

SUPPLEMENTARY INFORMATION

Effective separation of the actinides Am(III) and Cm(III) by electronic modulation of Bis-(1,2,4-triazin-3- yl)phenanthrolines

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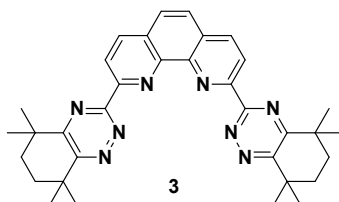
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1.0 Experimental Procedures

General procedure

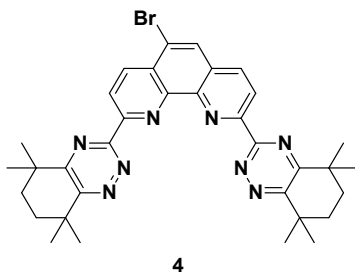
NMR spectra were recorded using either a Bruker AMX400 or an Avance DFX400 instrument. Deuterated chloroform (CDCl_3) and Deuterated DMSO (dimethyl sulfoxide- d_6) were used as solvents. Chemical shifts (δ values) were reported in parts per million (ppm) with the abbreviations s, d, t, q, qn, sx, dd, 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 as Nujol[®] mulls (N) on a Perkin Elmer RX1 FT-IR instrument. All the melting points were determined on a Gallenkamp melting point apparatus. 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 $[\text{MH}]^+$ or $[\text{M} + \text{Na}]$. The instrument used was Xcalibur Tune 2.1 (SP1).

2,9-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (3)



To a suspension of 1,10-phenanthroline-2,9-dicarbohydrazonamide (0.58 g, 2 mmol) in THF (75 mL) was added 3,3,6,6-tetramethylcyclohexane-1,2-dione (0.74 g, 4.4 mmol, 2.2 eq). Triethylamine (3.5 mL, 25.3 mmol) 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 Et₂O (25 mL). The insoluble solid was filtered and washed with further Et₂O (25 mL) and allowed to dry in air to afford the ligand **3** as a yellow solid (0.92 g, 83 %); Mp (247-250 °C); ¹H NMR (400.1 MHz, CDCl₃) δ_H (ppm) = 1.55 (s, 12H), 1.58 (s, 12H), 1.89 (s, 8H), 7.95 (s, 2H), 8.48 (d, *J* = 8.4 Hz, 2H), 8.90 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100.6 MHz, CDCl₃) δ_C (ppm) = 29.3, 29.9, 33.7, 36.7, 37.6, 123.5, 127.6, 129.9, 137.4, 146.5, 153.9, 161.4, 163.3, 165.1; C₆₈H₇₆N₁₆ [2M + Na] requires *m/z* 1139.6331; (FTMS + c ESI) MS found *m/z* 1139.6345; IR ν_{max} / cm⁻¹ = 3490, 2962, 2931, 2866, 2224, 1622, 1588, 1554, 1516, 1499, 1472.

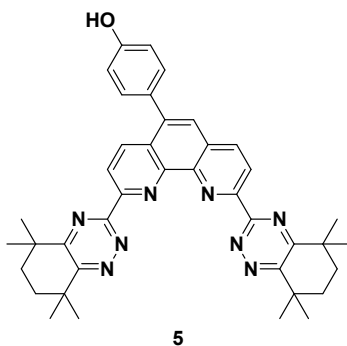
5-Bromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (4)



To a suspension of 5-bromo-1,10-phenanthroline-2,9-dicarbohydrazonamide (1.47 g, 3.9 mmol) in 1,4-dioxane (200 mL) was added 3,3,6,6-tetramethylcyclohexane-1,2-dione (1.72 g, 10.2 mmol, 2.6 eq). Triethylamine (6 mL, 42.7 mmol) was added and the mixture was heated under reflux for 3 days. After allowing the solution to cool to room temperature, the solvent was evaporated and the

