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Synthesis of functionalised BTPhen derivatives - effects on solubility and americium extraction

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Separation of the minor actinides (Am/Cm) from spent nuclear fuel post-PUREX process is expected to play a key part in new reprocessing methodologies. To date, a number of selective americium extractants from the BTPhen ligand family have been identified. In this investigation, we synthesise 24 novel BTPhens with additional functionality to determine the effects on solubilities and americium extraction capabilities. The data obtained will allow for tuning of steric/electronic properties of BTPhens in order to assist future extractant design.

Introduction

In nuclear fuel reprocessing, separation of the minor actinides (Am/Cm) from the lanthanides potentially offers alternative waste management options. The removal of these elements, which account for ~1% by mass but ~90% of the long lived radiotoxicity of high level waste from fuel reprocessing, could reduce both the duration of the radiological hazard and the volumes of high level waste.[1-3] One proposed approach partitioning of the minor actinides (and/or Np) after the PUREX process and transmutation by irradiation into short lived and/or stable isotopes.[4-5] To achieve this, selective extraction methods where single/groups of actinides are separated from neutron absorbing poisons (lanthanides) are required. In addition, such methods could be utilised to obtain pure minor actinide fractions in other applications, such as environmental analysis.[6-7] Such separation procedures require highly selective extractants that fulfil a wide range of criteria (e.g. resistance to radiolysis/acidity, comprising of CHON only (to reduce the generation of secondary waste streams), fast forward/reverse kinetics). Targeted ligand design has allowed access to a handful of ligand families that meet some/all of these criteria for Am/Ln separations. Currently, the main CHON-based extractant families are bis-triazinylpyridines (BTPs), bis-triazinylbipyridines (BTBPs) and bis-triazinylphen-anthrolines (BTPhens). Geist et al. provide an extensive review of the design/development of these ligand families.[8] In the main, the initial ligand designs aimed at resolving practical separation issues (e.g. poor acidic stability, slow extraction kinetics, low solubility).[9-10] Functionalisation of a large set of ligands with specific non CHON moieties has not yet been fully explored, so there is potential for further functionalisation to alter the electronics of the system and affect physical properties, and hence improve Am (III)/Ln (III) extraction. As sets of groups away from CHON have not been extensively investigated previously for BTPhens, it is of interest to future extractant design to see the effect that electron withdrawing/donating groups have on solubility and extraction. We therefore aimed to synthesise sets of BTPhen ligands with additional functionality (with BTBPs, BTPhens are currently the most promising for SANEX (Selective ActiNide EXtraction) processes)[11] to explore the effects on solubility, acidic stability and Am/Ln extraction capability. This would be analysed using separation factors (SF) which are defined as the ratio of distribution co-efficient between the organic and aqueous phases for Am/Eu as representative An(III)/Ln(III). BTPhens are soft-N donor ligands which exploit the enhanced covalency of the minor actinide *f*-orbitals via metal-nitrogen interactions,[12] we were therefore interested in the effect of changing the electronics of the system on Am extraction. From a practical standpoint, we were interested in simplifying the synthesis of these functionalised BTPhens by employing commercially available starting materials and a single precursor that could be made on a large scale. This allows for the generation of numerous easily accessible extractants with additional functionality without extensive synthetic chemistry. The phenanthroline moiety of the ligand is easily accessible in four synthetic steps, but functionalisation of this backbone requires harsh reaction conditions and/or protecting group chemistry as it is electron rich which can make obtaining a library of compounds for screening difficult.[9] However, some previously synthesised BTPhens such as the benchmark $CyMe_4$BTPhen require a 1,2-diketone which is not commercially available. Our strategy was therefore, a divergent functionalised BTPhen synthesis in which addition of a variety of differently functionalised commercially available diketones to a non-functionalised phenanthroline backbone would afford functionalised ligands. We designed three families of BTPhens

