_2 =0.43 for Eu) at an ionic strength of 5.0.[40] $\beta_1$of Yb was estimated between 0.1 and 0.25 due to the lack of information about Yb(III), and its corresponding $LogK_{ex}$ values are provided in range values corresponding to the estimated values of β_1, 0.1 and 0.25 (Table 1). From the distribution data, the apparent extraction equilibrium constants can be estimated. The average values of $LogK_{ex}$ for La(III), Eu(III) and Yb(III) with the ligand are 3.19, 4.53 and 4.55-5.21, respectively (Table 1).

3.2.3. Effect of temperature

The effect of temperature on the extraction of lanthanides from 5 M HNO_3 by 1 mM of CR4-Tz-DODGA in toluene / iso-octanol (90/10 v/v) was studied at a temperature range varying from 25 to 45 °C. The distribution ratio for Ln(III) was found to decrease with increasing temperature, indicating the extraction process to be exothermic (Figure 5). The change in the enthalpy (ΔH) can be calculated using the Van't Hoff relationship where R is the gas constant:

$$LogK_{ex} = -\frac{\Delta H}{2.303R}.\frac{1}{T} + \frac{\Delta S}{2.303R} \quad (5)$$

From the plot of $logK_{ex}$ versus 1/T, straight lines were obtained as shown in Figure 6. The ΔH values were determined from the slopes of the straight lines (2.01 for Yb(III), 1.79 for Eu(III), and 1.57 for La(III)), while the entropy values were estimated to a first approximation from the intercept values (-1.25 for Yb(III), -1.41 for Eu(III), and -2.09 for La(III)).

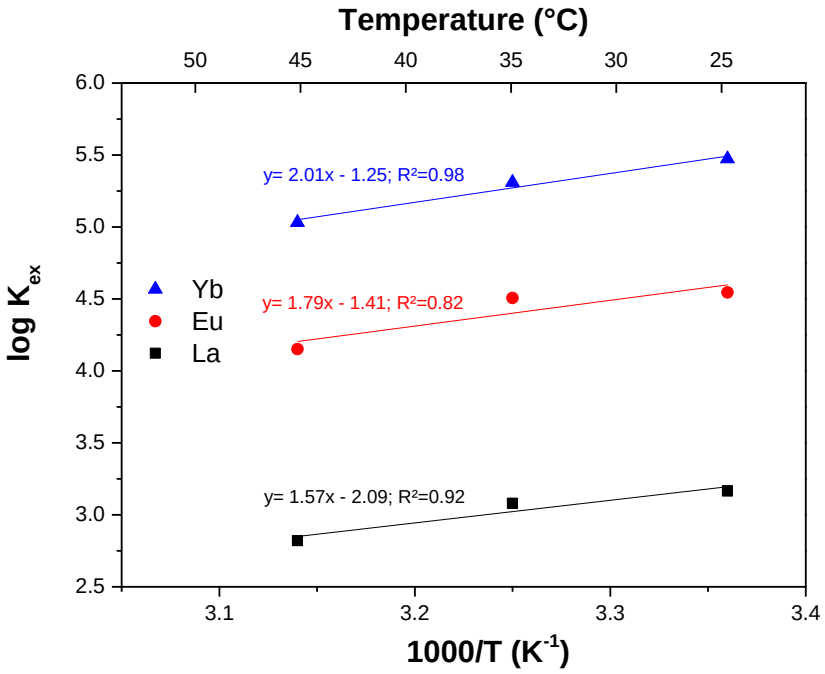


Figure 6: *Effect of temperature on the apparent extraction equilibrium constants logK_{ex}. Organic phase: 1 mM CR4-Tz-DODGA in toluene / iso-octanol (90/10 v/v); Aqueous phase: 1 mM $Ln(NO_3)_3$ in 5M in HNO_3.*

In addition, the free energy change, ΔG, for the extraction at 298 K was obtained from Gibbs's Helmholtz equation.

$$\Delta G = \Delta H - T\Delta S = -2.303RT \text{ Log } K \qquad (6)$$

The thermodynamic parameters, ΔH, ΔS, and ΔG for the extraction of CR4-Tz-DODGA are summarized in Table 2. The results indicate that the extraction mechanism is similar for REEs regarding the entropy and enthalpy factors that can affect the extent of the metal ion extraction.

The overall enthalpy change depends on several contributing factors, such as, (i) dehydration of the metal ions (ΔH_1), (ii) formation of neutral extracted species (ΔH_2), and (iii) dissolution of the metal complex in the organic phase (ΔH_3).

The negative ΔH values suggest that the complexation between Ln(III) metal nitrate species and the neutral extractant molecule is exothermic (Table 2).

The negative entropy change (−ΔS) suggests the presence of a few water molecules in the primary coordination sphere of Ln(III). Interestingly, the change in the Gibbs free energy (−ΔG) follows the order: ΔG(Yb) > ΔG(Eu) > ΔG(La) which is the same order for the extraction efficiency. The negative values of ΔG at room temperature indicate that the extraction reactions are spontaneous. The more negative ΔG value for Yb(III) indicates that the formation of the dissolved Yb(III) : CR4-Tz-DODGA complex is thermodynamically more favored in comparison to the dissolved complexes of Eu(III) and La(III).[41]

Table 2: *Thermodynamic parameters (ΔH, ΔS, and ΔG) for the extraction of La(III), Eu(III) and Yb(III) at 298K.*

System	Slope	Intercept	$\Delta H_{(kJ/mol)}$	$\Delta S_{(J/mol)}$	$\Delta G_{(kJ/mol)}$
YbL2	2.01	-1.25	-38.45	-24.03	-31.29
EuL2	1.79	-1.41	-34.26	-27.07	-26.19
LaL2	1.57	-2.09	-30.10	-39.94	-18.19

Organic phase: 1 mM CR4-Tz-DODGA in in toluene / iso-octanol (90/10 v/v)*;*
Aqueous phase: 1 mM $Ln(NO_3)_3$ in 5 M HNO_3.