remaining semi-solid residue was triturated with ice-cold Et₂O (400 mL). The insoluble solid was filtered and washed with further ice-cold Et₂O (400 mL) and allowed to dry in air to afford the **4** as a yellow solid (1.23 g, 49 %); Mp (197-200 °C); ¹H NMR (400.1 MHz, CDCl₃) δ_H (ppm) = 1.54 (s, 12H), 1.56 (s, 12H), 1.90 (s, 8H), 8.29 (s, 1H), 8.39 (d, *J* = 8.0 Hz, 1H), 8.86 (d, *J* = 8.4 Hz, 1H), 8.88 (d, *J* = 8.4 Hz, 1H), 8.95 (d, *J* = 9.4 Hz, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ_C (ppm) = 29.3, 29.8, 33.6, 33.8, 36.7, 37.5, 122.0, 124.0, 124.1, 128.9, 129.8, 130.6, 136.3, 137.3, 146.0, 146.9, 154.4, 154.7, 161.1, 161.3, 163.3, 163.4, 165.0, 165.1; C₃₄H₃₇N₈Br [MH]⁺ requires *m/z* 637.2397 and 639.2377; (FTMS + p ESI) MS found *m/z* 637.2392 and 639.2371; IR ν_{max} / cm⁻¹ = 3531, 3486, 2959, 2927, 2865, 1644, 1609, 1510, 1475, 1452, 1439.

4-(2,9-Bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[1,2,4]triazin-3-yl)-1,10-phenanthroline-5-yl)phenol (5)



A suspension of 5-bromo-2,9-bis(5,5,8,8-tetramethyl-5,6,7,8-tetrahydrobenzo[e][1,2,4]triazin-3-yl)-1,10-phenanthroline (0.51 g, 0.8 mmol), tetrakis(triphenylphosphane)palladium(0) (0.04 g, 0.04 mmol, 0.05 eq), (4-hydroxyphenyl)boronic acid (0.13 g, 0.9 mmol, 1.1 eq) and K₂CO₃ (0.15 g, 1.1 mmol, 1.4 eq) in degassed EtOH (75 mL) was heated to reflux for 18 h under nitrogen. The solution was allowed to cool to room temperature and filtered and the remaining solid residue was washed with EtOH (20 mL). The filtrate was evaporated and the solid residue was taken up in DCM (150 mL) and water (100 mL) was added. The organic layer was washed with saturated brine (100 mL) and dried over MgSO₄. The filtrate was evaporated and the solid was triturated with Et₂O (100 mL). The insoluble solid was filtered and washed with Et₂O (50 mL) and allowed to dry in air to afford **5** as a yellow solid (0.31 g, 59 %); Mp (250-252 °C); ¹H NMR (400.1 MHz, CDCl₃) δ_H (ppm) = 1.58 (s, 12H), 1.61 (s, 12H), 1.93 (s, 8H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 7.67 (s, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.76 (d, *J* = 8.8 Hz, 1H), 8.87 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100.6 MHz, CDCl₃) δ_C (ppm) = 29.3, 29.9, 33.8, 36.7, 37.6, 115.6,

122.9, 123.7, 127.0, 128.2, 129.5, 129.5, 130.0, 136.3, 137.3, 140.2, 145.3, 146.5, 153.2, 153.3, 157.7, 161.0, 161.3, 163.5, 163.6, 165.2, 165.3; C₄₀H₄₃N₈O [MH]⁺ requires m/z 651.3554; (FTMS + p ESI) MS found m/z 651.3553; IR ν_{\max} / cm⁻¹= 3399, 2962, 2931, 2865, 1611, 1587, 1514, 1471, 1456, 1389, 1365.

