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Multidentate extracting agents based on calix[4]arene scaffold – U^{VI}/Eu^{III} separation studies

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ABSTRACT

The development of new ligand systems for solvent extraction demands knowledge of the fundamental chemistry behind these processes. Thus, herein, we report the synthesis and structural characterization of a 6-hydroxymethylpyridine functionalized calix[4]arene (L²). Its complexation behavior towards the divalent uranyl cation as well as the trivalent europium cation was spectroscopically studied. In solution the formation of two uranyl complex species with L² was proven by spectrophotometric titration experiments, with stability constants of $\log \beta_{1:1} = 5.82 \pm 0.04$ and $\log \beta_{2:1} = 5.57 \pm 0.05$, and of one europium complex species ($\log \beta_{1:1} = 6.85 \pm 0.03$). In addition, the concept of the desired proper planar binding pocket for the linear uranyl cation has been verified in solution. Moreover, comparative U^{VI} and Eu^{III} extraction studies with L² and a structure related 8-hydroxyquinoline modified calix[4]arene (L¹) were performed in which the effects of various conditions such as pH of the aqueous phase, presence of relevant anions (sulfate, phosphate, carbonate) and competitive extraction with ethylenediaminetetraacetic acid (EDTA) were investigated. It has been shown that both macrocyclic ligands offer a strong chelate effect, which enables them to extract even stable uranyl hydrolysis species. With these ligands, the selective separation of U^{VI} from Eu^{III}-containing solutions is possible under a variety of conditions.

Keywords: calix[4]arene / uranium(VI) / europium(III) / liquid-liquid extraction / spectroscopic properties

1 Introduction

1.1 Motivation

The development of efficient liquid-liquid extraction processes is an ongoing task in fields of recovery of rare earths [1-4], waste treatment [5-7] and recycling procedures [8-10]. In some of these contexts, the separation of uranium is of great concern as rare earth deposits often contain this radioactive element which must be separated efficiently before the rare earths can be processed further [11]. Moreover, due to chemotoxic properties of all uranium isotopes, special process conditions and specific extracting agents are demanded [12-16]. In general, good extracting agents should have high solubility in nonpolar organic solvents, phase disengagement properties, and high selectivity towards a specific metal cation. With regard to environmental aspects it would be preferable to extract at more circumneutral pH values than working under strongly acidic conditions. Multidentate ligands that are characterized by a preorganized binding pocket, showing a strong chelate effect as well as high solubility in organic solvents, have been identified as a promising class of molecules for the complexation of metal ions [17-27]. Among others, calix[4]arene-based ligands have proven their suitability as extracting agents as they can be tailored to exactly bind a specific metal ion [28-36]. A prominent example which proves the potential of these compounds is the calix[4]arene derivative with the well-established extracting moiety CMPO (carbamoymethylphosphine oxide) [37] attached to the upper rim. The resulting ligand clearly exceeds the extraction efficiency for the separation of lanthanides and actinides compared to CMPO alone [38, 39]. So mostly, these chalice-like molecules are used as scaffolds for the construction of large organic ligand systems where the binding pocket for guest molecules is not coercively the cavity itself [40-45]. With regard to their modifiability Böhmer et al. [46] has already described these *tert*-butyl-phenol based macrocycles as molecules with almost unlimited possibilities.

However, studies of particular interest are those that lead to an improved knowledge of fundamental chemistry, eventually increasing selectivity of new ligand systems for extraction [47, 48]. One essential part is the understanding of the coordination chemistry of the target metal cation. For the hexavalent uranium a planar binding pocket would be preferable as it can coordinate to the basal plane of the linear uranyl cation (UO_2^{2+}). Thus, 8-hydroxyquinoline and similar heteroaromatic ring systems seem to be promising [49]. Additionally, reliable thermodynamic data are required to associate a correct speciation to the dynamic equilibria in solution and thus, to develop process understanding.

1.2 General concept

Recently, we reported the good extraction ability of an 8-hydroxyquinoline based calix[4]arene (Figure 1, L^1) towards U^{VI} [50] as well as trivalent lanthanides (Eu^{III} , Tb^{III}) [51]. Based on that well-working system, a structurally related 6-hydroxymethylpyridine based calix[4]arene was synthesized (Figure 1, L^2), which led to substantial cost savings during synthesis. The combination of Schiff bases [52] and heteroaromatic units [53] with the rigid macrocyclic backbone is expected to enhance the chelate effect [54] and to preorganize the binding pocket. Consequently, the affinity of the ligand for metal ions can be controlled. This could pave the way to very selective extracting agents to separate U^{VI} from lanthanide-containing concentrates under a wide range of conditions, e.g., relevant for water

purification purposes, waste treatment or metal recycling. Moreover, the macrocyclic backbone enhances the solubility in nonpolar organic solvents, which is indispensable for an application as extracting agent.

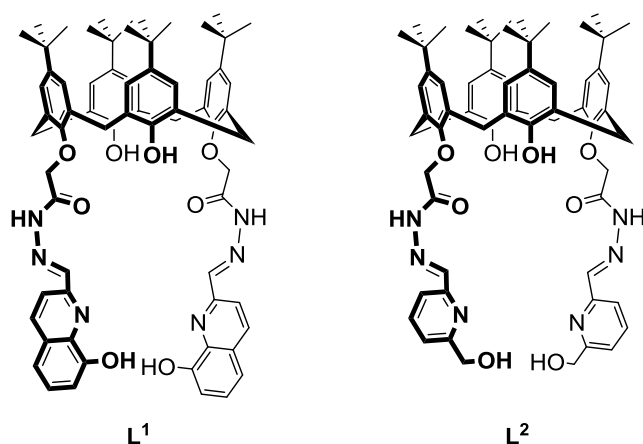


Figure 1. Calix[4]arene-based ligands with 8-hydroxyquinoline (left) and 6-hydroxymethylpyridine (right) substituents at the lower rim.

