

Synthesis and screening of modified 6,6'-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-2,2'-bipyridine ligands for actinide and lanthanide separation in nuclear waste treatment

Article

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Synthesis and Screening of Modified CyMe4-BTBP Ligands for Actinides/Lanthanides Separation in Nuclear Waste Treatment

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Synthesis and Screening of Modified CyMe₄-BTBP Ligands for Actinides/Lanthanides Separation in Nuclear Waste Treatment

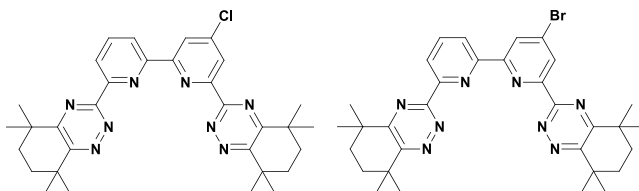
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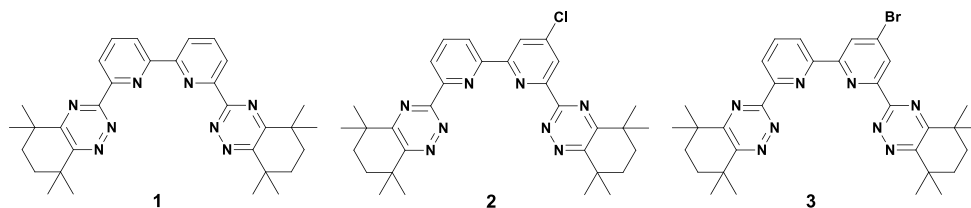
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Effects of chloro/bromo substitution at the 4-position of the pyridine ring of 6,6'-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-2,2'-bipyridine (CyMe₄-BTBP) have been studied with regard to the extraction of Am(III) from Eu(III) and Cm(III) from 0.1 – 3 M HNO₃. Similarly to CyMe₄-BTBP, a highly efficient ($D_{Am} > 10$ at 3 M HNO₃) and selective ($SF_{Am/Eu} > 100$ at 3 M HNO₃) extraction was observed for Cl-CyMe₄-BTBP and Br-CyMe₄-BTBP in 1-octanol but in the absence of a phase-transfer agent.

Separation of minor actinides (Am and Cm) from lanthanides (Ln) potentially offers alternative waste management options in nuclear fuel reprocessing. The removal of these elements, which accounts for ~0.1 wt% but ~90% of the long lived radiotoxicity, could reduce both the duration of the radiological hazard and the volumes of high level waste.¹ One proposed approach currently being pursued is “Partitioning and Transmutation” whereby the radioactive minor actinides (particularly Am and Cm) are first separated from the non-radioactive lanthanides using a selective solvent extraction process (SANEX process), and then converted into less radiotoxic elements by neutron induced fission.²

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5 However to achieve this, it is first necessary to separate single/groups of minor actinides from the
6 neutron absorbing poisons (lanthanides). Although the chemical properties of An(III) and Ln(III) are
7 similar, it has been shown that ligands containing soft *N*-donor atoms are capable of separating trivalent
8 actinide ions [An(III)] from trivalent lanthanide ions [Ln(III)].^{2c, 3} The selectivity of these reagents for
9 An(III) over Ln(III) is believed to arise from a slightly more covalent interaction between the *N*-donor
10 atoms and the *5f* orbitals of An(III).⁴ Within the soft *N*-donor ligands, *bis*-(1,2,4-triazine) ligands show
11 the highest selectivities and optimum extraction performance to date. Among these, the quadridentate
12 6,6'-*bis*-(1,2,4-triazin-3-yl)-2,2'-bipyridine (BTBP) family members have been the focus of intensive
13 research.⁵ One particular BTBP, known as CyMe₄-BTBP **1** (Figure 1), is chemically stable in HNO₃ and
14 shows good stability versus radiation.⁶ It is also able to extract Am(III) and Cm(III) from HNO₃ with
15 high selectivity over Ln(III).^{5c, 6-7} Due to its advantageous properties, several processes have been
16 developed using CyMe₄-BTBP **1**.⁸