^1H and ^{13}C NMR spectra

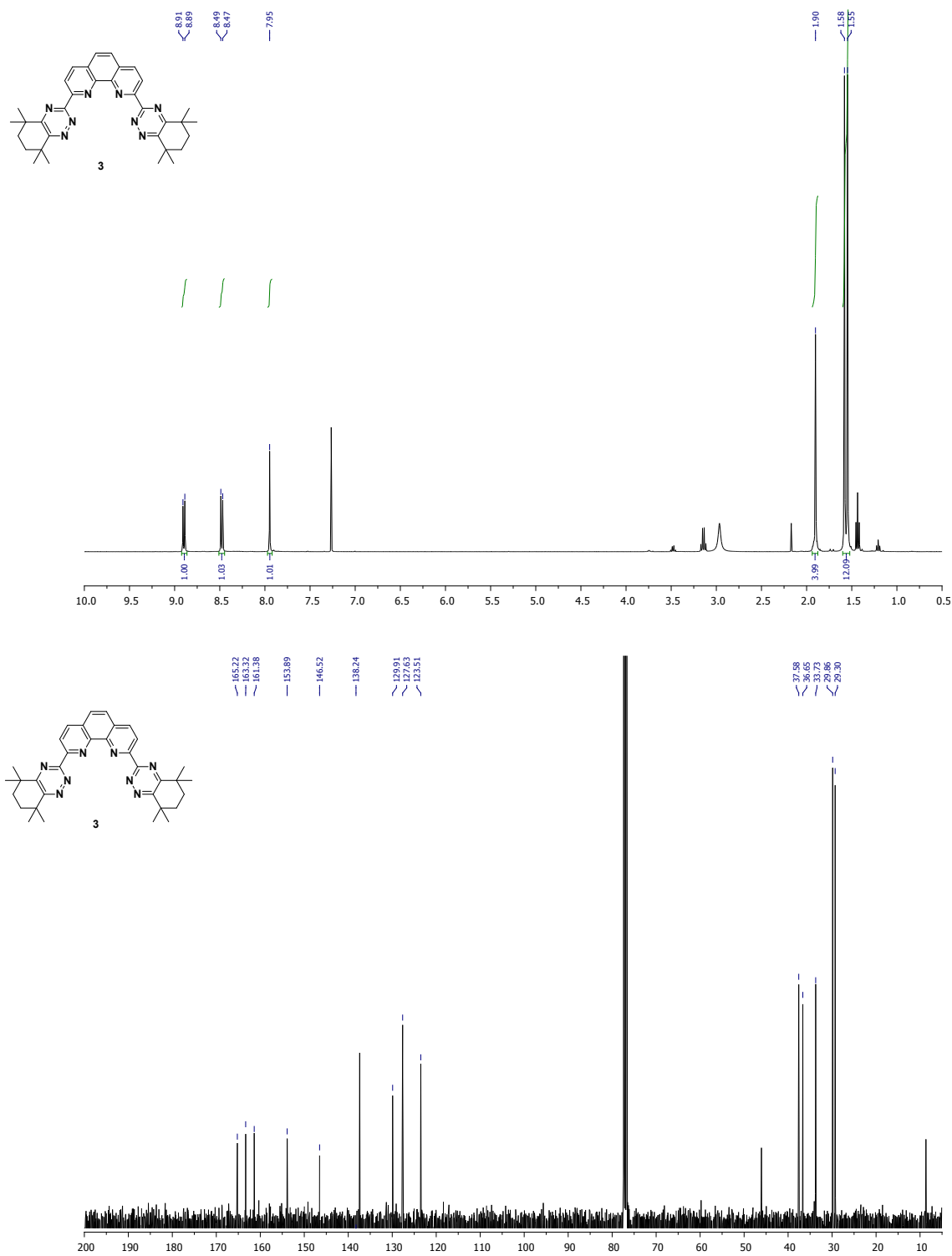


Figure S1. ^1H and ^{13}C NMR spectra of CyMe₄-BTPPhen **3**.

