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A Hydrolytically Stable Complexant for Minor An Separation from Ln in Process Relevant Diluents†

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The evaluation of bis-1,2,4-triazine complexants containing eight-carbon, alkoxy-functionalized phenyl substituents for selective minor actinide extraction in simulated high level waste is reported. The complexant retained chemoselective extraction efficiency of actinides over lanthanides while breaking through the hydrolytic stability and nonpolar diluent solubility barrier that limits many BTP complexants. Thus, we report a BTP complexant that is readily soluble in both kerosene and isooctanol without forming precipitates, emulsions, or third phase formations after contact with nitric acid and extracts $^{241}Am^{3+}$ from $^{154}Eu^{3+}$ Separations and spectroscopic data are reported herein.

A persistent research challenge lies within the long-term radiotoxicity of spent nuclear fuel (SNF), a byproduct of nuclear energy. After plutonium and uranium are extracted through the PUREX process, [1] the major contributors to the residual heat load are the minor actinides (An) specifically, americium, curium, and neptunium which remain present in the acidic raffinate. The partitioning and transmutation (P&T) strategy[2] is proposed as a method to lessen the heat load by partitioning the minor An from the lanthanides (Ln) for transmutation in advanced fast-neutron reactors.[3]

To implement the P&T strategy, a process to extract the minor An from the neutron-poisoning fission Ln in nitric acid conditions pertinent to the PUREX raffinate is required.[4] Numerous soft nitrogen- and sulfur-donor complexants have been developed for liquid-liquid separations[5] since Kolarik’s seminal report in 1999[6] which first disclosed that soft-N-donor ligands could facilitate chemoselective separations of the minor An from contact with up to 1 M $HNO_{3(aq)}$. Specifically, the tridentate 2,6-bis-(1,2,4-triazin-3-yl)pyridines (BTPs) have shown the most promise in leveraging the increased covalent character of the metal-complexant bond of the 5*f* orbitals, as opposed to the more contracted 4*f* orbitals,[7] while also meeting process-relevant criteria for performance such as suitable equilibration time, solubility in nonpolar diluents, as well as hydrolytic and radiolytic stability. However, the purposeful pursuit of a complexant that simultaneously meets all criteria for the selective actinide extraction (SANEX) process[8] continues.[9]

For instance, the first generation (alkyl-substituted) BTPs were susceptible to hydro- and radiolytic degradation.[10] Furthermore, N-donor complexants such as CyMe$_4$-BTP,[11] CA-BTP,[12] and MOB-BTP[13] were insoluble in purely nonpolar diluents such as kerosene, while the latter two also form precipitation when contacted with HNO_3 concentrations greater than 3 M. Despite solubility and acid-contact limitations of MOB-BTP, the complexant demonstrated improved separations performance for ^{241}Am over ^{154}Eu at lower complexant concentration compared to benchmark complexants.[13b] Experimentation building upon this success led to a convergent synthetic strategy to afford tetraalkoxy-functionalized BTPs reported elsewhere.[14] Recent disclosures have described $^{241}Am/^{154}Eu$ separations data of the 3,3’dibutyloxy-BTP in isooctanol[15] and FS-13.[16] While the butyloxy- derivative was a significant step forward in BTP solubility, the octyloxy- complexant was hypothesized to have greater solubility in nonpolar diluents. Potentially greater extraction efficiency due to the higher electron-donating ability of the alkoxy side chains was also postulated. This communication, presents $^{241}Am^{3+}/^{154}Eu^{3+}$ separations data and spectroscopic results with 3,3’-dioctyloxy-BTP complexant.

The synthesis of 3,3’-dioctyloxyphenyl-bis-1,2,4-triazinyl-2,6-pyridine [3,3’dioctyloxy-BTP, (**1**)] is described in Scheme 1 below. Treatment of pyridine-2,6-biscarbonitrile with hydrazine hydrate afforded the bis-hydrazonimide which was condensed with 3,3’-dioctyloxybenzil, obtained from 3,3’-