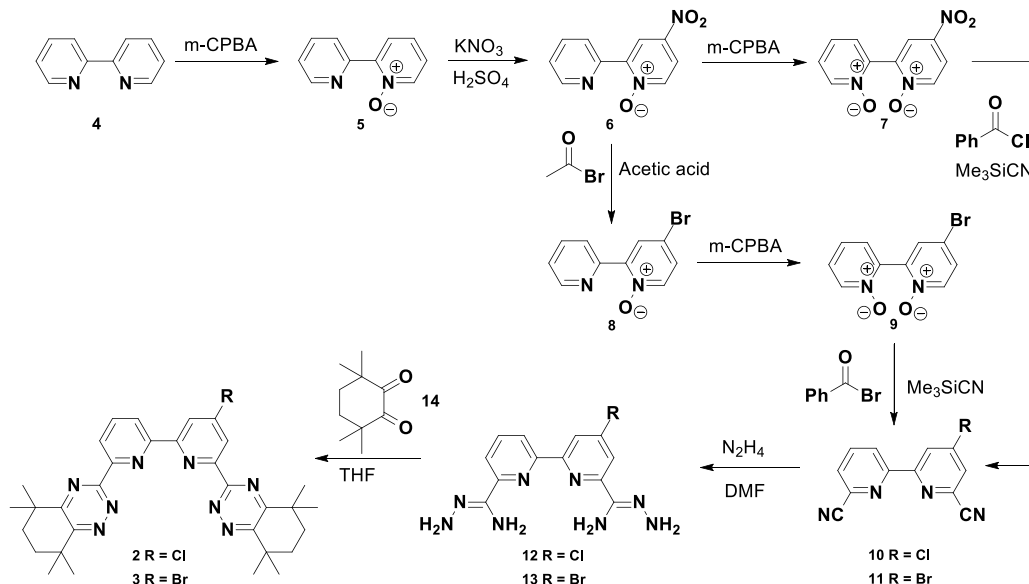
36 **Figure 1.** Structural formulae of CyMe₄-BTBP **1**, Cl-CyMe₄-BTBP **2** and Br-CyMe₄-BTBP **3**.

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39 Unfortunately the solubility of CyMe₄-BTBP **1** is rather low in preferred diluents such as 1-octanol
40 and cyclohexanone and a phase transfer agent DMDOHEMA (*N,N*-dimethyl-*N,N'*-
41 dioctyl[(hexyloxy)ethyl]malonamide) is needed to improve the otherwise slow extraction kinetics.⁹ In
42 this study, an attempt was made to improve the solubility of CyMe₄-BTBP **1** without modifying the
43 metal binding site or introducing benzylic hydrogens into the structure, and our results are reported
44 herein.
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50 The modified CyMe₄-BTBP ligands **2** and **3** were synthesized using the methodology previously
51 used to synthesize **1**.¹⁰ Mono-oxidation of the 2,2'-bipyridine **4** with *m*-chloroperbenzoic acid (*m*-
52 CPBA) in CH₂Cl₂ afforded 2,2'-bipyridine-1-oxide **5**.¹¹ This was first nitrated to 4-nitro-2,2'-bipyridine-
53 1-oxide **6** and was then further oxidized with *m*-CPBA to the corresponding *bis-N*-oxide **7**.¹¹ In the case
54 of Br-CyMe₄-BTBP **3**, the nitro group was substituted with bromine using acetyl bromide in acetic acid
55 followed by oxidation with *m*-CPBA to afford 4-bromo-2,2'-bipyridine-1,1'-dioxide **9**.¹¹ The *bis-N*-
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Oxide **9** was converted into the di-carbonitrile **11** by a Reissert-Henze reaction with trimethylsilyl cyanide and benzoyl bromide in CH_2Cl_2 .¹² When the same procedure was applied to 4-nitro-2,2'-bipyridine-1,1'-dioxide **7** using trimethylsilyl cyanide and benzoyl chloride in CH_2Cl_2 , the di-carbonitrile **10** was obtained in addition to the nucleophilic substitution of the nitro group with the chloride ion. The di-carbonitriles **10** and **11** were then treated with hydrazine hydrate in dimethylformamide (DMF) to generate the new di-carbohydrazonamides **12** and **13** in 91% and 74% yield, respectively. Finally, the condensation of **12** and **13** with tetramethylcyclohexane-1,2-dione **14** furnished the modified $\text{CyMe}_4\text{-BTBP}$ ligands **2** and **3** (Scheme 1).