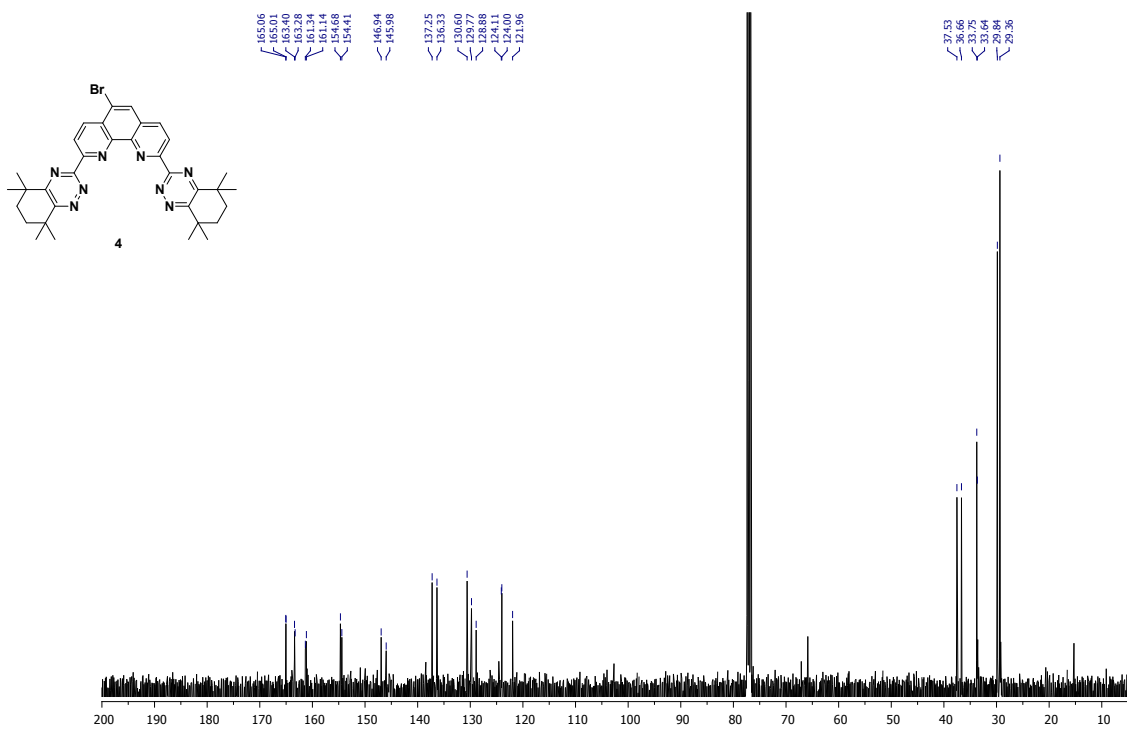
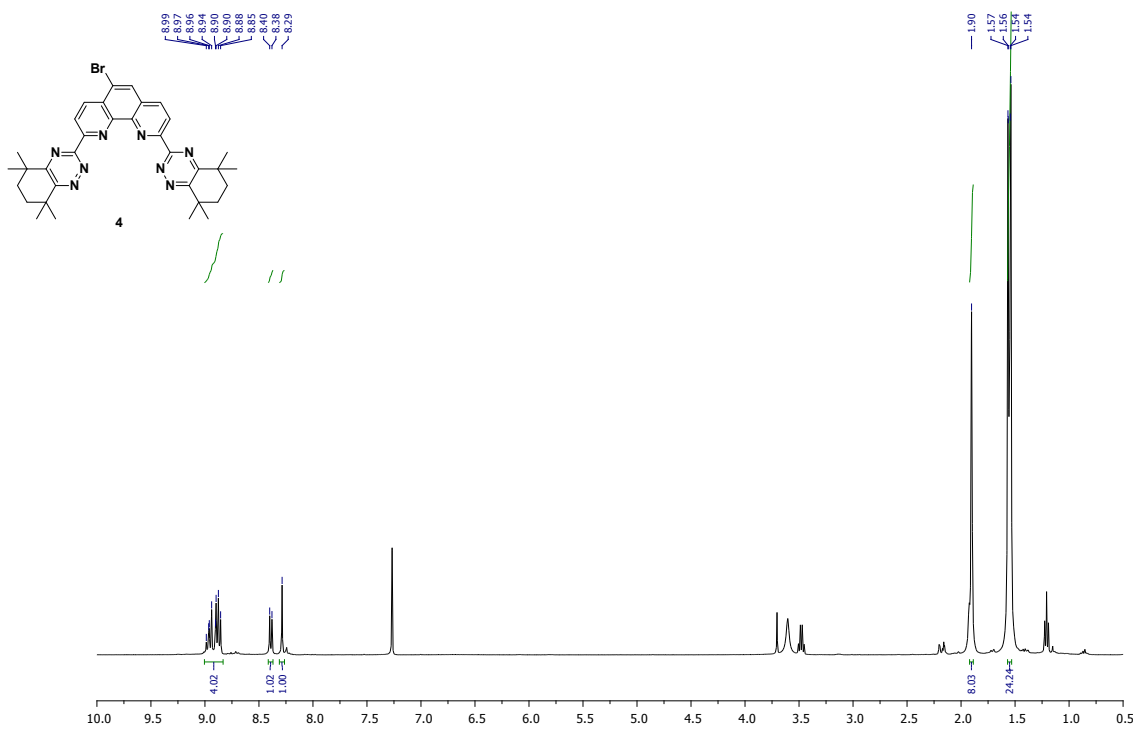


Figure S2. ¹H and ¹³C NMR spectra of 5-BrCyMe₄-BTPhen **4**.