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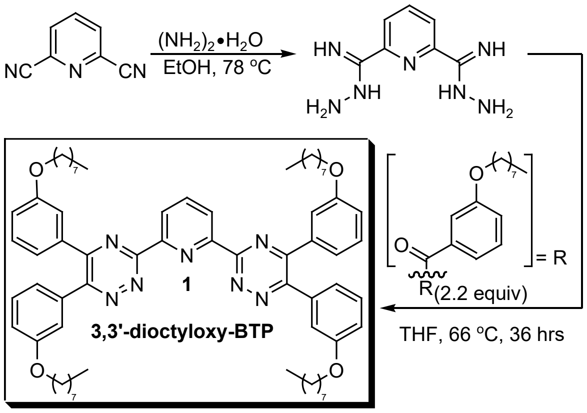

Scheme 1 Synthesis of 3,3'dioctyloxy-BTP

dimethoxy benzil, in THF. The synthetic strategy is convergent, scalable, and of low per gram cost.

Safety Considerations. ***Caution!*** *The ^{241}Am and ^{154}Eu solutions used in this work were highly radioactive. All manipulation of these samples was performed in a dedicated radiological facility using well-established radiological safety protocols.*

Small-scale dissolution experiments demonstrated the measured solubility of **1** was 664 mM in isooctanol and 248 mM in kerosene. To the best of our current knowledge at the time of publication, **1** is the first BTP complexant to be soluble in kerosene at any concentration in the absence of a surfactant or phase modifier. While **1** had high solubility in kerosene, preliminary results demonstrated slower equilibration time at higher acid concentrations and therefore, a 50*v*/50*v* diluent mixture of kerosene and isooctanol was evaluated.

In order to assess the ability of **1** as a potential complexant for the SANEX process, a series of separations assays were performed as a function of time, initial $HNO_{3(aq)}$ concentration, and initial concentration of **1**. Distribution ratios of the respective metal (D_M) (equation 1) were determined via γ-spectroscopy and used to calculate separation factors (*SF*) (equation 2). Full experimental details are included in the electronic supporting information.

$$D_M = \frac{[M]org}{[M]aq} \qquad \textit{Equation (1)}$$

$$SF_{Am(III)/Eu(III)} = \frac{D_{Am(III)}}{D_{Eu(III)}} \qquad \textit{Equation (2)}$$

An equilibration study of **1** at 25 mM in a Kerosene/isooctanol (50*v*/50*v*) diluent mixture contacted with 1 M $HNO_{3(aq)}$ spiked with either $^{241}Am^{3+}$ or $^{154}Eu^{3+}$ was executed resulting in the data disseminated in Fig. 1a. Equilibrium was achieved at 60 minutes with an average D_{Am} of 2.02. The change in distribution values after 60 minutes are within experimental error. At 30 minutes, 52% extraction from the aqueous to the organic phase was observed. An additional 8% extraction was realized from 30 to 45 minutes and 6% further from 45 to the equilibrium point of 60 minutes. The *D* values for $^{154}Eu^{3+}$ remained within experimental uncertainty throughout the 120 minutes, D_{Eu} = 0.0125 – 0.0141. Based on these results, a contact time of 60 minutes was selected for all subsequent experiments.

With confirmation of the optimized contact time of 60 minutes observed, effort focused on performing a $[HNO_{3(aq)}]$ study to ascertain the utility of **1** dissolved in kerosene/isooctanol at higher acid concentrations (Fig. 1b). The D_{Am} continued to increase with increasing concentration of $HNO_{3(aq)}$ up to 3 M with a slight decrease from 3 to 4 M followed by an increase from 4 to 5 M. The origins of the D_{Am} decrease at 4M $HNO_{3(aq)}$ remained elusive. A maximum D_{Am} of 13.43 was achieved at 3 M acid (Figure 1b), corresponding to 92% extraction. The distribution ratio of $^{154}Eu^{3+}$ follows the same trend as $^{241}Am^{3+}$, with a maximum D_{Eu} value of 0.0885 at 3 M corresponding to an 8% extraction. The highest separation factor was 155 at 2 M $HNO_{3(aq)}$. No third-phase formation or poor phase disengagement wereobserved, even at the highest acid concentration. This is an improvement over previous BTP complexants that limit either complexant or $HNO_{3(aq)}$ concentration due to formation of precipitates during phase contact.[17]