The combination of hard (O) with soft (N or S) donor atoms in proximity to each other allows the separation of $5f$ and $4f$ elements [55-59] and thus, to control the selectivity of the ligand by varying the extraction parameters. Both ligands, L^1 and L^2 , exhibit two oxygen and two nitrogen donor atoms at each substituent (Figure 2). Hence, by complexation of a metal cation at least three five-membered rings can be formed and it is possible to establish a coordination number of eight (only by ligand donor atoms) as described for the dinuclear Eu^{III} complex [51]. In addition, since the ligands were designed as complexing agents mainly for U^{VI} a flat rigid binding pocket was in mind. Due to the linear arrangement of UO_2^{2+} it is advantageous to have a planar binding pocket (sp^2 nature of the aromatic units as well as $\text{C}=\text{N}$) which can coordinate to the basal plane of the coordination polyhedron of the uranyl cation as shown for our previously reported mononuclear U^{VI} complex with L^1 [50].

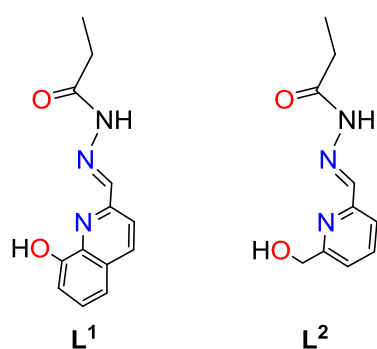


Figure 2. Tetradentate binding pocket of one substituent of the calix[4]arene-based ligands.

In general, stability against radiolysis and at acidic/basic conditions is an important requirement for extracting agents with regard to an application in spent fuel processing. However, the main application of the present calix[4]arene-based ligands is foreseen for environmentally related separation problems. Hence, due to the low activity of natural uranium (isotope mixture with ^{238}U as major component) no radiolytic damages of the ligands are expected or have been observed in our experiments. Moreover, the calix[4]arene-based ligands are stable in the pH range 3 – 9, otherwise

the imine bond would hydrolyze (Scheme S1). Thus, their direct application for the separation of U^{VI} from highly acidic rare earth concentrates of leached ores is not possible, only after an additional process step during which the pH is raised.

The main differences between L¹ and L² are the different solubilities mainly resulting from the heteroaromatic units and the unequal pK_a values of the hydroxyl groups, which clearly influence the extraction behavior of the ligands (see section below). The pK_a values for 8-hydroxyquinoline [60] and methanol in water are approximately 9 and 15, respectively. The ability of aprotic solvents like acetonitrile and chloroform to stabilize a proton is quite low, consequently, the importance of internal hydrogen bonding is significant [61]. The pK_a values for calixarenes in acetonitrile have been determined by selective titration with bases using a spectrophotometric method [62]. In this, a variety of organic bases were used in order to indirectly determine the protonation grade of the calixarenes. However, this requires that the electronic spectrum of the calix[4]arene-based ligand itself has no absorption bands in the wavelength region where the used base absorbs. In our systems this would be very difficult and therefore, we did not determine the explicit acid strengths of L¹ and L².

In this work, we present the synthesis of ligand L² and its coordination properties towards Eu^{III} and U^{VI} by determination of stability constants as well as stoichiometries of formed complexes in acetonitrile solution. Acetonitrile was used as a representative and photochemically stable, aprotic solvent with the advantage of ensuring sufficient solubility of the calix[4]arene-based ligands, the metal salts, and the as-formed complex species. The concentrations of the ligand and of the metal salts have been chosen with respect to the applied analytical methods. Additionally, we compared L¹ and L² concerning their extraction properties towards U^{VI} and Eu^{III} in dependence on pH, studied the influence of relevant anions and the competitive extraction with EDTA. Based on the results, we summarized and identified favorable and basic conditions for the separation of U^{VI} from lanthanide-containing solutions for both functionalized calix[4]arene ligands L¹ and L².

2 Results and discussion

2.1 Synthesis and characterization

5,11,17,23-Tetra-*p*-*tert*-butyl-25,27-bis[(6-hydroxymethyl)pyridine-2-carbaldehyde-hydrazone-carbonylmethoxy]-26,28-dihydroxycalix[4]arene (L²)

The new calix[4]arene-based ligand L² was synthesized via a modular synthesis procedure starting from *p*-*tert*-butylcalix[4]arene in overall four steps, similar to L¹ [51]. L² was characterized by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy, attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and elemental analysis (cf. section 4.4 and supplementary material Figures S1–S4). The flexibility of L² in solution demands heating to 90 °C for the NMR measurements. Thus, the ¹H NMR spectrum (DMSO-*d*₆) does not show a sharp signal pattern of a 2,6 disubstituted pyridine with two doublets and one triplet, but two doublets and one broad singlet in the region between 7.3 and 7.9 ppm. The hydroxyl group as well as imine proton generate a singlet at 11.6 and 7.8 ppm, respectively. The pair of doublets (²J_{HH} = 13.1 Hz, 3.46 ppm, 4.37 ppm) induced by the bridging methylene groups of the calix[4]arene is entirely consistent with the expected C_{2v} symmetrical structure. The ESI mass

spectrum reveals one major peak at m/z 1053.5 which corresponds to the Na^+ adduct of L^2 ($[\text{L}^2+\text{Na}^+]^+$). In the ATR FT-IR spectrum of L^2 the characteristic N–H as well as C=O vibrations of the carbonyl-hydrazone units were observed at 3431 cm^{-1} and 1698 cm^{-1} which is in good correspondence to data published previously [50, 51].

2.2 Spectrophotometric titrations

To determine the stability constants and complex stoichiometries of L^2 with U^{VI} as well as Eu^{III} in solution, a series of UV/Vis spectrophotometric batch titrations [63] was carried out in acetonitrile containing a supporting electrolyte to ensure a constant ionic strength. Figure 3 (left) shows the change of the UV/Vis absorption spectra with increasing concentration of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. The spectrum of L^2 (black line) is characterized by a strong band with a maximum at 200 nm attributed to π – π^* transitions of the calix[4]arene backbone (not influenced by complexation, not shown in Figure 3) and one absorption at 290 nm with a shoulder at 303 nm corresponding to n – π^* / π – π^* transitions of the aromatic units. With increasing metal ion concentration the absorption band at 290 nm decreases and due to charge-transfer transitions a new broad absorption band with maxima at 318 nm and 330 nm as well as a broad shoulder at 363 nm evolves. These findings indicate the involvement of the pyridine ring in complexation and suggest that a 1:1 stoichiometry is the limiting complex under the described conditions (Figure S5). However, factor analysis of the absorption spectra by the program suite HypSpec [64] affirmed the presence of the free ligand and two successive uranyl L^2 complexes and conditional stability constants of the $[(\text{UO}_2)(\text{L}^2)]$ and $[(\text{UO}_2)_2(\text{L}^2)]$ complexes ($\log \beta_{1,1} = 5.82 \pm 0.04$, $\log \beta_{2,1} = 5.57 \pm 0.05$) were calculated. Applying these data, the species distribution shown in Figure 3 (right) was derived.