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using three families of commercially available diketones (isatin, benzil and aliphatic groups), which were firstly tested for their solubility in common nuclear reprocessing solvents and acidic stability. The ligands were then tested in Am/Eu separations to determine $SF_{Am/Eu}$, with any very promising ligands subsequently tested on more complex matrices as described in our previous work reported in the supplementary information with kinetic data.[13]

Experimental

All reagents were purchased from Sigma Aldrich and were of analytical grade. All of the diketones used in the ligand cross coupling reactions are commercially available. Anhydrous acetonitrile was used as purchased (Sigma Aldrich) and handled under Schlenk line conditions (under N_2). All melting points were determined using a Stuart Scientific SMP10 apparatus and are uncorrected. NMR spectra were recorded for solutions in $CDCl_3$, d_4-MeOH or d_6-DMSO on a Bruker Avance III instrument (400 MHz) and were referenced to the residual solvent signal. Compound assignments were determined using COSY and HMQC experiments. Coupling constants (*J* values) are quoted to the nearest 0.1 Hz. IR spectra were recorded for solid samples using a Bruker Alpha-P ATR spectrometer. Preparative column chromatography was performed using Sigma-Aldrich silica gel (technical grade, 60 Å, 220–240 mesh, 35–75 μm) and the flash technique.[14] Compositions of solvent mixtures are quoted as ratios of volume. Organic solutions were dried with anhydrous magnesium sulfate. Low resolution mass spectra were measured on a Micromass Platform II instrument with electrospray ionisation (University of Manchester). Nano-electrospray accurate mass measurements were performed by EPSRC National Mass Spectrometry Facility (NMSF) in Swansea. All radionuclides used were provided from calibrated stocks in the School of Chemistry, University of Manchester. Micropipettes of 100 μL, 0.1–1 mL and 2–10 μL were calibrated on a 4 d.p. balance with >18 MΩ Millipore deionised water in the temperature range 18–22 °C and were found to be within their stated range. All acid solutions were made from Aristar® grade concentrated solutions and were diluted with >18 MΩ Millipore deionised water. All solutions were considered to have expired within one month of preparation. Gamma counting was performed using a Pb/Cd/Cu shielded Canberra 2020 coaxial HPGe gamma spectrometer with an Ortec 919E multi-channel analyser. Gamma spectroscopy was performed against a standard of known activity counted in the same geometry and analysed using the diagnostic photon energies of ^{241}Am (59.5 keV) and ^{152}Eu (121.8 keV).

Ligand Synthesis

Amidrazone **1** was synthesised as previously reported from commercially available neocuproine.[15] Amidrazone **1** was then reacted on 200 mg scale in THF (10 mL) in the presence of triethylamine (0.1 mL) with 2.1 equivalents of each of 26 diketones at reflux. The reactions were monitored by TLC (dichloromethane/MeOH) and took up to 3 d. The solvent was removed in vacuo and the solids were purified by column chromatography (dichloromethane/MeOH) to obtain compounds **2-27** (analytical data in Supplementary Information). $CyMe_4BTPhen$ and $Me_4BTPhen$ were synthesised and purified as previously reported.[16-17]

Solubility screening of BTPhen Ligands

Each of the ligands 2-27 was added to 1 mL of the three high immiscibility industrially relevant solvents, 1-octanol, dodecane and cyclohexanone, until the compound was at the solubility limit (at 18-20°C). The solubility (mmol) was then calculated by dividing by the molecular weight of the compound (x 1000) to give the solubility of the compounds in mmol.