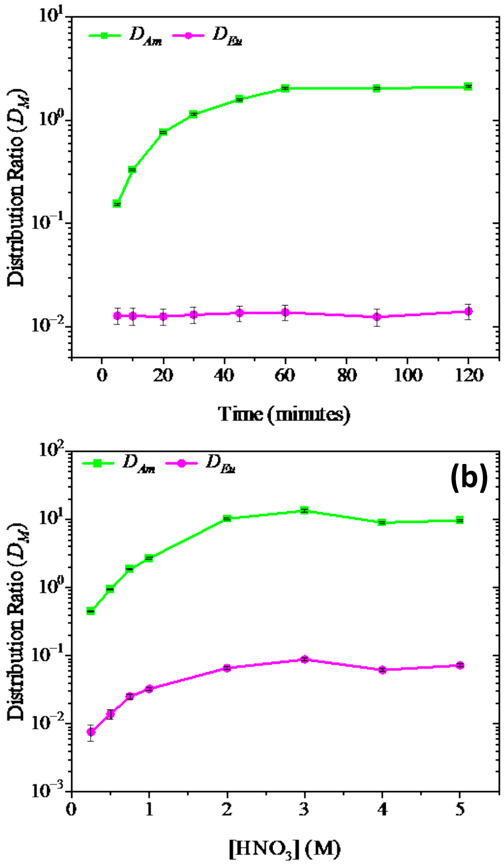

Fig. 1 Solvent extraction of $^{241}Am^{3+}$ and $^{154}Eu^{3+}$ by **1** (25 mM) in kerosene/isooctanol(50*v*/50*v*) mixture as a function of (a) contact time with 1 M $HNO_{3(aq)}$ and (b) initial $HNO_{3(aq)}$ concentration at 60 minutes contact time

The distribution ratios of both $^{241}Am^{3+}$ and $^{154}Eu^{3+}$ increased with increasing complexant concentration under a constant initial acid concentration of 5 M (Fig. 2a). The highest *D* values were observed at 75 mM with D_{Am} = 111 (95% extraction) and D_{Eu} = 0.946 (48% extraction) resulting in a *SF* of 117. The SF's were relatively constant between 12.5 and 75 mM complexant

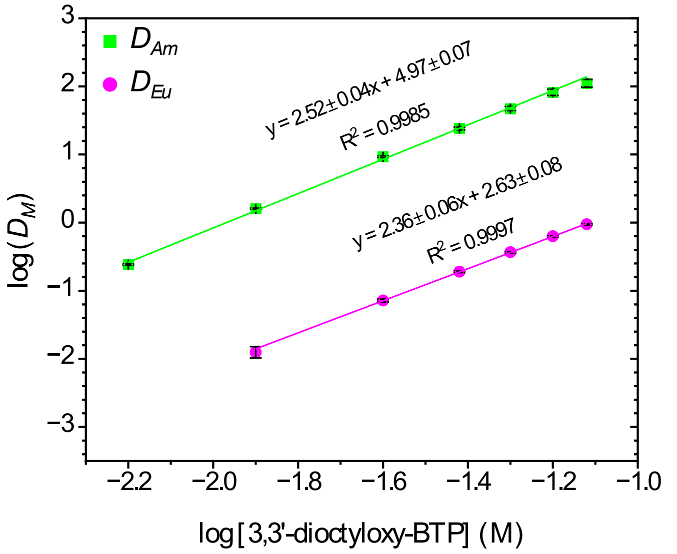

Fig. 2 Solvent extraction of $^{241}Am^{3+}$ and $^{154}Eu^{3+}$ by **1** in kerosene/isooctanol (50*v*/50*v*).

concentrations ranging from 117 to 129. While the D_{Am} values are higher in comparison to theisooctanol only data, the D_{Eu} values are also higher, resulting in lower separation factors. A slope of 2.48±.04 and 2.41 ± 0.02 were observed for $^{241}Am^{3+}$ and $^{154}Eu^{3+}$, respectively, as shown in Fig. 2b. The slope analysis suggested a mixture of 2:1 and 3:1 complexant-to-metal ion complexes is being formed during extraction at 5 M $HNO_{3(aq)}$ (equation 3).

$$M^{3+}_{(aq)} + 3NO^{-}_{3(aq)} + n\mathbf{1}_{(org)} \leftrightarrow M(NO_3)_3(\mathbf{1})_{n(org)} \quad \textit{Equation}\ (3)$$

Additionally, spectroscopic titrations were performed with $Nd(NO_3)_3$ and $Eu(NO_3)_3$ to gain more information into the metal speciation. Changes in the absorption spectra of **1** in the range of 220 to 450 nm at different metal/ligand (M/L) ratios are shown in Fig. 3. The λ_{max} of **1** appeared at 301 nm and initially decreased in intensity before gradually shifting and intensified upon addition of $Nd(NO_3)_3$. Isosbestic points present are indicative of the presence of two consecutive equilibria.