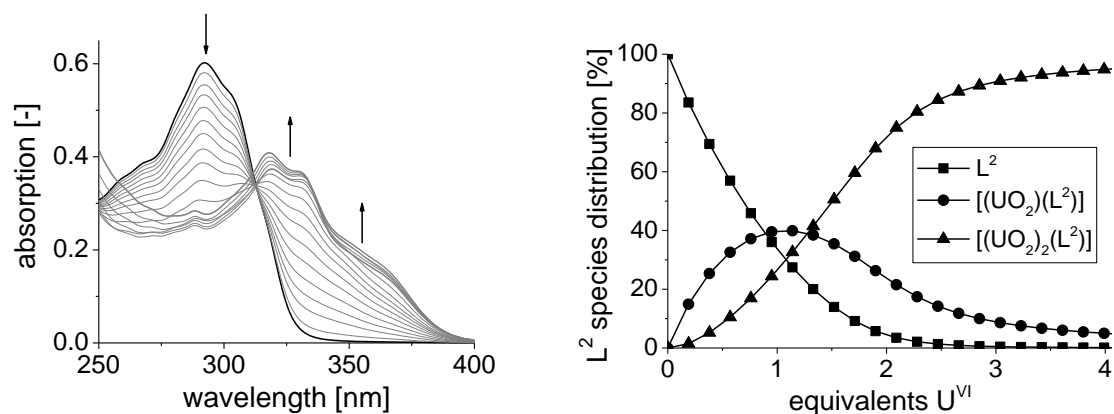


Figure 3. UV/Vis spectra of batch titration of L^2 ($2.5 \cdot 10^{-5}\text{ M}$) with increasing U^{VI} concentration (0 – 4 eq.) in 10^{-2} M NaClO_4 acetonitrile solution (left) and distribution of the L^2 species as a function of U^{VI} equivalents (right).

In accordance with this, ESI mass spectra of acetonitrile/methanol solutions containing $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and L^2 in different molar ratios also revealed 1:1 as well as 2:1 uranium-ligand complex species (Figure S8). In addition, with this method, nitrate anions acting as co-ligands, which cannot be detected by spectrophotometric investigations, were identified.

In the batch titrations of L^2 with Eu^{III} similar changes of the electronic spectra were observed with increasing amounts of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Figure S6). For europium, nonlinear least-square refinements

with HypSpec converged consistently for a speciation model involving 1:1 complex species ($\log \beta_{1:1} = 6.85 \pm 0.03$). Compared to these results, the spectrophotometric titrations of L^1 and Eu^{III} (Figure S7) showed also an inflection point at one equivalent of Eu^{III} indicating a 1:1 stoichiometry. However, this analysis method cannot clearly differentiate between a 1:1 and a possible 2:2 stoichiometry which was found for Eu^{III} and L^1 in the solid state [51]. Thus, in line with the isolated solid complex $[Eu_2(L^2)_2]$ we propose also in solution a polynuclear (2:2) complex species with L^2 , which is additionally consistent with the isolated tetranuclear Eu^{III} complex with L^2 in solid state (cf. supplementary material, section 6). Table 1 summarizes the respective stability constants of L^1 and L^2 with the trivalent europium cation as well as the divalent uranyl cation. In general, both ligands form 1:1 (2:2) complexes with Eu^{III} , which are slightly more stable than the U^{VI} species. Moreover, with L^2 and the uranyl cation at least two complex species are formed under the given conditions. These findings agree well with the recently reported U^{VI} complexes with L^1 concerning the stoichiometry as well as stability constants [50]. For the separation of U^{VI} from lanthanide-containing solutions, a 2:1 complex stoichiometry ($[(UO_2)_2(L^2)]$) would be more efficient since two metal cations are complexed by one ligand (extracting agent). However, the complexes formed in acetonitrile solution have not coercively a relationship to the structure of the extracted species in chloroform. Nevertheless, the coordination mode of the binding pocket of the calix[4]arene-based ligands could be clearly identified and is in agreement with all analytical results obtained in solution as well as in solid state.

Table 1. Stability constants $\log \beta$ for L^1 and L^2 with Eu^{III} and U^{VI} .

	Eu^{III}	U^{VI}
L^1	$\log \beta_{1:1} = 7.53 \pm 0.04$ [65]	$\log \beta_{1:1} = 5.94 \pm 0.02$ [50] $\log \beta_{2:1} = 6.33 \pm 0.01$ [50]
L^2	$\log \beta_{1:1} = 6.85 \pm 0.03$	$\log \beta_{1:1} = 5.82 \pm 0.04$ $\log \beta_{2:1} = 5.57 \pm 0.05$

Errors represent two standard deviations.

2.3 Liquid-liquid extractions

For a better understanding of the extraction behavior of the calix[4]arene-based ligands, comprehensive extraction studies were performed under a variety of conditions. Due to leaching of ores with acids [2, 66-68] the aqueous concentrates contain additional components, namely sulfate or phosphate. Carbonate plays a role for more environmentally relevant scenarios, e.g., for the separation of metal ions from aqueous solution to attenuate environmental contamination. Thus, the influence of these anions (sulfate, phosphate, carbonate) on the U^{VI} and Eu^{III} extractability was examined in addition to the pH dependence. The corresponding aqueous speciations of U^{VI} and Eu^{III} (Figure S15 and S17) were calculated as a function of pH value in absence and presence of sulfate, phosphate or carbonate by using the speciation code EQ3/6 [69]. For this, U^{VI} and Eu^{III} thermodynamic data compiled in the OECD/NEA Thermochemical Database [70] and in the Thermo-Chimie database (version 9b0) from ANDRA [71] with addition of recently determined thermodynamic data of Eu^{III} phosphates [72] were applied.