Scheme 1 Synthesis of Cl-CyMe₄-BTBP **2** and Br-CyMe₄-BTBP **3**.¹⁰⁻¹²



Preliminary solvent extraction experiments were then carried out to determine the ability of Cl-CyMe₄-BTBP **2** and Br-CyMe₄-BTBP **3** to extract Am(III), Cm(III) and Eu(III). Solutions of **2** and **3** in 1-octanol (0.03 M) were contacted (200 min) with nitric acid solutions (0.1 – 3 M) spiked with ²⁴¹Am, ²⁴⁴Cm and ¹⁵²Eu radiotracers. The distribution ratios, *D*, were calculated as the ratio between the radioactivity (α - and γ - emissions) of each isotope in the organic and in the aqueous phase. The separation factor, $SF_{\text{Am/Eu}} = D_{\text{Am}} / D_{\text{Eu}}$ or $SF_{\text{Am/Cm}} = D_{\text{Am}} / D_{\text{Cm}}$. The solubility of CyMe₄-BTBP **1** is rather low in 1-octanol (~ 10 mmol/L) and is only slightly better in cyclohexanone (~ 20 mmol/L). However, both **2** and **3** showed higher solubility than **1** in both 1-octanol (> 170 mmol/L) and

cyclohexanone (> 230 mmol/L) in line with previous observations that nonsymmetrical ligands possess far higher solubility than symmetrical ligands due to its higher entropy of dissolution.^{9b, 10c}

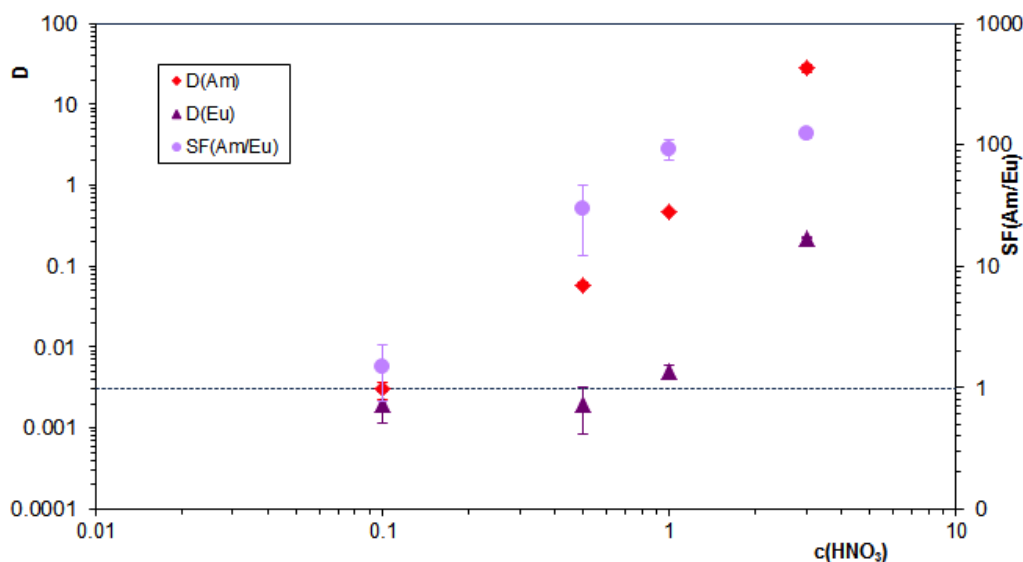


Figure 2. Extraction of Am(III) and Eu(III) by Cl-CyMe₄-BTBP **2** in 1-octanol as a function of nitric acid concentration.

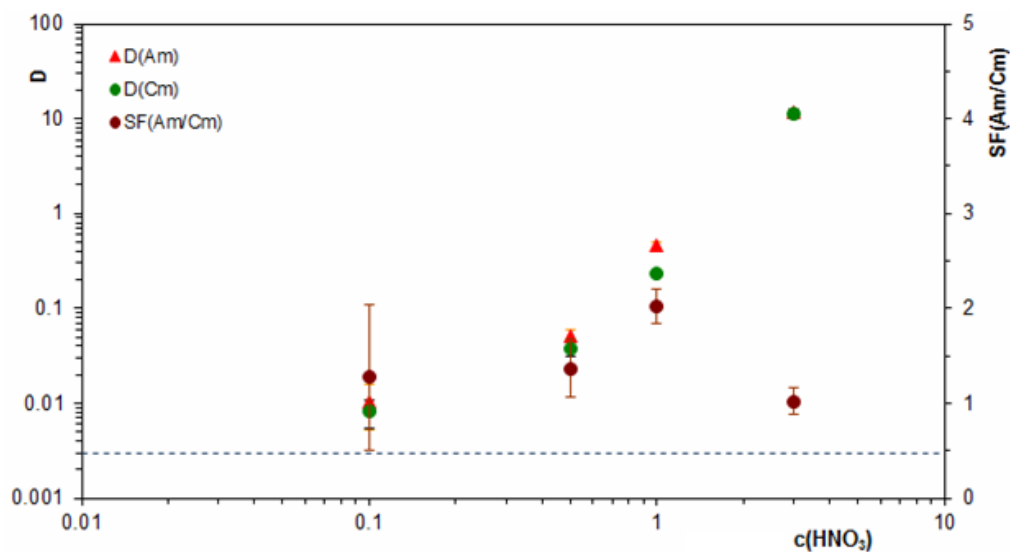


Figure 3. Extraction of Am(III) and Cm(III) by Cl-CyMe₄-BTBP **2** in 1-octanol as a function of nitric acid concentration.