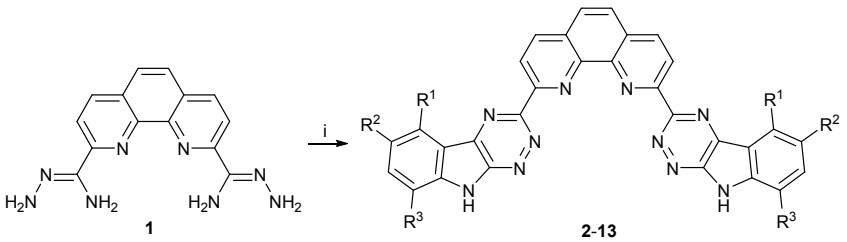
Am/Eu Separations with BTPhen Ligands

A 1 mM solution of the ligands described below in 1-octanol was contacted with 0.1-5 M HNO_3/HCl (1 mL) solution containing ^{241}Am (III)/^{152}Eu (III) (10/50/100 Bq each) in for 1.5 h using a vortex mixer in initial studies. For the separation factor values reported, the ligands (1 mM, 1 mL) in 1-octanol was contacted with 3 M HNO_3/HCl (1 mL) solution containing ^{241}Am (III)/^{152}Eu (III) (100 Bq each) for 1.5 h using a vortex mixer. The metal was then back-stripped for 1 h with 0.1 M HCl on a vortex mixer. The resulting acidic phases were separated and counted by gamma spectroscopy against a standard of known activity in the same geometry.

Results and Discussion

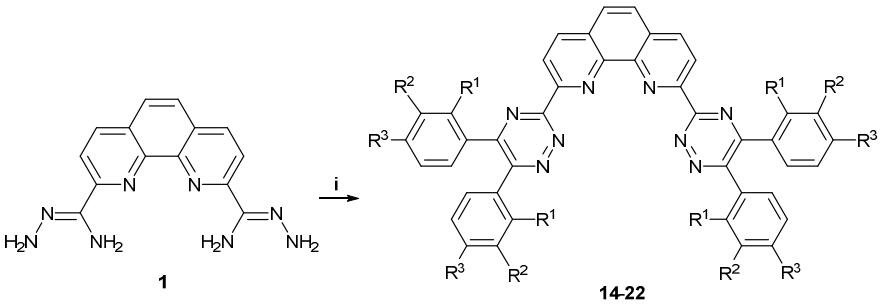
Ligand Synthesis

Twenty six BTPhen ligands were synthesised by reaction of amidrazone **1**[17] with commercially available diketones from three families: isatin, benzil and aliphatic (Schemes 1-3)



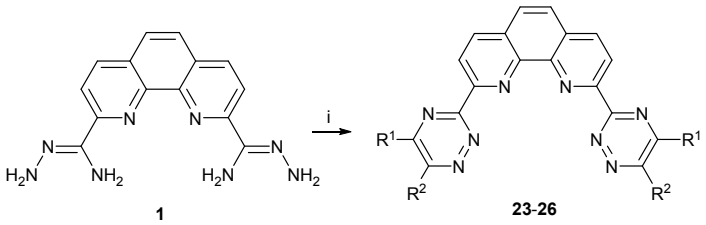
2 $R^1 = R^2 = R^3 = H$
5 $R^1 = R^2 = H$, $R^3 = Br$
8 $R^1 = R^3 = H$, $R^2 = Br$
11 $R^1 = R^3 = H$, $R^2 = CH_3$
3 $R^1 = R^2 = H$, $R^3 = F$
6 $R^1 = R^3 = H$, $R^2 = F$
9 $R^1 = R^3 = H$, $R^2 = I$
12 $R^1 = R^3 = H$, $R^2 = OCF_3$
4 $R^1 = R^2 = H$, $R^3 = Cl$
7 $R^1 = R^3 = H$, $R^2 = Cl$
10 $R^1 = R^3 = H$, $R^2 = NO_2$
13 $R^1 = R^3 = Cl$, $R^2 = H$

Scheme 1. Synthesis of istain-BTPhens. *Reagents*: (i) diketone, Et_3N, THF, Δ, <72 h.