Dependence on pH

Firstly, to determine optimal pH conditions for the selective separation of U^{VI} from lanthanide-containing solutions, aqueous phases containing 10^{-5} M Eu^{III} and 10^{-5} M U^{VI} were extracted by $4 \cdot 10^{-5}$ M chloroform solutions of ligand L^1 or L^2 (Figure 4). Both ligands extracted U^{VI} in nearly quantitative yield in just one extraction step over a wide pH range. Due to the different pK_a values of the aromatic units, the U^{VI} extraction by L^1 is very high already at pH 4 whereas the U^{VI} extraction by the less acidic L^2 reaches comparable yields at $pH > 5.5$. Commercially applied separation processes mostly work under highly acidic conditions, since e.g. sulfuric acid is applied to leach uranium and lanthanides from rare-earth ores, whereby simultaneously hydrolysis of the uranyl cation is prevented [73, 74]. Interestingly, both ligands extract U^{VI} even at higher pH values (> 5) where the uranyl cation forms a variety of hydrolysis species [75] though they just differ by a loss of one to three protons from the first hydration shell of the uranyl unit. Even when the $[(UO_2)_2CO_3(OH)_3]^-$ species is dominant (pH 6 – 10, atmospheric conditions) extraction percentages of 95 % and above were reached. Thus, either this species is dissociated enforced by complexation of the uranyl ion by the calix[4]arene-based ligands or is actually extracted in its original form. Though, the latter is rather unlikely due to the large ion size. The reason for this is the strong chelate effect of the calix[4]arene-based ligands [76]. Substantiated by distribution experiments at pH 6 and 8 (Figure S9), we propose for uranium a 2:1 complex with L^2 and a 1:1 stoichiometry with L^1 [50] formed during the extraction. This is in good agreement with the complexes observed in acetonitrile as well as the solid structure $[UO_2(L^1)(NO_3)](NO_3)$ [50]. Indeed, this holds for all mononuclear uranyl hydrolysis species, which were actually extracted by each substituent. The slight decrease in extraction efficiency of the L^2 ligand at pH 9 is most probably related to the emergence of the uranyl tricarbonato complex. Nevertheless, to establish the exact structure of the extracted species at each pH value and the underlying mechanisms require further investigations, especially in the case of the aqueous uranyl oligomers and ternary hydrolysis species (Figure S16). In contrast, the trivalent europium cation is extracted by both ligands only at $pH > 7$ suggesting that a higher deprotonation degree of the ligands is required. This was already shown by extraction experiments monitored by radiotracing the trivalent ^{160}Tb and ^{152}Eu [51]. In addition, the solid state structure of the uranyl complex with L^1 [50] supports the assumption of a lower deprotonation degree of the ligand by coordinating a divalent metal cation. For the U^{VI} and Eu^{III} extraction by L^1 and L^2 , the distribution ratios (D) are found to increase with the pH value with a slope of about one (Figure S13). That means, that one hydrogen ion is released into solution by the formation of U^{VI} and Eu^{III} complexes with these ligands.

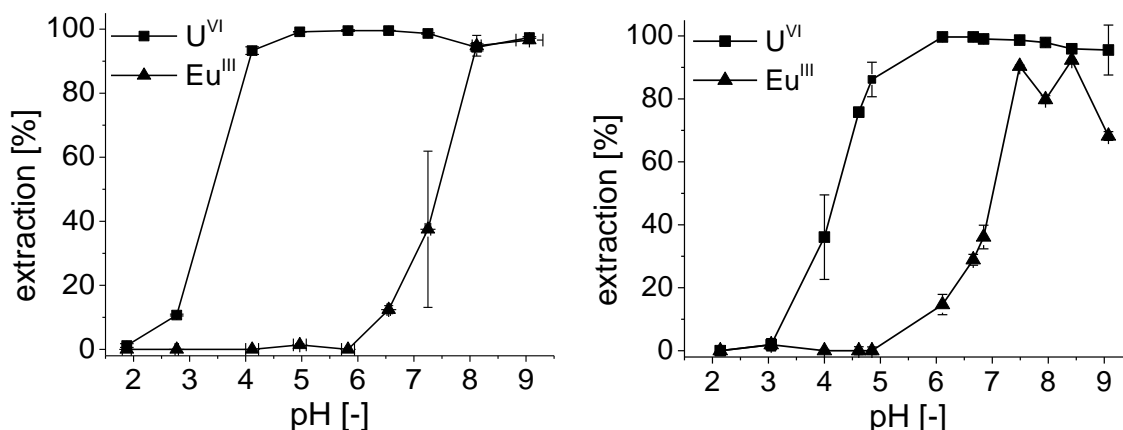


Figure 4. pH dependence of the extraction of U^{VI} and Eu^{III} by L^1 ([50], left) and L^2 (right).

Influence of sulfate

Figure 5 shows the impact of sulfate anions on the extraction of Eu^{III} and U^{VI} as function of pH value of the aqueous phase. For U^{VI} the high extraction percentages observed for both extractants were not influenced as the affinity of the flat binding pocket of the ligands (towards the basal plane of UO_2^{2+}) is higher than that of the spherical (tetrahedral) sulfate anion. This is in good agreement with the small stability constants of the uranyl sulfate complex $[(UO_2)(SO_4)](aq)$ occurring at acidic conditions. In contrast to U^{VI} , Eu^{III} sulfate species are significant until pH 7.5 (Figure S17). Consequently, the percentage extraction of Eu^{III} with L^2 is decreased in the presence of 10^{-3} M sulfate, whereby simultaneously, the separation factors ($SF_{U/Eu}$) of L^2 are enhanced in the higher pH range. For L^1 the extraction curve of Eu^{III} is shifted to lower pH values, which could be explained by a decrease of the effective charge of the $[Eu(SO_4)]^+$ species, which were actually extracted. The stronger chelate effect of L^1 actually renders the europium extractability more environmentally friendly (near at circumneutral pH values). And it ensures still a good separation ability between U^{VI} and Eu^{III} (see Tables 2 and S1).