The distribution ratios for Am(III) and Eu(III) (D_{Am} and D_{Eu}) and the separation factors for Am(III)

over Eu(III) ($SF_{Am/Eu}$) for Cl-CyMe₄-BTBP **2** in 1-octanol as a function of nitric acid concentration of the aqueous phase are shown in Figure 2. For **2**, the highest D_{Am} value observed was 28 ± 3 at 3 M HNO₃ and the highest separation factor obtained was 124 ± 12 at 3 M HNO₃. The D values for Eu(III) remained less than 0.3 over most HNO₃ concentrations. The D values for both Am(III) and Eu(III) increased with increasing nitric acid concentration and this trend is also observed with CyMe₄-BTBP **1** and other BTBPs. Distribution ratios for Am(III) and Cm(III), and the separation factors at different nitric acid concentrations were also examined (Figure 3). Again the D values for both Am(III) and Cm(III) increased with increasing nitric acid concentration resulting in a small but significant $SF_{Am/Cm} = 2.2 \pm 0.2$ at 1 M HNO₃.

The extraction of Am(III) and Eu(III) from nitric acid by Br-CyMe₄-BTBP **3** in 1-octanol is shown in Figure 4. The D values for Am(III) and Eu(III) increased with increasing nitric acid concentration in the aqueous phase resulting in a maximum separation factor of 112 ± 11 at 3 M HNO₃. The extraction of Am(III) and Cm(III) from nitric acid by **3** in 1-octanol is shown in Figure 5. In this case the maximum separation factor obtained was 1.9 ± 0.4 at 0.5 M HNO₃. Separation factors for Cl-CyMe₄-BTBP **2** and Br-CyMe₄-BTBP **3** ($SF_{Am/Eu}$ = estimated to be > 110 at 3 M HNO₃) are similar to that observed for CyMe₄-BTBP **1** ($SF_{Am/Eu} = 100 - 120$) in solvent extraction experiments but means that separation of Am(III) from Eu(III) from HNO₃ is possible without use of a phase transfer agent such as DMDOHEMA.^{2c}

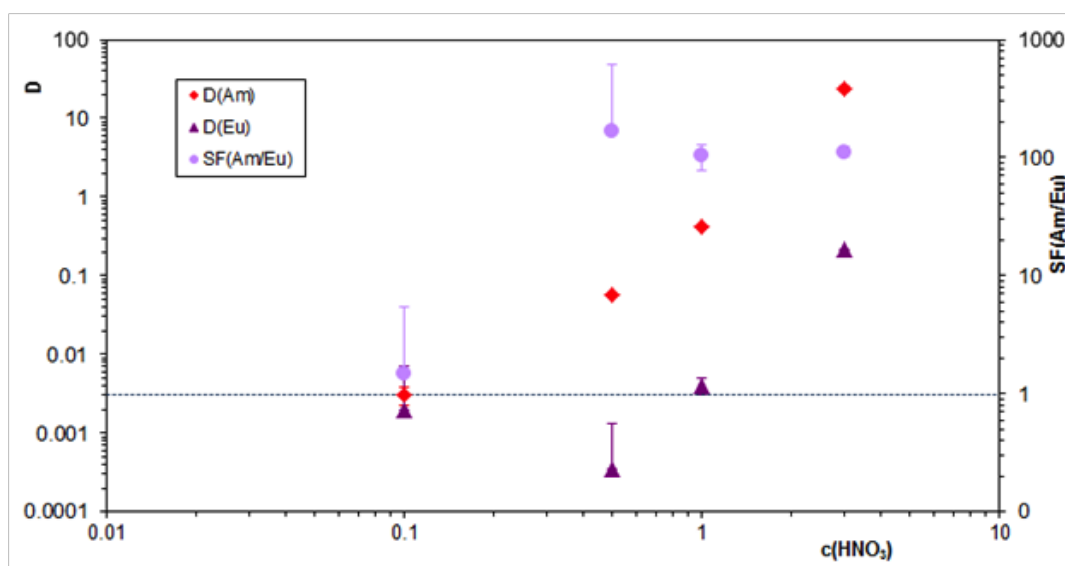


Figure 4. Extraction of Am(III), Cm(III) and Eu(III) by Br-CyMe₄-BTBP **3** in 1-octanol as a function of nitric acid concentration.