Mathematical analysis of the UV-vis titration data was performed using Hypspec software.[18] Prior to running the model, the unrestricted factor analysis in HypSpec revealed four mathematically significant light absorbing species, however the fourth was close to a singular value. Therefore, the best-fit model, based on equation 4, was initially engaged with consideration of the formation of two metal/ligand complexes, ML and ML_2, and compared with the fit of a three complex model by adding ML_3.

$$M^{3+} + xL \rightleftarrows M(L)^{3+}_{x} \qquad \textit{Equation}\ (4)$$

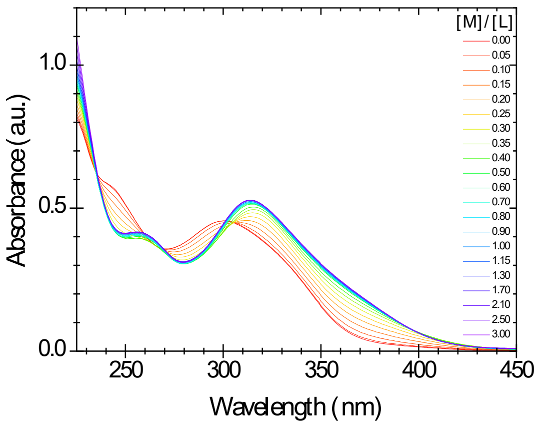

Fig. 3 UV-Vis Spectrum of **1** upon addition of $Nd(NO_3)_3$. Solvent system 99% acetonitrile/ 1% water (*v*/*v*). [**1**] = 1.5×10^{-5} M, [$Nd(NO_3)_3$] = $7.5\times10^{-7} – 4.5\times10^{-5}$ M.

Table 1 Stability Constants (Log β) for the Formation of Nd(III) and Eu(III) Complexes with **1**(L) at 298K ± 1K

Metal	Reaction	log β
Nd^{3+}	$L + Nd^{3+} \rightleftharpoons NdL^{3+}$	6.38 ± 0.45
	$2 L + Nd^{3+} \rightleftharpoons NdL_2{}^{3+}$	14.87 ± 0.37
	$3 L + Nd^{3+} \rightleftharpoons NdL_3{}^{3+}$	22.43 ± 0.57
Eu^{3+}	$L + Eu^{3+} \rightleftharpoons EuL^{3+}$	7.01 ± 0.0.04
	$2 L + Eu^{3+} \rightleftharpoons EuL_2{}^{3+}$	16.27 ± 0.04
	$3 L + Eu^{3+} \rightleftharpoons EuL_3{}^{3+}$	21.65 ± 0.0.04

The best fit was obtained with consideration of three complexes and the formation (stability) constants are reported in Table 1. The larger stability constants can be explained by previous observations from the literature,[19] such as titrations performed in acetonitrile typically have larger stability constants than when the stronger solvating methanol is the diluent due to the higher desolvation energy requirement. Additionally, smaller percentages of added water to the solvent along with increased alkyl chain length has been shown to lead to higher stability constants.[20]

In Summary, the high solubility of **1** in nonpolar, process-relevant, diluents was a first for a BTP complexant. The increased hydrocarbon chain of the alkoxy-functionalized aryl groups led to improved solubility in kerosene and isooctanol. The complexant was able to successfully extract $^{241}Am^{3+}$ with good separation over $^{154}Eu^{3+}$ over a range of $HNO_{3(aq)}$ concentrations, 0.25–5.0 M, without the formation of precipitates, emulsions, or a third phase. Slope analysis suggested a mixture of 1:3 and 1:2 metal:ligand complexes during extraction at 5 M $HNO_{3(aq)}$. UV-vis titration data supported the slope analysis results. Further exploration of this complexant in other diluents, along with $^{241}Am^{3+}$ decomplexation, full Ln series extraction, and Ln/$^{241}Am^{3+}$ competition experiments are underway and will be reported in due course.

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Conflicts of interest

There are no conflicts to declare.

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