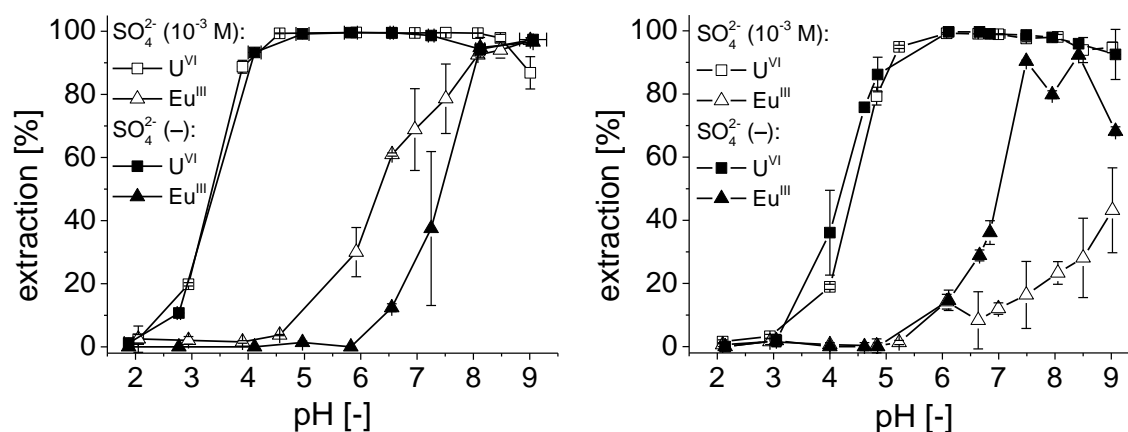


Figure 5. pH dependence of the extraction of U^{VI} and Eu^{III} by L^1 (left) and L^2 (right) in absence and presence of 10^{-3} M sulfate.

Influence of phosphate

Extractions in the presence of 10^{-3} M phosphate (Figure 6) indicate the impact of the formation of metal phosphate species on the extraction efficiencies of both extractants. Based on the U^{VI} speciation

(Figure S15) at pH > 3.5 the predominating aqueous species are $[\text{UO}_2(\text{HPO}_4)](\text{aq})$ and $[\text{UO}_2(\text{PO}_4)]^-$. The U^{VI} extraction percentage with both ligands decreases rapidly with increasing pH value. Most probably this is caused by these complexes being sterically oversized for direct extraction by the ligands. However, with further increasing pH values (> 7.5) the U^{VI} extraction increases again since the uranyl phosphate species transforms to the ternary uranyl hydroxo carbonate species $[(\text{UO}_2)_2\text{CO}_3(\text{OH})_3]^-$, which can be extracted by the calix[4]arene ligands as already shown in Figure 4. The phosphate also affects the aqueous speciation of Eu^{III} . In pH range 5 – 8.5, the $[\text{Eu}(\text{HPO}_4)]^+$ complex governs the speciation (Figure S17). This high affinity of the tetrahedral trivalent phosphate anion to the spherical europium cation decreases the percentage extraction below 20 % for both calix[4]arene-based ligands.

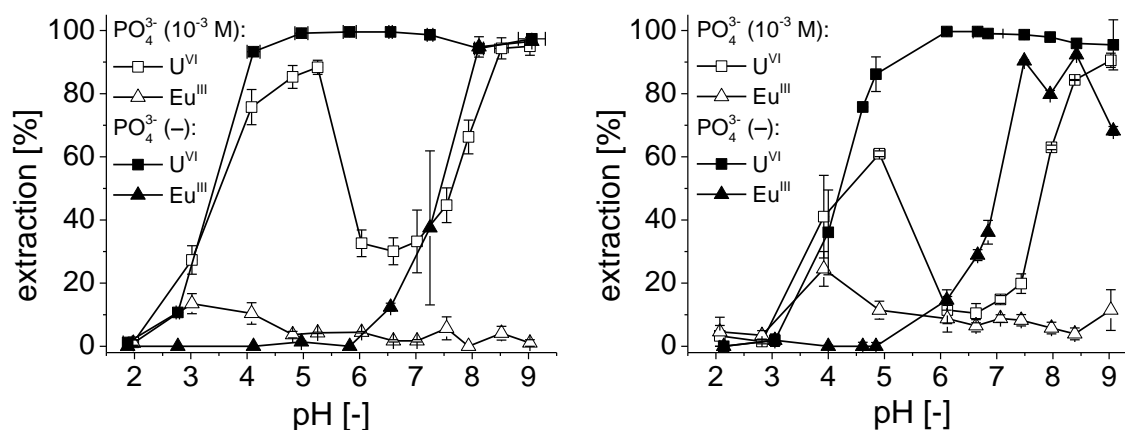


Figure 6. pH dependence of the extraction of U^{VI} and Eu^{III} by L^1 (left) and L^2 (right) in absence and presence of 10^{-3} M phosphate.

Influence of carbonate

As expected in the case of U^{VI} , a high concentration of carbonate considerably influences the speciation and the extraction behavior. At pH 6 – 8, mainly the $[(\text{UO}_2)_2\text{CO}_3(\text{OH})_3]^-$ species predominates (Figure S15), which can be extracted by both L^1 and L^2 as already shown in the previous experiments. Due to the planarity of the carbonate anion it fits optimal to the basal plane of the linear UO_2^{2+} moiety and the resulting uranyl carbonate complex $[(\text{UO}_2)(\text{CO}_3)_3]^{4-}$, predominating between pH 8 and 10, is very stable. Even more important, this species is highly negatively charged and therefore, the affinity of the calix[4]arene-based ligands towards this anionic species is rather weak. Thus, at pH ≥ 8 the extraction efficiencies of both ligands towards U^{VI} are significantly decreased. In case of europium, at pH 7 – 9 the positively charged carbonate complex $[\text{Eu}(\text{CO}_3)]^+$ is the dominant species [77]. Thus, similar to the influence of the sulfate anion the effective charge of the potentially extracted species is lowered and consequently, the extraction curve is shifted to lower pH values for L^1 . Analog results were observed for L^2 . The deprotonation degree of L^2 is apparently more influenced by the amphoteric properties of the bicarbonate system due to its higher $\text{p}K_{\text{a}}$ value compared with L^1 . This results in larger margins of errors for the pH values in the region 6 – 8 (Figure S12) as well as for the extraction percentage in dependence on pH value.