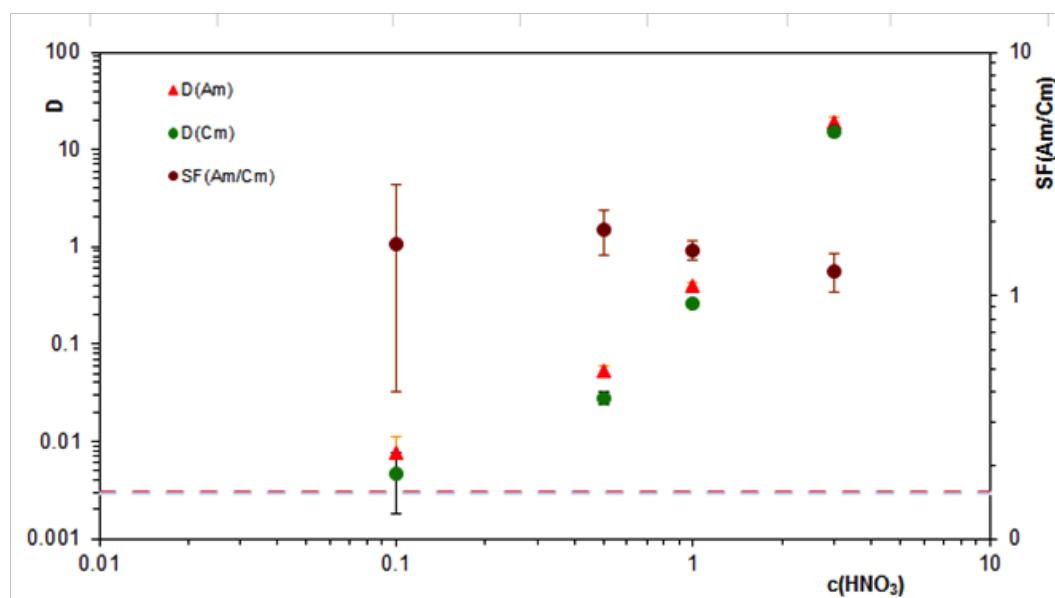


Figure 5. Extraction of Am(III) and Cm(III) by Br-CyMe₄-BTBP **2** in 1-octanol as a function of nitric acid concentration.

In summary, the synthesis and extraction of Am(III), Cm(III) and Eu(III) from HNO₃ by the two new BTBP ligands (Cl-CyMe₄-BTBP **2** and Br-CyMe₄-BTBP **3**) is described. Compared to CyMe₄-BTBP **1**, a far higher solubility in 1-octanol and cyclohexanone was observed by **2** and **3**. The distribution ratios and separation factors for Am(III) over Eu(III) obtained without using a phase transfer agent for **2** and **3** were similar to that observed for **1** with use of a phase transfer agent.

EXPERIMENTAL SECTION

General Methods. All reagents and solvents were of commercial grade and purified prior to use when necessary. NMR spectra were recorded on a 400.1 MHz spectrometer. Deuterated chloroform (CDCl₃) and deuterated DMSO (dimethyl sulfoxide-d₆) were used as solvents. Chemical shifts (δ values) were reported in parts per million (ppm) with the abbreviations s, d, t, q, qn, sx, dd, ddd and br denoting singlet, doublet, triplet, quartet, quintet, sextet, double doublets, doublet of doublets of doublets and broad resonances respectively. Coupling constants (J) are quoted in Hertz. IR spectra were recorded on an infrared spectrometer. Melting points were determined on a melting point detector. Mass spectra (m/z) were recorded under conditions of electrospray ionisation (ESI). The ions observed were quasimolecular ions created by the addition of a hydrogen ion denoted as [MH]⁺ or [M + Na].

Typical Procedure for the preparation of di-carbohydrazonamides (12-13). To a suspension of di-carbonitriles (9.2 mmol for **10** and 5.7 mmol for **11**) in DMF (50 mL) was added hydrazine hydrate

(64%, 50 mL) and the suspension was stirred at room temperature for 3 days. Water (200 mL) were added and the solid was filtered and washed with Et₂O (50 mL) and allowed to dry in a vacuum oven (40 °C) to yield the di-carbohydrazonamide.