14 $R^1 = R^2 = R^3 = H$
17 $R^1 = R^2 = H$, $R^3 = OMe$
20 $R^1 = R^2 = H$, $R^3 = CH_3$
15 $R^1 = R^2 = H$, $R^3 = Cl$
18 $R^1 = R^2 = H$, $R^3 = F$
21 $R^1 = R^2 = H$, $R^3 = NMe_2$
16 $R^1 = R^3 = H$, $R^2 = OMe$
19 $R^1 = R^2 = H$, $R^3 = Br$
22 $R^1 = Cl$, $R^2 = R^3 = H$

Scheme 2. Synthesis of benzil-BTPhens. Reagents: (i) diketone, Et3N, THF, Δ, <72 h.



23 $R^1 = R^2$ = indan
24 R^1 = Me, R^2 = Et
25 R^1 = Me, $R^2 = {}^nPr$
26 $R^1 = R^2$ = Et

Scheme 3: Synthesis of aliphatic (and indan) BTPhens. *Reagents*: (i) diketone, Et_3N, THF, Δ, <72 h.

Solubility Testing in Common Reprocessing Solvents

Increasing the solubility of BTPhens is of interest for their application to reprocessing methodology as the ligands typically have solubility in 1-octanol of <20 mM. Increased solubility would allow for smaller volumes of organic phase to be used and reduce secondary waste. To determine the effects of additional functionalisation on solubility, ligands **2-26** were dissolved in three high immiscibility industrially relevant solvents representative of three solvent groups (1-octanol (alcohol), dodecane (aliphatic), cyclohexanone (cyclic ketones)) to determine their solubility (Table 1-3). We reasoned that specific functional groups such as methoxy or chloride would improve solubility of the ligands in polar solvents where bromide or iodide may potentially show the reverse trend. These alterations in the design could help improve promising extractants by tuning the solubility in process relevant solvents such as dodecane and 1-octanol. Also, cyclohexanone was reasoned to allow for stacking effects with these ligands/functional groups which we hoped would allow for trends based on functionalisation to be significant.

Table 1. Solubilities of isatin- (and indan) BTPhens in industrially relevant solvents.

Solubility / mM	Indan-BTPhen **23**	Isatin-BTPhen **2**	7-F-isatin-BTPhen **3**	7-Cl-isatin-BTPhen **4**	7-Br-isatin-BTPhen **5**
1-Octanol	8.0	8.1	2.2	8.0	6.0
Dodecane	5.0	6.2	3.8	3.0	3.0
Cyclohexan-one	22.0	98.0	50.7	100.0	42.0
	5-CF_3-isatin-BTPhen **12**	5-Me-isatin-BTPhen **11**	5-F-isatin-BTPhen **6**	5-Cl-isatin-BTPhen **7**	5-Br-isatin-BTPhen **8**
1-Octanol	3.8	8.3	11.0	9.0	7.0
Dodecane	1.9	2.3	2.9	2.1	2.1
Cyclohexan-one	194.0	47.7	56.2	57.0	41.0
	4,7-Cl_2-isatin-BTPhen **13**	5-I-isatin-BTPhen **9**	5-NO_2-isatin-BTPhen **10**		
1-Octanol	17.0	1.9	2.3		
Dodecane	3.0	1.3	2.0		
Cyclohexan-one	105.0	40.9	47.0		

All isatin-BTPhen ligands had low solubility (<6.2 mM) in dodecane, and additional functionality had a detrimental effect on the solubility in straight chain solvents. This implies that functionalization in similar extractants ultimately may not improve in a process relevant non-polar solvent. Solubility was generally higher in 1-octanol for all ligands which mirrors previous solubility studies and implies that perhaps functionality in certain positions could be used to improve solubility. In cyclohexanone, much higher solubilities (22–194 mM) were observed, and addition of the CF_3 group markedly improved solubility, which could be useful for future ligand design if increased solubility in a cyclic solvent is required. Overall, the cyclohexanone data shows the effects of electron withdrawing groups on this general class of isatin-BTPhen ligands and shows that functionalisation to be counter-productive in most cases.