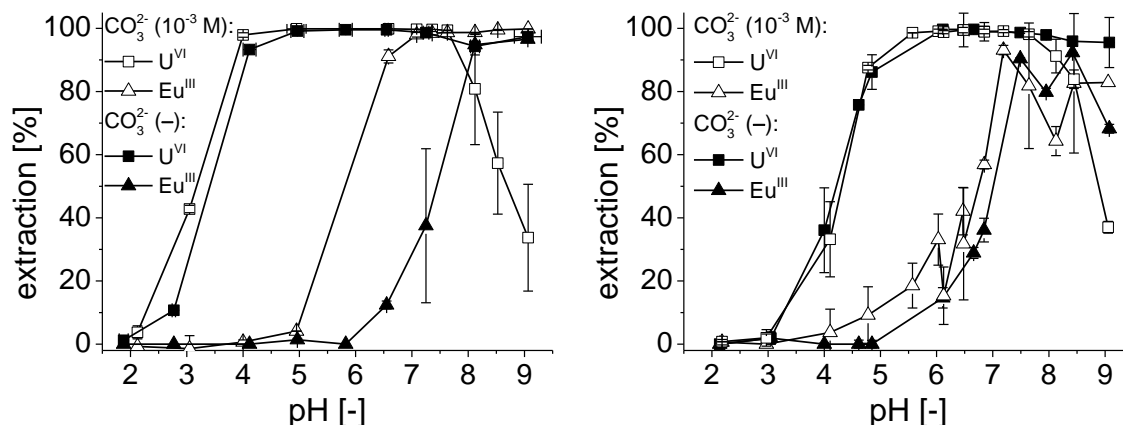


Figure 7. pH dependence of the extraction of U^{VI} and Eu^{III} by L¹ (left) and L² (right) in absence and presence of 10⁻³ M carbonate.

Competitive extraction with EDTA

The simultaneous use of different extracting agents in solvent extractions is a common instrument to enhance separation efficiencies [78, 79]. Here, EDTA was dissolved in the aqueous phase in order to change the separation ability of the resulting extraction system. In general, EDTA forms very stable metal complexes. For instance, the mononuclear europium complex has a stability constant of $\log K_{1:1} = 15.35$ (pH 7.38) [80]. Conditional stability constants of uranyl EDTA complexes are $\log K_{1:1} = 7.95$ and $\log K_{2:1} = 17.85$ (pH 3) [81]. Interestingly, in the presence of equimolar amounts of EDTA (10⁻⁵ M) in the aqueous solution, the trivalent europium cation is retained in the aqueous phase over the whole pH range whereas the U^{VI} extraction is almost unaffected as observed for both ligands (Figure 8). This does not correspond to the conditional stability constants of the metal EDTA complexes. Due to the possible higher negative charge of the EDTA molecule, the affinity of L¹ and L² towards the trivalent europium cation is smaller under the given conditions. Actually, in case of L¹ U^{VI} is still extracted in nearly quantitative yield even when 10⁻⁴ M EDTA was applied (Figure S11). In contrast, excess EDTA (10⁻⁴ M) vastly affects extraction percentage of ligand L² by complexing both metal cations in the aqueous phase (Figure S11). Thus, solely in the presence of equimolar amounts of EDTA, the trivalent europium is entirely complexed by the aminopolycarboxylic acid in the aqueous phase whereas the uranyl cation is selectively extracted by both calix[4]arene-based ligands. However, when EDTA is present at higher concentrations, the chelate effect of L² is not strong enough to effectively extract U^{VI}.

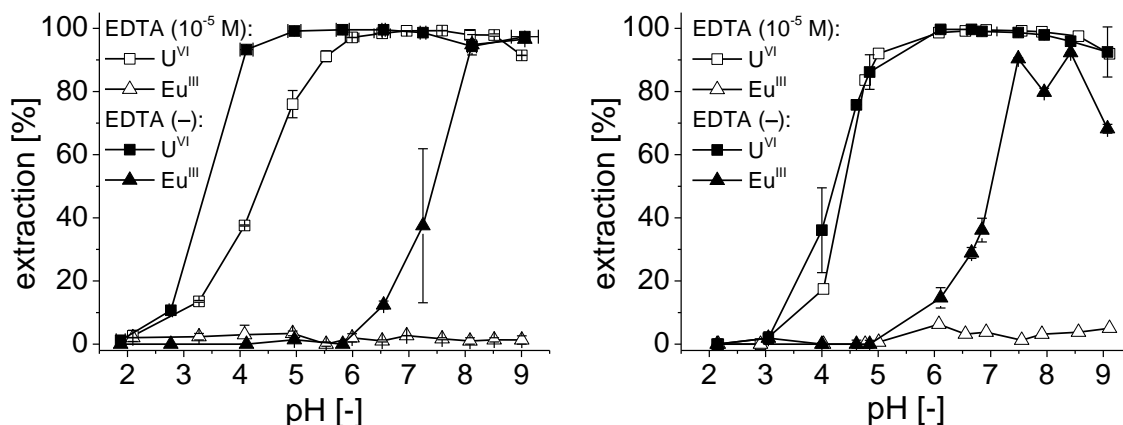


Figure 8. pH dependence of the extraction of U^{VI} and Eu^{III} by L^1 (left) and L^2 (right) in absence and presence of 10^{-5} M EDTA.

In summary, both calix[4]arene-based ligands are able to separate U^{VI} selectively from Eu^{III} -containing solution under a variety of conditions in laboratory scale. Moreover, successful back extractions (stripping) of metal ions were carried out by extracting the loaded organic phase with an aqueous phase at acidic pH. Table 2 summarizes the parameters and results of the liquid-liquid extractions of U^{VI} and Eu^{III} by the macrocyclic ligands. Thus, favorable conditions for the separation of U^{VI} from lanthanide-containing solutions by both calix[4]arene-based ligands, L^1 and L^2 , have been identified (cf. $SF_{U/Eu}$ in Tables 2, S1 and S2). For this, the 8-hydroxyquinoline based calix[4]arene L^1 seems to be slightly more efficient due to the rigid and more planar binding pocket as well as the lower pK_a value compared with the 6-hydroxymethylpyridine based calix[4]arene L^2 .

Table 2. Extraction parameters for L^1 and L^2 with Eu^{III} and U^{VI} .