4-chloro-[2,2'-bipyridine]-6,6'-bis(carbohydrazonamide) (12). Yellow solid (2.6 g, 91% yield); mp > 300 °C. ¹H NMR (400.1 MHz, DMSO-*d*₆) δ_H (ppm) = 5.51 (br s, 4H, 2 × NH₂), 6.0 (d, *J* = 16.0 Hz, 4H, 2 × NH₂), 7.90 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 7.6 Hz, 1H), 8.73 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ_C (ppm) = 118.7, 119.4, 120.2, 120.4, 137.2, 141.9, 143.2, 144.1, 151.6, 152.0, 153.1, 155.2; C₁₂H₁₃N₈Cl [MH]⁺ requires *m/z* 305.1024 and 307.0995; (FTMS + p ESI) MS found *m/z* 305.1026 and 307.0995; Expected for C₁₂H₁₃N₈Cl: % C, 47.30; H, 4.30; N, 36.75; Cl, 11.63, found: % C, 46.97; H, 4.18; N, 36.49; Cl, 11.10; IR ν_{max} / cm⁻¹ = 3301 (N-H), 3182 (N-H), 3096 (N-H), 1616, 1556, 1434, 1362, 1278.

4-bromo-[2,2'-bipyridine]-6,6'-bis(carbohydrazonamide) (13). Yellow solid (1.5 g, 74% yield); mp > 300 °C. ¹H NMR (400.1 MHz, DMSO-*d*₆) δ_H (ppm) = 5.48 (br s, 4H, 2 × NH₂), 6.00 (d, *J* = 16.4 Hz, 4H, 2 × NH₂), 7.91 (t, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 7.2 Hz, 1H), 8.10 (d, *J* = 1.6 Hz, 1H), 8.65 (d, *J* = 7.2 Hz, 1H), 8.84 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100.6 MHz, DMSO-*d*₆) δ_C (ppm) = 120.1, 120.5, 121.9, 122.2, 133.2, 137.2, 141.8, 143.2, 151.6, 152.0, 152.8, 154.9; C₁₂H₁₃N₈Br [MH]⁺ requires *m/z* 349.0519 and 351.0499; (FTMS + p ESI) MS found *m/z* 349.0520 and 351.0499; Expected for C₁₂H₁₃N₈Br: % C, 41.28; H, 3.75; N, 32.07; Br, 22.88, found: % C, 41.52; H, 3.67; N, 31.30; Br, 23.35; IR ν_{max} / cm⁻¹ = 3309 (N-H), 3185 (N-H), 3096 (N-H), 1645, 1622, 1558, 1466, 1431.

Typical Procedure for the preparation of BTBP Ligands (2-3). To a suspension of diamide dihydrazide (1.5 mmol) in THF (100 mL) was added tetramethylcyclohexane-1,2-dione **14** (3.3 mmol). Triethylamine (9 mL) was added and the mixture was heated under reflux for 3 days. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with DCM (25 mL). The filtrate was evaporated and the solid was triturated with petroleum ether (40-60 °C) (100 mL). The insoluble solid was filtered and washed with petroleum ether (40-60 °C) (50 mL) and allowed to dry in air to yield the BTBP ligand.

*3,3'-(4-chloro-[2,2'-bipyridine]-6,6'-diyl)bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[*e*][1,2,4]triazine) (2)*. Yellow solid (0.9 g, 95% yield); mp 180-182 °C. ¹H NMR (400.1 MHz, CDCl₃) δ_H (ppm) = 1.48 (s, 12H, 4 × CH₃), 1.54 (s, 12H, 4 × CH₃), 1.90 (s, 8H, 4 × CH₂), 8.06 (dd, *J* = 7.6 Hz, 1H), 8.52 (d, *J* = 2 Hz, 1H), 8.56 (d, *J* = 7.6 Hz, 1H), 8.93 (d, *J* = 7.6 Hz, 1H), 8.97 (d, *J* = 1.6 Hz, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ_C (ppm) = 29.3, 29.8, 33.3, 33.8, 36.6, 37.3, 123.0,

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5 123.3, 124.0, 124.4, 138.0, 146.3, 153.0, 154.2, 155.0, 157.5, 160.0, 160.7, 163.2, 163.5, 164.5, 164.6;
6 $C_{32}H_{37}N_8Cl$ [M + Na] requires m/z 591.2722 and 593.2692; (FTMS + p ESI) MS found m/z 591.2724 and
7 593.2694; Expected for $C_{32}H_{37}N_8Cl$: % C, 67.53; H, 6.53; N, 19.68; Cl, 6.23, found: % C, 64.10; H,
8 6.78; N, 18.00; Cl, 5.88; analysis suggests $C_{32}H_{37}N_8Cl \times H_2O$: calcd. % C, 65.46; H, 6.69; N, 19.08; Cl,
9 6.04; IR ν_{max} / cm^{-1} = 2961 (C-H), 2930 (C-H), 2867 (C-H), 1706, 1636, 1621, 1561, 1509, 1455, 1385.