The benzil-BTPhens are generally less soluble than the isatin-BTPhens in octanol/dodecane. The amine functionalised benzil-BTPhen **21** showed higher solubility than the other ligands in 1-octanol which could be useful for ligand design (the resulting ligand would also still adhere to the CHON principle and amine/amides would potentially increase electron donation into the overall system). Solubility was highest in cyclohexanone for all ligands, with 2,2'-dichlorobenzil-BTPhen **22** showing the highest solubility (128 mM). This potentially shows that multiple chloride insertion can improve solubility in design of BTPhen ligands in specific solvents and positions.

Table 2: Solubilities of benzil-BTPhens in industrially relevant solvents.

Solubility / mM	Benzil-BTPhen **14**	2,2'-Cl_2-benzil-BTPhen **22**	3,3'-$(MeO)_2$-benzil-BTPhen **16**	4,4'-F_2-benzil-BTPhen **18**	4,4'-Br_2-benzil-BTPhen **19**
1-Octanol	2.5	4.0	2.2	2.3	1.1
Dodecane	1.6	2.0	1.3	2.1	1.0
Cyclo-hexanone	50.0	128.1	9.2	42.0	11.5
Solubility / mM	4,4'-$(MeO)_2$-benzil-BTPhen **17**	4,4'-Me_2-benzil-BTPhen **20**	4,4'-Me_2N-benzil-BTPhen **21**	4,4'-Cl_2-benzil-BTPhen **15**	
1-Octanol	3.0	2.6	15.0	2.7	
Dodecane	2.0	2.3	2.6	1.5	
Cyclo-hexanone	78.7	40.1	63.8	36.1	

Table 3: Solubilities of aliphatic BTPhens in industrially relevant solvents.

Solubility / mM	MeEt-BTPhen **24**	MePr-BTPhen **25**	Et_2-BTPhen **26**
1-Octanol	14.4	2.2	6.1
Dodecane	2.3	2.2	2.2
Cyclohexanone	14.9	99.8	157.6

For the aliphatic BTPhen ligands, the solubility trends are similar to those previously reported by Asfar *et al.* for BTPhen/BTBP where increasing the aliphatic chain length increased the solubility in alcohol and cyclic ketone based solvents at the expense of acidic and radiolytic stability.[9]

Acid Stability of Functionalised BTPhens

All the BTPhens synthesised were stable when contacted with 3 M HNO_3 (typically the molarity of high active raffinate) for 24 h. However, acid concentrations higher than this led to decomposition of the ligands in all cases; this is markedly different to the stability of $CyMe_4$BTPhen/BTBP which are stable in 4 M HCl/HNO_3 overnight. In terms of ligand design, additional functionality appears to reduce acidic stability.

Am/Eu Separations by Functionalised BTPhens

Initial testing of Am (III)/Eu (III) separation for one ligand from each family was carried out prior to a full screen. The ligands (1 mM in 1-octanol) were contacted with a solution of $^{241}Am/^{152}Eu$ (10 Bq each) in 0.1-4 M HCl/HNO_3 for 1.5 h. The results were very similar to those of our previous work applying $CyMe_4$BTPhen to complex matrices so, for separations with the functionalised BTPhens we used the same extraction procedure but with the aqueous phase as 3 M HNO_3 (concentrations set at 1 mM in 1-octanol). Using this procedure, Am/Eu separation was carried out for each BTPhen ligand in triplicate (with $CyMe_4$BTPhen as a control). This allowed for distribution ratios which are defined as the distribution of the ion between organic and aqueous phase D_{Am}/D_{Eu} and $SF_{Am/Eu}$ which is the ratio of the two metal ion distribution ratios to be calculated (Tables 4-6).

Table 4: $SF_{Am/Eu}$ for isatin-BTPhens, determined by gamma spectroscopy (1 mM in 1-octanol, 3 M HNO_3).