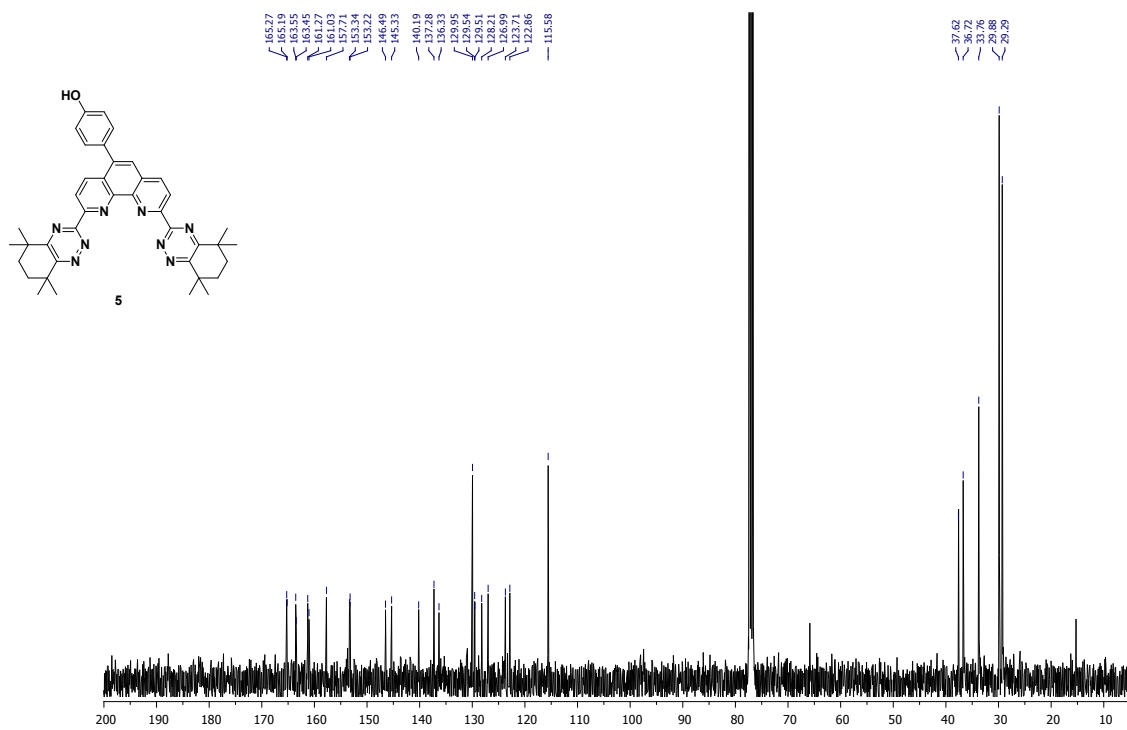
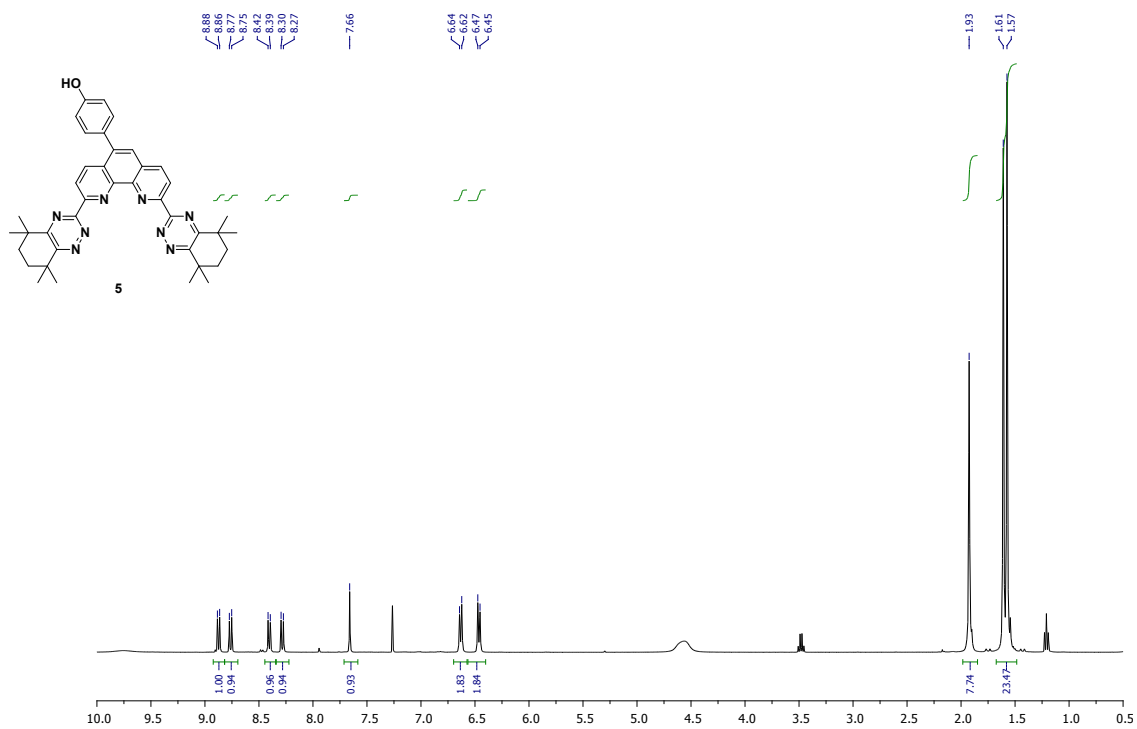