	Eu^{III}		U^{VI}	
	L^1	L^2	L^1	L^2
pH	pH 8 – 9	pH 7 – 8	pH 4 – 9	pH 6 – 9
efficiency^[a]	> 95 %	90 %	> 95 %	> 95 %
extraction	4 h	4 h	4 h	4 h
back extraction	92 % [51] (1 h, pH 4)	–	74 % (19 h, pH 3)	31 % (19 h, pH 3)
stoichiometry^[a]	–	–	1:1 [50]	2:1
$SF_{U/Eu}$				
pH = 5			> 6000 [51]	> 200
pH = 5 (PO_4^{3-}) ^[b]			170	12
pH = 5 (SO_4^{2-}) ^[b]			917	930
pH = 5 (CO_3^{2-}) ^[b]			2468	105
pH = 5 (EDTA) ^[c]			160	1150

^[a] pH 8, ^[b] $c(\text{anion}) = 10^{-3}$ M, ^[c] $c(\text{EDTA}) = 10^{-5}$ M.

3 Conclusions

To arrive at new insights into the complexation characteristics of calix[4]arene derivatives with respect to the U^{VI} and Eu^{III} metal cations, a comprehensive spectroscopic, modeling and preparative approach was followed, developed and applied. In a first step, a new calix[4]arene-based ligand L^2 with a carbonyl-hydrazone-6-hydroxy-methylpyridine moiety was synthesized and structurally characterized. Due to the applied modular synthesis, further calix[4]arene-based ligands are conceivable and easily synthetically accessible to vary the extracting properties in a well-defined way. The distinct differences in functionality between the two extractants, combined with the variation of selected boundary conditions (pH, content of sulfate, phosphate, carbonate, EDTA as co-ligand) allowed to derive proposals for the extracted species and the mechanisms behind. This was further supported by the coordination properties of L^2 towards U^{VI} and Eu^{III} which were spectroscopically determined in acetonitrile solution. The third important pillar to achieve a better process understanding on a molecular level was the derivation of complex stoichiometries and stability constants of 1:1 and 2:1 complexes with U^{VI} and of a 1:1 species with Eu^{III} . The same holds for the already earlier established compound L^1 . Moreover, the speciation patterns found both in acetonitrile and chloroform by a multi-method study are internally consistent providing a high degree of confidence to the derived findings.

The comprehensive U^{VI} and Eu^{III} extraction studies performed with both ligands circumstantiate the strong chelate effect by extracting even the U^{VI} hydrolysis species at $pH > 4$. Moreover, the extraction efficiency of L^1 towards U^{VI} is nearly unaffected by anionic additives, except for a high phosphate concentration. However, a typical source for U^{VI} and rare earth elements occurring together in nature are phosphate minerals such as monazite or apatite [2, 68]. Thus, the extraction conditions and the affinity of the binding pocket of the ligand would have to be further modulated for such an application. The extraction of Eu^{III} is much stronger influenced by accompanying anionic ligands possibly due to the higher positive charge of the cation. Especially the competitive extraction with equimolar amounts of EDTA enables the selective separation of U^{VI} from Eu^{III} over the whole pH range by retaining the trivalent europium cation in the aqueous phase.

In conclusion, the thermodynamic constants derived in this work as well as the extraction results with regard to the influence of several anions provide a basis for assessing the suitability of these macrocyclic multidentate ligands for metal ion separation under environmentally or industrially relevant conditions. The high extraction efficiency even at circumneutral pH values would allow the reduction of contamination problems more environmentally compatible than working under strongly acidic conditions. Potential applications extending into the technical scale, however, require further studies. For instance, studies on the effect of additional competing ions, such as Ca^{2+} , Mg^{2+} , Ba^{2+} , Al^{3+} or Fe^{3+} , present in natural environments or in leached ore concentrates as well as studies on the effect of higher sulfate or phosphate concentrations on the extraction efficiency of the calix[4]arene-based ligands have to be performed.

4 Experimental section

4.1 Materials and general methods

Caution! Natural uranium consists of radioactive nuclides including long-lived α -emitters (^{235}U , $t_{1/2} = 7.04 \cdot 10^8$ years and ^{238}U , $t_{1/2} = 4.47 \cdot 10^9$ years) and is also chemically toxic. Special precautions as well as appropriate equipment and facilities for radiation protection are required for handling this material.

Generally, all experiments were performed at (25 ± 0.1) °C under aerobic conditions and reagent-grade chemicals were used. Acetonitrile (VWR), chloroform (Sigma Aldrich), ethanol (VWR), ethyl bromoacetate (Alfa Aesar), hydrazine monohydrate (Sigma Aldrich), NaOH (Roth), $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Chemapol), $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar), Eu_2O_3 (Sigma Aldrich), Na_2SO_4 (Merck), $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Merck), Na_2CO_3 (Roth), EDTA (Merck), HClO_4 (Merck), triethylamine (Sigma Aldrich), NaClO_4 anhydrous (Alfa Aesar), $(n\text{Bu})_4\text{NPF}_6$ anhydrous (Alfa Aesar) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (Merck) were used as purchased from commercial sources without further purification. A stock solution of UO_2^{2+} was prepared by diluting $\text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ (Chemapol) in 0.01 M HClO_4 . Elemental analyses were carried out with a VARIO EL elemental analyzer. ATR FT-IR spectra were recorded with a Bruker VECTOR 22 FT-IR spectrophotometer on a ZnSe crystal plate. NMR spectra were recorded with a Varian UnityNova 400 spectrometer at 363 K [^1H : 300.21 MHz; ^{13}C (^1H): 100.63 MHz]. Chemical shifts refer to solvent signals. ESI mass spectra were recorded with a Agilent 6538 UHD Accurate-Mass Q-TOF LC-MS.

4.2 Spectrophotometric titrations

Spectrophotometric measurements with $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were performed on a TIDAS 100 spectrophotometer (J&M Analytik) in the wavelength range between 190 and 700 nm with 0.1 nm interval using 10 mm quartz glass cuvettes. As supporting electrolyte 10^{-2} M NaClO_4 was used to ensure a constant ionic strength. For the batch titrations with $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ the UV/Vis absorption spectra were recorded with a JASCO V-570 UV/Vis/NIR spectrophotometer and $(n\text{Bu})_4\text{NPF}_6$ was used as supporting electrolyte. The complex stability constants were calculated by the nonlinear regression program HypSpec (version 1.1.18, Protonic Software) [64]. In the fitting algorithm, the pH was not considered, as acetonitrile is an aprotic solvent.