Ligand	$SF_{Am/Eu}$
$CyMe_4$BTPhen	350
Indan-BTPhen **22**	2
Isatin-BTPhen **2**	4
5-Me-isatin-BTPhen **11**	37
5-CF_3-isatin-BTPhen **12**	10
5-F-isatin-BTPhen **6**	3
5-Cl-isatin-BTPhen **7**	3
5-Br-isatin-BTPhen **8**	1
5-I-isatin-BTPhen **9**	1
5-NO_2-isatin-BTPhen **10**	3
7-F-isatin-BTPhen **3**	8
7-Cl-isatin-BTPhen **4**	8
7-Br-isatin-BTPhen **5**	3
4,7-Cl_2-isatin-BTPhen **13**	3

All isatin-BTPhens achieved separation of Am from solution (>40% Am extracted within 1.5 h), however, they all co-extracted Eu (III) (5-27%), resulting in low separation factors. The overall observed trend is that secondary functionalisation of these extractants appears to reduce Am (III) extraction and favours Eu (III) co-extraction lowering the separation factor. However, it is interesting to note that 5-Me-isatin-BTPhen is the only ligand with an electron donating group in the family, and this shows the highest $SF_{Am/Eu}$. From this data, isatin-BTPhens do not appear to be viable ligands for Am (III) extraction due to low separation factor In addition to this it can perhaps be shown that the addition of electron withdrawing halogens to these systems reduces the metal-nitrogen interaction with Am (III) and reduces the observed selectivity.

Table 5: $SF_{Am/Eu}$ for aliphatic BTPhens, determined by gamma spectroscopy. (1 mM in 1-octanol, 3 M HNO_3).

Ligand	$SF_{Am/Eu}$
$CyMe_4$BTPhen	350
Me_4BTPhen	122
Et_4BTPhen **25**	105
Me_2Et_2BTPhen **23**	40
Me_2Pr_2BTPhen **24**	60

The aliphatic BTPhen ligands were seen to have decreasing Am extraction capability with increasing chain length when symmetrical. It is interesting to note that the unsymmetrical ligands Me_2Et_2BTPhen and Me_2Pr_2BTPhen had lower separation factors even though there is no great increase in chain length. The unsymmetrical ligand design shows that symmetrical extractants would be preferred in the design of BTPhen extractants both in a selectivity and stability context. This is an interesting observation as, until now the majority of reported ligands have been generally symmetrical in design.

Table 6: $SF_{Am/Eu}$ for benzil-BTPhens, determined by gamma spectroscopy. (1 mM in 1-octanol, 3 M HNO_3).

Ligand	$SF_{Am/Eu}$
$CyMe_4$BTPhen	350
Benzil-BTPhen **14**	16
4,4-F_2-benzil-BTPhen **18**	30
4,4-Cl_2-benzil-BTPhen **15**	78
4,4-Br_2-benzil-BTPhen **19**	146
3,3-$(MeO)_2$-benzil-BTPhen **16**	71
4,4-$(MeO)_2$-Benzil-BTPhen **17**	284
2,2-Cl_2-benzil-BTPhen **22**	17
4,4-Me_2-benzil-BTPhen **20**	99

Overall, the benzil-BTPhens show higher $SF_{Am/Eu}$ than either of the other two ligand families. In addition, functionalisation appears to increase separation factors. For the 4,4-disubstituted ligands, an increase in $SF_{Am/Eu}$ can be seen with increasing electron donating ability of the substituent (OMe>Me>Br>Cl>F). The donation of electron density into the triazine moieties may assist the covalent interactions required to complex Am (III) over Eu (III). Substituents at the 2- or 3-positions did not result in high separation factors, probably due to steric hindrance (2,2-Cl_2-benzil-BTPhen) or due to the *ortho/para* directing effect of the substituents (3,3-$(MeO)_2$-benzil-BTPhen). These results highlight the importance of electronics in the design of selective BTPhen extractants, in particular the methoxy benzil group is of interest due to its high separation factor and adherence to the CHON principle. From these results, we think a $CyMe_4$BTPhen extractant functionalised with electron-donating groups (e.g. ester, methyl, methoxy) would potentially improve both the solubility and observed extraction data and that from our work many groups can be ignored as potential functionalisation candidates (e.g. NO_2/I). Overall it is clear that functionalisation can both improve and hinder the solubility/stability in these systems and that the position and type of functionalisation is an important consideration when designing these extractants.