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14 *3,3'-(4-bromo-[2,2'-bipyridine]-6,6'-diyl)bis(5,5,8,8-tetramethyl-5,6,7,8-*
15 *tetrahydrobenzo[e][1,2,4]triazine) (3).*

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17 Yellow solid (0.8 g, 86% yield); mp 108-110 °C. 1H NMR (400.1 MHz, $CDCl_3$) δ_H (ppm) = 1.48 (s,
18 12H, 4 \times CH_3), 1.54 (s, 12H 4 \times CH_3), 1.90 (s, 8H, 4 \times CH_2), 8.05 (dd, J = 7.6 Hz, 1H), 8.56 (d, J = 7.6
19 Hz, 1H), 8.68 (s, 1H), 8.93 (d, J = 7.6 Hz, 1H), 9.13 (s, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ_C (ppm) =
20 29.3, 29.8, 33.3, 33.8, 36.6, 37.3, 123.3, 124.4, 126.0, 127.0, 134.9, 138.0, 153.0, 153.9, 154.9, 157.2,
21 159.9, 160.7, 163.2, 163.5, 164.5, 164.6; $C_{32}H_{37}N_8Br$ [MH] $^+$ requires m/z 613.2397 and 615.2377;
22 (FTMS + p ESI) MS found m/z 613.2396 and 615.2376; Expected for $C_{32}H_{37}N_8Br$: % C, 62.64; H, 6.08;
23 N, 18.25; Br, 13.02, found: % C, 60.97; H, 6.19; N, 17.41; Br, 12.91; analysis suggests $C_{32}H_{37}N_8Br \times$
24 H_2O : calcd. % C, 60.85; H, 6.22; N, 17.74; Br, 12.65; IR ν_{max} / cm^{-1} = 2961 (C-H), 2927 (C-H), 2864 (C-
25 H), 1718, 1615, 1558, 1506, 1455, 1427, 1388.

26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

EXTRACTION STUDIES

General Procedure. Experiments were performed extracting $^{241}Am(III)$, $^{244}Cm(III)$ and $^{152}Eu(III)$ from
 HNO_3 (500 μL) into 30 mmol/L BTBP in 1-octanol (500 μL). After phase separation, $^{241}Am(III)$ and
 $^{152}Eu(III)$ were determined by gamma counting in 300 μL aliquots of both phases. $^{241}Am(III)$ and
 $^{244}Cm(III)$ were determined by alpha spectrometry. The distribution ratios, D , were calculated as the
ratio between the radioactivity (α - and γ - emissions) of each isotope in the organic and in the aqueous
phase. The separation factor, $SF_{Am/Eu} = D_{Am} / D_{Eu}$ or $SF_{Am/Cm} = D_{Am} / D_{Cm}$. All extraction experiments
were carried out in duplicate and error bars in the figures represent standard deviations.

ASSOCIATED CONTENT

Supporting Information

1H , ^{13}C , COSY and HSQC NMR spectra for compounds **12**, **13**, **2** and **3**. Data for solvent extraction
measurements.