Figure S3. ¹H and ¹³C NMR spectra of 5-(4-hydroxyphenyl)-CyMe₄-BTPhen **5**.

2.0 Extraction Results

General Procedure

Experiments were performed extracting $^{241}\text{Am(III)}$, $^{244}\text{Cm(III)}$, $^{152}\text{Eu(III)}$ (1 kBq/mL each), all lanthanides (La(III)–Lu(III) except Pm(III)), and Y(III) (20 mg/L) from HNO_3 (500 μL) into 30 mmol/L BTPPhen in 1-octanol (500 μL). After phase separation, $^{241}\text{Am(III)}$ and $^{152}\text{Eu(III)}$ were determined by gamma counting ((Packard Cobra Auto Gamma 5003) in 300 μL aliquots of both phases. $^{241}\text{Am(III)}$ and $^{244}\text{Cm(III)}$ were determined by alpha spectrometry (Canberra 7401); inactive lanthanides were determined by ICP-MS (Perkin-Elmer Elan 6100). An error of 20 % was estimated for the distribution ratios measurements, which were not repeated.

Table S1 Extraction of Am(III) and Eu(III) by CyMe₄-BTPPhen **3** as a function of nitric acid concentration (* gamma measurement).

[HNO ₃] Initial (mol/L)	D_{Am}^*	D_{Eu}^*	SF _{Am/Eu}
0.1	1043.4	1.6	667.0
0.3	1967.6	3.1	634.2
1	560	4.2	133.1
3	335.4	4.6	72.6

Table S2 Extraction of Am(III) and Cm(III) by CyMe₄-BTPPhen **3** as a function of nitric acid concentration (* alpha measurement).

[HNO ₃] Initial (mol/L)	D_{Am}^{**}	D_{Cm}^{**}	SF _{Am/Cm}
0.1	377.0	300.1	1.3
0.3	501.3	512.9	1.0
1	369.3	298.3	1.2
3	238.9	210.5	1.1

Table S3 Extraction (reported in mg/L) of Ln(III) and Y(III) from nitric acid (0.1 – 3 M) by a 0.03 M solution of CyMe₄-BTPPhen **3** in 1-octanol.

Metal	[HNO ₃] Initial (mol/L)			
	0.1	0.3	1	3
Y	0.0267	0.0475	0.0309	0.0137
La	0.0218	0.0314	0.0189	0.0131
Ce	0.174	0.2846	0.1711	0.1333
Pr	0.6809	1.0217	0.6115	0.52
Nd	1.5877	2.4023	1.456	1.3203
Sm	2.3121	4.2039	3.9317	4.2924
Eu	1.4755	3.0832	4.253	4.6439
Gd	0.6238	1.323	2.1708	1.3628
Tb	0.5455	1.1354	2.2244	0.9335
Dy	0.3101	0.6687	0.998	0.3773
Ho	0.1764	0.362	0.3593	0.1262
Er	0.1123	0.1915	0.1404	0.0507
Tm	0.0659	0.1062	0.0613	0.0235
Yb	0.0494	0.0692	0.0375	0.02
Lu	0.028	0.035	0.0215	0.0114

Table S4 Extraction of Am(III) and Eu(III) by 5-Br-CyMe₄-BTPPhen **4** as a function of nitric acid concentration (* gamma measurement).