Modelling of $[AmL]^{3+}$ complexes of benzil-BTPhen ligands

The bond lengths in the $[AmL]^{3+}$ complexes (minima complexes presented in the Supplementary information) were calculated using density functional theory (DFT; Gaussian 09)[19] in the same manner as that reported by Xiao *et al*[18] for the benzil-BTPhen ligand family. The functional used was B3LYP. With light atoms, the standard Pople-style polarized valence triple 6-311G(d,p) basis set was used for geometry optimization. Small-core RECPs which replace 60 core electrons for Am and 28 electrons for Eu were also used.

All the chemical species were firstly optimized at the B3LYP/6-311G(d,p)/RECP level and natural bond order (NBO) analysis was undertaken. The resulting bond lengths (Am-N_2) lie in the 2.36-2.38 Å range which agrees well with previously reported calculations for BTPhens.[19] The shorter bond lengths when compared with (Eu-N_2) [18] No trends were observable in these data. The NBO analysis allowed a population analysis of the triazine nitrogen atoms in BTPhen ligands (used to complex Am (III)) for the additional functional groups (Table 7). The results suggest that, relative to benzil-BTPhen, all functional groups add additional electron density into the triazine system which we expected, which could potentially lead to stronger interaction when complexing with Am (III). Overall, none of our computational analysis accounted for the observed reduction in selectivity seen when specific functionalisations were undertaken.

Table 7: Calculated additional electron population on triazine nitrogens calculated by DFT (Gaussian 09, B3LYP; N/A = not applicable)

Ligand	Additional population of triazine nitrogen / % of one electron
benzil-BTPhen	N/A
2,2-Cl_2-benzil-BTPhen	5.178
3,3-$(MeO)_2$ benzil-BTPhen	1.200
4,4-$(MeO)_2$ benzil-BTPhen	3.174
4,4-F_2-benzil-BTPhen	3.314
4,4-Cl_2-benzil-BTPhen	2.124
4,4-Br_2-benzil-BTPhen	2.316
4,4-Me_2-benzil-BTPhen	2.124

Conclusions

From the three families of functionalised BTPhens synthesised, selectivity factors for Am (III)/Eu (III) separation were obtained to determine the effects of ligand design on Am extraction. The isatin-BTPhens showed poor separation factors due to Eu co-extraction so this group of ligands would not be viable. The aliphatic BTPhen ligands showed decreasing separation factors

with increasing chain length, and the unsymmetrical members of this family showed lower separation factors than symmetrical ligands. The benzil-BTPhens were the most promising group of ligands, showing the highest $SF_{Am/Eu}$ values, which improved when electron donating groups were present, an interesting point for future ligand design. The benzil-BTPhens were also tested for Am extraction from a more complex matrix containing lanthanides and fission products. For most benzil-BTPhens, co-extraction of the lanthanides (10-15%) was observed, apart from the 4,4-fluoro (attributed to slow extraction kinetics). Overall, the ligands synthesised do not show a great improvement on the current benchmark ligands such as $CyMe_4$BTPhen. However, this study highlights how additional functionality on BTPhens can be used to modify properties such as solubility and Am (III) extraction and potentially underpins the design of future Am/Cm selective extractants for reprocessing methodologies. Future work will attempt to synthesise additional diketones with electron donating groups to yield more data on the effects on selectivity to fill in the majority of potential groups. Also work on functionalising the $CyMe_4$BTPhen system should be attempted in light of these observations with electron donating CHON groups to attempt to resolve problems with slow phase transfer kinetics and to attempt to improve the system which could potentially be used in the proposed SANEX process.

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