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REFERENCES

1. Higginson, M. A.; Kyle, N. D.; Marsden, O. J.; Thompson, P.; Livens, F. R.; Heath, S. L. *Dalton Trans.* **2015**, 44 (37), 16547-16552.
2. (a) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B.; Hubscher-Bruder, V.; Videva, V.; Arnaud-Neu, F.; Stamberg, K.; Vyas, S. *Inorg. Chem.* **2013**, 52 (9), 4993-5005; (b) Hudson, M. J.; Harwood, L. M.; Laventine, D. M.; Lewis, F. W. *Inorg. Chem.* **2012**, 52 (7), 3414-3428; (c) Kolarik, Z. *Chem. Rev.* **2008**, 108 (10), 4208-52.
3. (a) Lewis, F. W.; Hudson, M. J.; Harwood, L. M. *Synlett* **2011**, 2011 (18), 2609-2632; (b) Dam, H. H.; Reinhoudt, D. N.; Verboom, W. *Chem. Soc. Rev.* **2007**, 36 (2), 367-77.
4. (a) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G. B.; Sypula, M.; Modolo, G.; Whittaker, D.; Sharrad, C. A.; Videva, V.; Hubscher-Bruder, V.; Arnaud-Neu, F. *Dalton Trans.* **2012**, 41 (30), 9209-9219; (b) Afsar, A.; Laventine, D. M.; Harwood, L. M.; Hudson, M. J.; Geist, A. *Chem. Commun.* **2013**, 49 (76), 8534-8536; (c) Afsar, A.; Harwood, L. M.; Hudson, M. J.; Westwood, J.; Geist, A. *Chem. Commun.* **2015**, 51 (27), 5860-5863.
5. (a) Drew, M. G. B.; Foreman, M. R. S. J.; Hill, C.; Hudson, M. J.; Madic, C. *Inorg. Chem. Commun.* **2005**, 8 (3), 239-241; (b) Foreman, M. R. S. J.; Hudson, M. J.; Geist, A.; Madic, C.; Weigl, M. *Solvent Extr. Ion Exch.* **2005**, 23 (5), 645-662; (c) Nilsson, M.; Ekberg, C.; Foreman, M.; Hudson, M.; Liljenzin, J. O.; Modolo, G.; Skarnemark, G. *Solvent Extr. Ion Exch.* **2006**, 24 (6), 823-843.
6. Aneheim, E.; Ekberg, C.; Fermvik, A.; Foreman, M. R. S. J.; Grüner, B.; Hájková, Z.; Kvičalová, M. *Solvent Extr. Ion Exch.* **2011**, 29 (2), 157-175.

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4
5 7. (a) Aneheim, E.; Grüner, B.; Ekberg, C.; Foreman, M. R. S.; Hájková, Z.; Löfström-Engdahl, E.;
6 Drew, M. G. B.; Hudson, M. J. *Polyhedron* **2013**, *50* (1), 154-163; (b) Magnusson, D.; Christiansen,
7 B.; Foreman, M. R. S.; Geist, A.; Glatz, J. P.; Malmbeck, R.; Modolo, G.; Serrano-Purroy, D.; Sorel,
8 C. *Solvent Extr. Ion Exch.* **2009**, *27* (2), 97-106.
9
10
11 8. (a) Modolo, G.; Wilden, A.; Daniels, H.; Geist, A.; Magnusson, D.; Malmbeck, R. *Radiochim. Acta*,
12 2013; *101*, 155-162; (b) Aneheim, E.; Ekberg, C.; Fermvik, A.; Foreman, M. R. S. J.; Retegan, T.;
13 Skarnemark, G. *Solvent Extr. Ion Exch.* **2010**, *28* (4), 437-458; (c) Aneheim, E.; Ekberg, C.;
14 Foreman, M. R. S.; Löfström-Engdahl, E.; Mabile, N. *Sep. Sci. Technol.* **2011**, *47* (5), 663-669.
15
16 9. (a) Lewis, F. W.; Harwood, L. M.; Hudson, M. J.; Drew, M. G.; Desreux, J. F.; Vidick, G.;
17 Bouslimani, N.; Modolo, G.; Wilden, A.; Sypula, M.; Vu, T. H.; Simonin, J. P. *J. Am. Chem. Soc.*
18 **2011**, *133* (33), 13093-102; (b) Retegan, T.; Drew, M.; Ekberg, C.; Engdahl, E. L.; Hudson, M. J.;
19 Fermvik, A.; Foreman, M. R. S.; Modolo, G.; Geist, A. *Solvent Extr. Ion Exch.* **2014**, *32* (7), 720-
20 736.
21
22 10. (a) Foreman, M. R. S.; Hudson, M. J.; Drew, M. G. B.; Hill, C.; Madic, C. *Dalton Trans.* **2006**,
23 (13), 1645-1653; (b) Geist, A.; Hill, C.; Modolo, G.; Foreman, M. R. S. J.; Weigl, M.; Gompper, K.;
24 Hudson, M. J. *Solvent Extr. Ion Exch.* **2006**, *24* (4), 463-483; (c) Lewis, F. W.; Harwood, L. M.;
25 Hudson, M. J.; Distler, P.; John, J.; Stamberg, K.; Núñez, A.; Galán, H.; Espartero, A. G. *Euro. J.*
26 *Org. Chem.* **2012**, *2012* (8), 1509-1519.
27
28 11. Kodama, K.; Kobayashi, A.; Hirose, T. *Tetrahedron Lett.* **2013**, *54* (40), 5514-5517.
29
30 12. Baxter, P. N. W.; Connor, J. A.; Schweizer, W. B.; Wallis, J. D. *J. Chem. Soc., Dalton Trans.* **1992**,
31 (20), 3015-3019.
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
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