[HNO ₃] Initial (mol/L)	D_{Am}^*	D_{Eu}^*	SF _{Am/Eu}
0.1	63.7	0.2	317.9
0.3	270.7	0.6	475.8
1	333.9	1.2	287.8
3	507.5	0.7	678.7

Table S5 Extraction of Am(III) and Cm(III) by 5-Br-CyMe₄-BTPPhen **4** as a function of nitric acid concentration (* alpha measurement).

[HNO ₃] Initial (mol/L)	D_{Am}^{**}	D_{Cm}^{**}	SF _{Am/Cm}
0.1	61.0	9.3	6.6
0.3	208.2	35.2	5.9
1	301.3	138.0	2.2
3	369.6	192.3	1.9

Table S6 Extraction (reported in mg/L) of Ln(III) and Y(III) from nitric acid (0.1 – 3 M) by a 0.03 M solution of 5-Br-CyMe₄-BTPPhen **4** in 1-octanol.

Metal	[HNO ₃] Initial (mol/L)			
	0.1	0.3	1	3
Y	1.81×10^{-3}	3.41×10^{-3}	4.87×10^{-3}	6.13×10^{-3}
La	2.38×10^{-3}	5.34×10^{-3}	7.39×10^{-3}	7.65×10^{-3}
Ce	0.0147	0.04	0.0549	0.0608
Pr	0.0513	0.1359	0.1796	0.2246
Nd	0.116	0.3228	0.4305	0.5575
Sm	0.2619	0.7306	1.2069	1.537
Eu	0.1929	0.5682	1.0878	0.7184
Gd	0.0805	0.2297	0.3686	0.189
Tb	0.0619	0.1703	0.2673	0.1513
Dy	0.0354	0.0876	0.1299	0.097
Ho	0.0216	0.0478	0.0653	0.0529
Er	0.0192	0.0341	0.0362	0.0278
Tm	0.0155	0.0237	0.0191	0.0171
Yb	0.0136	0.0186	0.0147	0.0124
Lu	0.01	0.0113	8.08×10^{-3}	6.19×10^{-3}

Table S7 Extraction of Am(III) and Eu(III) by 5-(4-hydroxyphenyl)-CyMe₄-BTPPhen **5** as a function of nitric acid concentration (* gamma measurement).

[HNO ₃] Initial (mol/L)	D_{Am}^*	D_{Eu}^*	SF _{Am/Eu}
0.1	27.9	0.5	54.6
0.3	70.1	1.2	59.1
1	1807.3	4.6	389.6
3	1581.0	5.1	311.3

Table S8 Extraction of Am(III) and Cm(III) by 5-(4-hydroxyphenyl)-CyMe₄-BTPPhen **5** as a function of nitric acid concentration (* alpha measurement).

[HNO ₃] Initial (mol/L)	D_{Am}^{**}	D_{Cm}^{**}	SF _{Am/Cm}
0.1	23.7	5.7	4.2
0.3	63.3	13.8	4.6
1	831.8	153.2	5.4
3	2496.3	1110.9	2.2

Table S9 Extraction (reported in mg/L) of Ln(III) and Y(III) from nitric acid (0.1 – 3 M) by a 0.03 M solution of 5-(4-hydroxyphenyl)-CyMe₄-BTPPhen **5** in 1-octanol.

Metal	[HNO ₃] Initial (mol/L)			
	0.1	0.3	1	3
Y	0.0188	0.0296	0.0158	6.61×10 ⁻³
La	0.0256	0.0372	0.025	0.0174
Ce	0.262	0.3674	0.2593	0.1711
Pr	0.7203	1.2413	1.0235	0.8784
Nd	0.8555	1.7828	2.605	2.3609
Sm	0.6576	1.4965	6.2924	9.1194
Eu	0.4787	1.1086	4.7113	5.2025
Gd	0.2546	0.5899	1.9159	1.0156
Tb	0.2219	0.5187	1.3779	0.5717
Dy	0.1509	0.3163	0.4965	0.1747
Ho	0.0927	0.1546	0.1141	0.0408
Er	0.0524	0.0651	0.0406	0.0164
Tm	0.0282	0.0291	0.0212	7.98×10 ⁻³
Yb	0.0221	0.0248	0.0256	0.012
Lu	0.018	0.0192	0.0299	0.0262