3.2.4. Extraction Kinetics

A study on the phase transfer kinetics indicated that equilibrium was attained quickly (Figure 7). The amount of Yb extracted increased rapidly, the values obtained after 15 minutes did not change after 60 minutes of shaking, a plateau is observed with a distribution ratio of approximately 98. Thus, the extraction rate of Yb by CR4-Tz-DODGA was not a limiting factor in the extraction process.

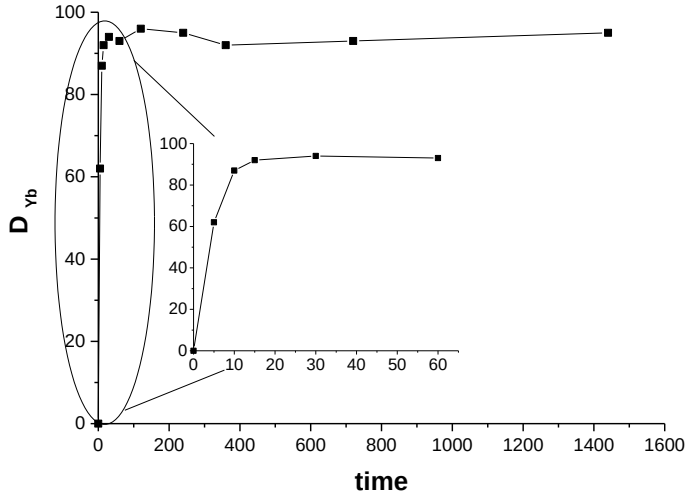


Figure 7: *Distribution ratio of Yb as a function of time.*
Organic phase: 5 mM CR4-Tz-DODGA in toluene / iso-octanol (90/10 v/v);
Aqueous phase: 1 mM $Yb(NO_3)_3$ in 5 M HNO_3.

3.3. Application to permanent magnets

Considering the performances of CR4-Tz-DODGA in the extraction of REEs, the extractability of Nd and Dy over Fe and B from a simulated leaching solution from permanent magnets was studied. A new set of experiments was performed at 5 M nitric acid with a total concentration of the metals fixed at 2 mM in the following proportions: 70% Fe, 10% Dy, 10% Nd, 10% B, to mimic a representative leaching solution of a Nd/Fe/B/Dy magnet. The concentration of CR4-Tz-DODGA was varied from 1-3 mM, which corresponds to (M:L) ratios

varying from 0.5-1.5. The data are presented in Table 3. The results show that the ligand selectively extracts Dy(III) with regards to the other cations. As shown in the previous study, the ligand was more selective towards the HREE with a Dy:Nd selectivity factor of > 45.

These results demonstrate the potential use of CR4-Tz-DODGA towards the selective extraction of REEs with regards to competitive ions, especially iron – $SF_{(Dy/Fe)}$ > 1000, which is the main competing ion in the nitric acid leaching solution.

Table 3: *Distribution coefficients and separation factors for Nd/Dy/Fe/B cations at 25°C.*

[Lig.]	D(Fe)	D(B)	D(Nd)	D(Dy)	SF(Dy/Nd)	SF(Dy/B)	SF(Nd/B)
1 mM	< 0.01	0.04	0.01	2.1	210	52.5	0.25
2 mM	< 0.01	0.02	0.10	6.8	68.0	340	5.0
3 mM	< 0.01	0.03	0.25	11.7	46.8	390	8.3

Organic phase: 1-3 mM CR4-Tz-DODGA in 90% toluene/10% iso-octanol (v/v);
Aqueous phase: 2 mM of cations 70% Fe. 10% Dy. 10% Nd. 10% B in 5 M HNO_3.

4. Conclusions

A new ligand CR4-Tz-DODGA, corresponding to a tetra-methylcavitand functionalized at the upper rim with four 1,2,3-triazole-DGA binding units containing n-octyl groups, was synthesized with a satisfactory yield of 65 % using a click reaction. Ligand-binding, at a concentration range from 1 to 5 mM, was investigated towards 1 mM mixtures of three rare earth elements (REEs): La(III), Eu(III), and Yb(III). The distribution coefficients and selectivity factors increased with an increase in nitric acid concentration. At 5 M HNO_3 with a 1 mM ligand concentration, no real extraction of light REE (La and Eu) was observed but approximately 77% of Yb was extracted, indicating a selective extraction for heavy REEs. By increasing the ligand concentration to 5 mM, it was possible to perform a mutual separation of REEs (24% of La, 83% of Eu and 99% of Yb are extracted). An extraction mechanism was proposed based on slope analysis and thermodynamic studies highlighting the differences between the LREEs and HREEs, which are linked to the extraction efficiency. These results allowed us to consider this ligand for the extraction of HREEs present in a solution mimicking a leaching solution of Nd/Dy/Fe/B magnets. The selective extractability of Dy with regards to the other species in such solutions opens up interesting applications for this ligand.

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