4.3 Liquid-liquid extractions

The U^{VI} and Eu^{III} extraction from the aqueous phase by L^1 and L^2 in chloroform was studied in the pH range from 2 to 9. The pH was adjusted by using a WTW pH benchtop meter (Portable meter ProfiLine pH 3110) equipped with a WTW pH microelectrode. A three-point calibration at room temperature with technical calibration buffers (HANNA instruments) was routinely performed before pH adjustment. Chloroform was used as organic phase with the advantage of sufficient solubility of the extractants and the as-formed complex species. Moreover, no extraction by the solvent itself and no significant uptake of the aqueous phase was observed. The general extraction procedure was as follows: The respective aqueous phase contained 10^{-5} M Eu^{III} and 10^{-5} M U^{VI} , in which Eu_2O_3 and 0.1 M

UO₂²⁺ in 0.01 M HClO₄ were used as starting material. For the studies of the impact of anions, Na₂SO₄, NaH₂PO₄·H₂O, Na₂CO₃ (10⁻³ M) or EDTA (10⁻⁴ or 10⁻⁵ M) were additionally to the metals dissolved in the aqueous phase.

The pH value was adjusted by diluted NaOH and HClO₄ solutions. Sodium tetraborate decahydrate was used as a pH stabilizer at a concentration of 13 mM in experiments with pH > 6. A 4 mL aliquot of the aqueous phase was added to 4 mL organic phase containing 4·10⁻⁵ M ligand. For liquid-liquid extraction, PFA (perfluoralkoxy polymer) vials (AHF analysentechnik AG) were used. The two-phase mixture was shaken for 12 h at 400 rpm by a Thermoshaker MKR 23 (Hettich Benelux B.V., Geldermalsen). After reaching equilibrium, the aqueous and organic phases were separated by centrifugation. Then, the final pH of the aqueous phase was determined. The initial and equilibrium concentrations of Eu^{III} and U^{VI} were determined by inductively coupled plasma mass spectrometry, ICP-MS (Elan 9000, Perkin Elmer). The extraction (%) values were calculated using Eq. (1) where c₀ is the initial concentration and c₁ the equilibrium concentration of the metal ion in the aqueous phase.

$$E (\%) = 100 \times \left(\frac{c_0 - c_1}{c_0} \right) \quad (1)$$

Distribution ratios (D) and separation factors (SF_{U/Eu}) were calculated using Eq. (2) and (3), respectively.

$$D = \left(\frac{c_0 - c_1}{c_1} \right) \quad (2)$$

$$SF_{U/Eu} = \left(\frac{D_U}{D_{Eu}} \right) \quad (3)$$

4.4 Synthetic procedures and characterization

5,11,17,23-Tetra-*p-tert*-butyl-25,27-bis[(8-hydroxyquinolinecarbaldehyde-hydrazone-carbonyl-methoxy)]-26,28-dihydroxycalix[4]arene (L¹) was synthesized as previously described [51]. 6-hydroxymethylpyridine-2-carbaldehyde was prepared according to the procedure given by Artali et al. [82].

5,11,17,23-Tetra-*p-tert*-butyl-25,27-bis[(6-hydroxymethylpyridine-2-carbaldehyde-hydrazone-carbonylmethoxy)]-26,28-dihydroxycalix[4]arene (L²). Ligand L² was prepared in four steps equal to L¹. Starting from *p-tert*-butylcalix[4]arene [83] the lower rim was substituted in 1,3 distal position with ethyl bromoacetate [84], followed by treatment with hydrazine monohydrate to give the corresponding hydrazide [85]. The hydrazide (0.5 g, 631 μmol) was dissolved in ethanol (30 mL). A solution of 6-hydroxymethylpyridine-2-carbaldehyde (173 mg, 1.26 mmol) in ethanol (5 mL) was added dropwise. The yellow solution was heated under reflux for 16 h. The obtained pale yellow precipitate was collected by filtration, washed with ethanol and dried in air to give the target compound. Yield: 508 mg (80 %). ¹H NMR (300 MHz, DMSO-*d*₆): δ [ppm] = 11.57 (s, 2H, OH), 7.79 (d, *J* = 7.7 Hz, 4H, py, HC=N), 7.62 (s, 2H, py), 7.53 – 7.29 (m, 2H, py), 7.13 (s, 4H, C₆H₂), 7.00 (s, 4H, C₆H₂), 5.10 (s, 4H, CH₂OH), 4.57 (s, 4H, CH₂), 4.38 (d, *J* = 13.0 Hz, 4H, Ar-CH₂-Ar), 3.44 (d, *J* = 13.1 Hz, 4H, Ar-CH₂-Ar), 1.25 (s, 18H, ^tBu), 1.05 (s, 18H, ^tBu). ¹³C NMR (101 MHz, DMSO-*d*₆): δ [ppm] = 162.25 (C_{carb}), 152.43 (HC=N), 150.22 (C₅H₃), 141.94 (C₅H₃), 137.41 (C₆H₂), 133.08 (C₆H₂), 128.18 (C₆H₂), 126.09 (C₆H₂), 125.61 (C₆H₂), 121.31 (C₅H₃), 119.48 (C₆H₂), 118.80 (C₅H₃), 64.72 (CH₂-R), 34.17 (C_{tert}), 33.96 (C_{tert}), 31.93 (Ar-CH₂-Ar), 31.79 (CH₃), 31.22 (CH₃). MS(ESI(+), MeCN): *m/z* calcd. C₆₂H₇₄N₆O₈Na [L²+Na⁺]⁺

1053.6; found: 1053.5. IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3431 $\nu(\text{N-H})$, 2956 $\nu(\text{C-H})$, 1698 $\nu(\text{C=O})$, 1585 $\nu(\text{C=N})$, 1201 $\nu(\text{C-O})$. UV/Vis (MeCN): λ_{max} [nm] (ϵ [$\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$]) = 202 (9759), 290 (3800). Elemental analysis $\text{C}_{62}\text{H}_{74}\text{N}_6\text{O}_8 + \text{EtOH}$ (1030.6 + 46.0): calcd. C 71.35, H 7.48, N 7.80; found C 71.45, H 7.72, N 7.82.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at

Declarations of interest

The authors declare no conflict of interest.

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